Tungsten
Sources, Metallurgy, Properties, and Applications
Tungsten

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Sources, Metallurgy, Properties, and Applications

Stephen W.H. Yih

and

Chun T. Wang

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To

K. C. Li, Senior

the founder of Wah Chang Corporation
who dedicated his life to the tungsten industry
Preface

Discovery of tungsten was relatively late in world history, probably because of the difficulty in extracting the metal from its minerals. Furthermore, due to its unusual refractory property, the consolidation and fabrication of tungsten was beyond the capability of the metal industry during the earlier years. This further prevented it from being amenable for shaping into convenient forms for utilization.

However, after the strengthening effect of the addition of tungsten in steel was recognized and the powder metallurgy technique for producing tungsten was developed, this highly refractory metal soon gained unique positions in the following major areas of application: (1) filaments in electrical lamps and electronic tubes, (2) tungsten addition in high-speed and other tool steels, and (3) tungsten carbide in tool materials and wear-resistant parts. The emergence of space vehicles and nuclear reactors in recent years further opened new fields of application for tungsten.

In Chapter 1, mineralogy and geological genesis of tungsten are discussed, followed by a description of current major mining operations in the United States and in the world in general. In the beneficiation section (Sec. 1.5), separate processes are treated, followed by illustrations of recent industrial practice.

In Chapter 2, various techniques of decomposition and purification of tungsten ores are treated, with emphasis on the trend of present development, followed by examples of industrial operations. Recycling of the metal is also discussed.

In Chapter 3, reduction of tungsten oxides, halides, and ores is treated, with the introduction of some new types of reduction furnaces and equipment. Production of ferrotungsten is also discussed.

In Chapter 4, powder metallurgy processing, its theoretical background, and the recently adopted arc-melting process are discussed in detail. Also discussed are electron-beam melting and other newly developed processes of consolidation.

In Chapter 5, wire drawing, still a major process of fabrication in the industry, is discussed in much detail, along with other new fabrication techniques for tungsten, from extrusion, forging, and rolling to tube-reducing. Descaling, machining, welding, and protective coating are also discussed.

In Chapter 6, structure and thermal, optical, and electrical properties are treated, followed by a discussion of mechanical properties, including comparison of ductility, hardness, and tensile and creep properties of tungsten of various purity and fabrication histories.
In Chapter 7, general and oxidation behavior of tungsten are discussed, followed by a discussion of properties of compounds of tungsten, tungstates, and tungsten bronzes.

In Chapter 8, emphasis is placed on preparation and mechanical properties of tungsten alloys and composites, including heavy alloys and metal-infiltrated tungsten. Also discussed are compositions and applications of steel, superalloys, and refractory alloys that contain tungsten.

In Chapter 9, preparations of tungsten carbides and their properties are treated, with emphasis on cemented tungsten carbide and some new trends in the industry.

In Chapter 10, applications of tungsten are discussed for various forms of end products.

In Chapter 11, the industry structure is outlined, the trend of usage and prospective substitutes are discussed, and future outlook is projected.

Appendix I presents a brief discussion on metallographic procedures for tungsten.

Appendix II treats various analytical procedures related to tungsten.

This book is intended to be as comprehensive as possible within the size of the volume; to cover the latest technical development in the industry; to serve as a handbook for scientists and engineers who are working in the fields of exploration, mining, extraction, reduction, consolidation, and fabrication of tungsten, its alloys, pseudoalloys, composites, tungsten carbides, and chemicals; to serve as a guide book for the end users who are interested in the properties or the processes of tungsten products; and to serve as an introduction for students who have particular interests in this field or for those who are about to enter into this field as their profession.

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Occurrence, Geology, Mining, and Beneficiation of Tungsten

1.1. DISCOVERY OF TUNGSTEN MINERALS

The tungsten mineral wolframite was known in the tin mines of the Saxony-Bohemia region, and later in Cornwall, long before the element itself was discovered (Weeks, 1945). J. F. Henckel regarded wolframite as an arsenical and ferruginous ore of tin. Similar views were held by J. G. Wallerius, A. Cronstedt, J. H. G. von Justi, and J. G. Lehmann (Li and Wang, 1955).

In 1781, the Swedish chemist Scheele, who had been working with a stony mineral, elucidated the composition of this mineral to be a compound of calcium with an unknown acid. The acid-forming element thus discovered was named tungsten by A. F. Cronstedt in 1755. He derived this name, from the Swedish words tung, meaning heavy, and sten, meaning stone. Later, in 1821, Leonhard honored Scheele by naming the mineral scheelite.

In 1783, the brothers J. J. and F. de Elhujar found that wolframite also contained tungsten, but with iron and manganese instead of calcium. They also succeeded, in collaboration with T. Bergmann, in obtaining metallic tungsten by the reduction of the oxide with carbon and were probably the first to prepare the metal (Li and Wang, 1955), to which they gave the name “wolfram.” The origin of this word is not quite clear, but it is assumed to be derived from the German words Wolf and Rahm or the Swedish word wulfriq. It was probably associated with the difficulties of extracting tin from cassiterite when it was contaminated with wolframite (Palache et al., 1951; Li and Wang, 1955). Later in 1863, Liebe described the nearly pure iron tungstate, which was found in Sierra Almagrera, Spain, and was named ferberite.

However, tungsten remained rarely known in the industry until Oxland (1847) patented his manufacturing process of sodium tungstate, tungstic acid, and the metal. Oxland (1857) also patented the manufacturing method of iron–tungsten alloys, but the metal itself found no application until nearly 50 years later, when it was used as electric filaments in incandescent lamps. More history of extraction, reduction, manufacturing, and application of tungsten will be discussed in the following chapters of this book when it is pertinent.
1.2. MINERALOGY

Minerals of tungsten that occur in sufficient abundance to be of economic significance can be divided into two groups — the wolframite group and the scheelite group. These two groups will be discussed in some length followed by brief mentions of other minerals in Sec. 1.2.3.

1.2.1. Wolframite Group

The wolframite group consists of three minerals — ferberite, wolframite, and huebnerite. The iron-rich mineral is ferberite, the manganese-rich one is huebnerite, and wolframite contains between 20 and 80% of each in their pure forms. The physical and chemical properties of these minerals are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ferberite</th>
<th>Wolframite</th>
<th>Huebnerite</th>
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<tr>
<td>Formula (pure)</td>
<td>FeWO₄</td>
<td>(Fe,Mn)WO₄</td>
<td>MnWO₄</td>
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<tr>
<td>WO₃ content (%)</td>
<td>76.3</td>
<td>76.5</td>
<td>76.6</td>
</tr>
<tr>
<td>Mn content (%)</td>
<td>0-3.6</td>
<td>3.6-14.5</td>
<td>14.5-18.1</td>
</tr>
<tr>
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<td>14.7-3.7</td>
<td>3.7-0</td>
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<tr>
<td>Crystal structure</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Lattice parametersb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.71</td>
<td>4.79</td>
<td>4.85</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.70</td>
<td>5.74</td>
<td>5.77</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.94</td>
<td>4.99</td>
<td>4.98</td>
</tr>
<tr>
<td>β</td>
<td>90°</td>
<td>90°26'</td>
<td>90°53'</td>
</tr>
<tr>
<td>Cleavage</td>
<td>Perfect in one</td>
<td>Perfect in one</td>
<td>Perfect in one</td>
</tr>
<tr>
<td>direction</td>
<td>direction</td>
<td>direction</td>
<td>direction</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>7.5</td>
<td>7.1-7.5</td>
<td>7.2-7.3</td>
</tr>
<tr>
<td>Color</td>
<td>Black</td>
<td>Dark gray to black</td>
<td>Reddish brown to black</td>
</tr>
<tr>
<td>Tenacity</td>
<td>Very brittle</td>
<td>Very brittle</td>
<td>Very brittle</td>
</tr>
<tr>
<td>Luster</td>
<td>Submetallic to</td>
<td>Submetallic to</td>
<td>Submetallic</td>
</tr>
<tr>
<td>metallic</td>
<td>metallic</td>
<td>metallic</td>
<td>adammantine</td>
</tr>
<tr>
<td>Fracture</td>
<td>Uneven</td>
<td>Uneven</td>
<td>Uneven</td>
</tr>
<tr>
<td>Hardness (Mohs)</td>
<td>5</td>
<td>5-5.5</td>
<td>5</td>
</tr>
<tr>
<td>Magnetism</td>
<td>Sometimes feebly</td>
<td>Slightly magnetic</td>
<td>—</td>
</tr>
<tr>
<td>magnetic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streak</td>
<td>Dark brown</td>
<td>Dark brown</td>
<td>Brownish red to greenish yellow</td>
</tr>
<tr>
<td>Diaphaneity</td>
<td>Opaque to translucent</td>
<td>Opaque</td>
<td>Opaque to translucent</td>
</tr>
<tr>
<td>Common form of occurrence</td>
<td>Well-defined</td>
<td>Irregular masses</td>
<td>Radiating groups of</td>
</tr>
<tr>
<td>crystals, massive</td>
<td></td>
<td>radiating groups</td>
<td>thin-bladed</td>
</tr>
<tr>
<td>crystalline</td>
<td></td>
<td>of bladed crystals</td>
<td>crystals</td>
</tr>
</tbody>
</table>

* Li and Wang, 1955.
* Palache et al., 1951.
At high temperature these three minerals form a continuous solid solution series of iron and manganese tungstates. Huebnerite and ferberite may occur together in a deposit, since the temperature of formation of many tungsten deposits is below the limit of miscibility. It has been suggested that the gap in miscibility between FeWO$_4$ and MnWO$_4$ at low temperatures could be used as a geological thermometer, provided that there is sufficient manganese present.

The detection of calcium in the wolframite series is probably due to inclusions of scheelite. Niobium, tantalum, and scandium have been detected in the wolframite series and are believed to be due to the presence of ScNbO$_4$ and FeNb$_2$O$_6$ and their corresponding tantalum compounds (Goldschmidt and Peters, 1931).

Ferberite was named after Rudolph Ferber of Gera, Germany. It is commonly elongated (010) and somewhat flattened (100); usually striated (001) (Palache et al., 1951). The crystals often have a wedge-shaped appearance (Fig. 1.1).

Wolframite is commonly short prismatic (100), less frequently long prismatic, and somewhat flattened or tabular (100), usually striated (001) (Palache et al., 1951) (Fig. 1.2).

Huebnerite was named in honor of Adolph Huebner of Freiberg, Germany. It is commonly prismatic to long prismatic (001), often flat tabular (100), striated or furrowed (001) (Palache et al., 1951) (Fig. 1.3).
Optical data as determined from polished surfaces of wolframite group minerals are as follows (Cameron, 1961): color gray, like sphalerite. Hardness E. Negative to all reagents. Shows cleavage in two directions. Reflection pleochroism very low, distinct at grain boundaries. Anisotropic effects are distinct. Extinction is inclined. Internal reflection with crossed Nicols and in oil is always visible, and seen rarely in air without crossed Nicols. Intensity of red color increases with rising

<table>
<thead>
<tr>
<th>Mineral</th>
<th>d Values of strongest lines (Å)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferberite(^a)</td>
<td>2.94 4.75 3.75 3.65 2.48 2.49 1.72 2.20</td>
<td>FeWO(_4)</td>
</tr>
<tr>
<td>Ferberite(^b)</td>
<td>2.94 4.69 3.75 3.24 2.47 2.35 2.19</td>
<td>FeWO(_4)</td>
</tr>
<tr>
<td>Wolframite(^c)</td>
<td>2.97 2.95 4.78 3.76 3.67 2.49 2.86 2.39</td>
<td>FeMn(WO(_4))(_2)</td>
</tr>
<tr>
<td>Wolframite(^d)</td>
<td>2.95 2.98 4.76 3.74 3.65 1.72 1.77 2.19</td>
<td>(Fe,Mn)WO(_4)</td>
</tr>
<tr>
<td>Huebnerite(^e)</td>
<td>3.00 2.95 4.84 3.78 3.70 2.50 2.88 1.73</td>
<td>MnWO(_4)</td>
</tr>
<tr>
<td>Scheelite(^f)</td>
<td>3.10 4.76 3.67 1.93 1.59 2.62 2.00 1.69</td>
<td>CaWO(_4)</td>
</tr>
<tr>
<td>Scheelite(^g)</td>
<td>3.11 1.60 1.94 1.25 4.77 1.69 1.56 1.09</td>
<td>CaWO(_4)</td>
</tr>
<tr>
<td>Anthoïnite(^h)</td>
<td>4.20 3.07 3.05 5.66 3.98 1.94 1.86 6.09</td>
<td>Al(WO(_4))(OH)(_2)</td>
</tr>
<tr>
<td>Anthoïnite(^i)</td>
<td>5.63 4.19 3.97 3.06 2.46 4.33 4.13 3.65</td>
<td>AlWO(_4)(OH)(_3)</td>
</tr>
<tr>
<td>Cuprotungstite</td>
<td>2.53 1.73 3.93 3.02 1.46 7.30 2.23 4.73</td>
<td>Cu(_2)WO(_4)(OH)(_2)</td>
</tr>
<tr>
<td>Ferritungstite</td>
<td>5.94 2.97 3.10 1.82 1.55 2.57 0.99 0.87</td>
<td>Ca(_2)Fe(_2)(WO(_4))(_9) H(_2)O</td>
</tr>
<tr>
<td>Raspite</td>
<td>3.22 2.76 2.62 2.71 1.81 3.59 3.48 2.91</td>
<td>PbWO(_4)</td>
</tr>
<tr>
<td>Russellite</td>
<td>3.12 1.64 1.92 2.71 1.25 1.22 1.58 1.11</td>
<td>B(_2)WO(_6)</td>
</tr>
<tr>
<td>Sanmartinite(^d)</td>
<td>2.93 2.91 3.73 4.69 3.62 2.47 2.46 2.86</td>
<td>ZnWO(_4)</td>
</tr>
<tr>
<td>Sanmartinite(^e)</td>
<td>2.93 1.70 2.47 4.68 3.62 1.76 3.73 2.18</td>
<td>(Zn,Fe,Ca,Mn)WO(_4)</td>
</tr>
<tr>
<td>Stolzite</td>
<td>3.25 2.02 1.66 2.73 3.01 1.78 1.93 1.63</td>
<td>PbWO(_4)</td>
</tr>
<tr>
<td>Tungstenite</td>
<td>6.18 2.28 2.73 2.67 1.83 1.58 3.09 1.53</td>
<td>WS(_2)</td>
</tr>
<tr>
<td>Tungstite</td>
<td>3.49 5.39 2.57 1.84 2.63 2.69 1.85 1.74</td>
<td>WO(_3) H(_2)O</td>
</tr>
</tbody>
</table>

\(^a\) ICCD, 1977.
\(^b\) Calculated pattern.
\(^c\) Sample from Tipserdorf, Olanitz, Germany.
\(^d\) Laboratory prepared sample.
\(^e\) Sample from Zehnwald, Bohemia.
\(^f\) Sample from Kernville, California.
\(^g\) Sample from Furstenberg, Schwarzenberg, Saxony.
\(^h\) Sample from Mt. Misogo, Kalima District, Belgian Congo.
\(^i\) Sample from Nyamulilo Mine, Uganda.
\(^j\) Sample from San Martin Province, San Luis, Argentina.
manganese content. It is difficult to distinguish between members of the wolframite series without chemical tests.

A field test for tungsten may be conducted in the following manner: Moisten a platinum wire bent into a loop about 3.2 mm across, and dip it into Na₂CO₃. Hold in a flame for 2 min to sinter. Fuse with a blow pipe flame; dip into powdered tungsten mineral and fuse again, after which the bead is plunged into 50% HCl. Heat the mixture over a flame until the bead is dissolved. If tungsten is present, the bead takes on a bright yellow color from the WO₃ formed. Add a few pieces of granulated zinc metal. If tungsten is present, a deep blue color appears.

X-ray data of these together with other minerals of tungsten are shown in Table 1.2.

1.2.2. Scheelite Group

The scheelite group contains only one economically important mineral — scheelite, CaWO₄ (Figs. 1.4 and 1.5). Molybdenum may substitute for tungsten in scheelite, forming a partial series with powellite, CaMoO₄, although most scheelite contains only a minor amount of molybdenum. The physical and chemical properties of scheelite are shown in Table 1.3. X-ray data for scheelite together with other minerals of tungsten are shown in Table 1.2.

Fig. 1.4. Scheelite on quartz — dark brown euhedral tetragonal crystals of octahedral habit perched on a quartz crystal, dimensions 5 × 4 cm, Tae Wha Mine, Chungchongpukdo, South Korea.

Fig. 1.5. Scheelite on quartz — dark brown euhedral tetragonal crystals of octahedral habit with quartz crystals, dimensions 4.5 × 4 cm, Tae Wha Mine, Chungchongpukdo, South Korea.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula (pure)</td>
<td>CaWO₄</td>
</tr>
<tr>
<td>WO₃ content (%)</td>
<td>80.6</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.257</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.373</td>
</tr>
<tr>
<td>a/c</td>
<td>1.2165</td>
</tr>
<tr>
<td>Cleavage</td>
<td>Good in four directions</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>5.4–6.1</td>
</tr>
<tr>
<td>Color</td>
<td>Pale yellow, brown, commonly white</td>
</tr>
<tr>
<td>Tenacity</td>
<td>Very brittle</td>
</tr>
<tr>
<td>Luster</td>
<td>Vitreous to resinous</td>
</tr>
<tr>
<td>Fracture</td>
<td>Uneven</td>
</tr>
<tr>
<td>Hardness (Mohs)</td>
<td>4.5–5</td>
</tr>
<tr>
<td>Magnetism</td>
<td>Nonmagnetic</td>
</tr>
<tr>
<td>Streak</td>
<td>White</td>
</tr>
<tr>
<td>Diaphaneity</td>
<td>Transparent to translucent</td>
</tr>
<tr>
<td>Common form of occurrence</td>
<td>Massive and in small grains; exists sometimes as pseudomorph after wolframite. Commonly as tetragonal crystals.</td>
</tr>
</tbody>
</table>

* Li and Wang, 1955.
* Palache et al., 1951.

Optical data for scheelite are as follows (Palache et al., 1951): The mineral is optically (+), \( n_o = 1.918, n_e = 1.934 \) (Hurlbut, 1971). (A plus sign indicates \( n_e < n_o \), \( n \) designates refractive index, subscript “e” designates extraordinary ray, and “o” designates ordinary ray.)

The fluorescence of scheelite can be used as a field test. It fluoresces a bright bluish white under the influence of shortwave ultraviolet radiation. The presence of molybdenum in the mineral modifies the color of fluorescence, changing it progressively from blue to cream, pale yellow, and orange as the content of molybdenum increases.

### 1.2.3. Minor Tungsten Minerals

#### 1.2.3.1. Anthoineite, \( Al(WO_4)(OH)\cdot H_2O \)

White chalky mass; hardness (in Mohs’ scale) = 1; specific gravity = 4.6. Found in placers at Mt. Misobo, Kalima district, Maniema, Belgian Congo (Palache et al., 1951). Anthoineite was named after Raymond Anthoine, a Belgian mining engineer. X-ray data of anthoineite are shown in Table 1.2.

#### 1.2.3.2. Cuprotungstite, \( Cu_2(WO_4)(OH)\)₂

Cuprotungstite is found as microcrystalline green masses. Luster is vitreous, also waxy to earthy. Strongly birefringent with a mean index of refraction of 2.15
(Palache et al., 1951). X-ray data are shown in Table 1.2. Cuprotungstite is a secondary mineral formed by the alteration of scheelite. It is found at Cave Creek, Maricopa County, Arizona, and also at La Paz, Mexico, and Llamuco near Santiago, Chile (Palache et al., 1951).

1.2.3.3. Ferritungstite, $\text{Ca}_2\text{Fe}^{3+}_2\text{Fe}^{3+}_2(\text{WO}_4)_3\cdot 9\text{H}_2\text{O}$

Ferritungstite is found as earthy coatings composed of microscopic hexagonal plates. Specific gravity: 5.57; color pale yellow to brownish-yellow. Optically (−), $n_o = 1.80$, $n_e = 1.72$ (Palache et al., 1951). (A negative sign indicates $n_o < n_p$) X-ray data are shown in Table 1.2. Ferritungstite is found as an alteration product of wolframite at the Germania Mine, Deer Trail District, in northeastern Washington and also in Cerro Liquinaste, Jujuy, Argentina (Palache et al., 1951).

1.2.3.4. Raspite, $\text{PbWO}_4$

Monoclinic; prismatic. Crystal habit usually tabular (100), striated parallel (010). Twinning common; cleavage perfect. Hardness = 2.5–3, specific gravity = 8.46. Color yellowish brown, light yellow, gray (Palache et al., 1951). Raspite was named for Charles Rasp, the discoverer of the Broken Hill Mines. X-ray data of this mineral are shown in Table 1.2; and optical data are shown in Table 1.4. Raspite is found at the Proprietary Mine, Broken Hill, New South Wales and also found in tin veins on the Cerro Estano, east of Guanajuato, Mexico (Palache et al., 1951).

1.2.3.5. Russellite, $\text{Bi}_2\text{WO}_6$

Tetragonal; scalenohedral. Crystal habit is fine-grained compact massive. Hardness = 3.5, specific gravity = 7.35. Color pale yellow to green (Palache et al., 1944). Russellite was named after the British mineralogist Arthur Russell. X-ray data of this mineral are shown in Table 1.2. Russellite occurs as an alteration product of native bismuth with wolframite at the Castle-an-Dinas Mine, St. Columb Major, Cornwall, England.

<table>
<thead>
<tr>
<th>Table 1.4. Optical Data of Raspite$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation$^b$</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>$X$</td>
</tr>
<tr>
<td>$Y \parallel b$</td>
</tr>
<tr>
<td>$Z \wedge c \sim 30^\circ$</td>
</tr>
</tbody>
</table>

$^a$ Palache et al., 1951.

$^b$ $X$, $Y$, and $Z$ in the indicatrix indicate, respectively, the directions of low, intermediate, and high refractive indices; $b$ and $c$ are crystal axes; $\wedge$ indicates the angle between two faces of a crystal.

$^c$ $2V$ is the optic axial angle in the mineral.
1.2.3.6. Sanmartinite, $\text{ZnWO}_4$

Monoclinic; prismatic. Crystal habit as fine granular masses and sometimes, microscopic tabular crystals. Cleavage perfect; luster resinous. Color dark brown to black. Microscopic crystals are reddish brown with red internal reflections. Specific gravity 6.70 (Palache et al., 1951). X-ray data are shown Table 1.2. Sanmartinite is found with willemite as an alteration of scheelite at Los Cerrillos, near San Martin, San Luis Province, Argentina.

1.2.3.7. Stolzite, $\text{PbWO}_4$

Tetragonal; pyramidal; Usually dipyramidal, also thick tabular. Prism faces horizontally striated, cleavage (001) imperfect, fracture conchoidal to even. Brittle. Hardness $= 2.5–3$; specific gravity $= 7.9–8.3$. Luster resinous. Color reddish brown, yellow, green, and red (Palache et al., 1951). Stolzite is optically uniaxial ($-$), $n_o = 2.27$; $n_e = 2.19$ (Palache et al., 1951). Stolzite was named in honor of Dr. Stolz of Teplitz, Bohemia, Germany. X-ray data are shown in Table 1.2. Stolzite is a secondary mineral found associated with limonite, cerussite, etc., in the oxidized zone of ore deposits containing primary tungsten minerals. It is found in the tin veins of Zinnwald, Germany, and with cerussite at Cumberland, England. It is also found at the Proprietary Mine, Broken Hill, New South Wales (Palache et al., 1951).

1.2.3.8. Tungstenite, $\text{WS}_2$

Tungstenite is hexagonal and found only massive in fine scaly aggregates. Hardness $= 2.5$; specific gravity $= 7.4$. Color dark lead gray; opaque (Palache et al., 1944). X-ray data are shown in Table 1.2. Tungstenite is pure white in polished sections with both anisotropism and pleochroism very strong. Tungstenite is found only at the Emma Mine, Little Cottonwood district, Salt Lake County, Utah.

1.2.3.9. Tungstite (Meymacite), $\text{WO}_3 \cdot \text{H}_2\text{O}$

Tungstite is orthorhombic. It is found massive, earthy, and as microscopic platy crystals. Cleavage (001) perfect. Hardness $= 2.5$. luster resinous. Color bright yellow to yellowish green. Transparent (Palache et al., 1944). X-ray data are shown in Table 1.2. Optical data of tungstite are shown in Table 1.5.

<table>
<thead>
<tr>
<th>Table 1.5. Optical Data of Tungstite (Meymacite)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation$^b$</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>$X \parallel c$</td>
</tr>
<tr>
<td>$Y$</td>
</tr>
<tr>
<td>$Z$</td>
</tr>
</tbody>
</table>

$^a$ Palache et al. (1944).

$^b$ $X$, $Y$, and $Z$ in the indicatrix indicate, respectively the directions of low, intermediate, and high refractive indices; $c$ is a crystal axis.

$^c$ $2V$ is the optic axial angle in the mineral.
Tungstite is an oxidation product of wolframite and other tungsten minerals. It has been found as an ore in considerable quantities at Easly and Juslee, east of La Paz, Bolivia. Pockets of tungstite have been found in some of the fergusonite mines in Boulder County, Colorado. It has also been found with huebnerite in the Anglo Saxon Mine near Silverton, Colorado; in the Ima Mine, Blue Wing District, Lemhi County, Idaho; and the Combination Mine at Black Pine, Montana.

1.3. GEOLOGY

1.3.1. General Information

The key to the geology of tungsten is an understanding of tungsten’s genetic relation to the igneous process and its associated ore deposits. All economic deposits of the four important tungsten minerals — scheelite, huebnerite, wolframite, and fergusonite — are formed through some sort of igneous activity. Considering the source for these tungsten ores, it is best to discuss and classify all deposits in terms of the magmatic-hydrothermal model.

The magmatic-hydrothermal model begins with a magma of any composition and from any source. As time progresses, the magma body will change its physical and chemical states. It will cool and may be intruded into a higher level of the earth’s crust. The net result of this change will be crystallization through the loss of temperature and pressure. As crystallization begins, relatively large amounts of iron, magnesium, calcium, and aluminium are used to form the basic rocks such as basalt and gabbro. This effectively enriches the remaining magma in silica, the alkalis, and a number of other compounds that will not fit into the structural framework of the common basic rock-forming minerals. As this crystallization proceeds, a series of rock types will form. The common intrusive varieties of this series consist, according to increasing silica content, of gabbro, diorite, granodiorite, monzonite, and granite.

The so-called “porphyry” copper deposits and the tin-tungsten deposits are two types of deposit that are often cited as requiring a specific magmatic source. While certain rock types have been found to relate to certain ore deposits, the idea of relating original magma source to certain ore deposits has not been sufficiently developed to be of any practical use at this time.

Goldschmidt (1954) classified tungsten as a mainly lithophile element (one that due to its chemical behavior was concentrated in the earth’s crust at an early time in its history). However, under certain reducing conditions, he found that tungsten would concentrate with iron as a siderophile element (one that was characterized by ready solubility in molten iron, hence concentrated in iron meteorites and probably in the earth’s core). This means that the earth’s interior (its mantle and core) might also be a source of tungsten. Aside from that crustal rocks contain more tungsten to begin with, tungsten deposits are related to igneous intrusions that appear to be products of crustal melting. Tungsten deposits of the western United States lie in two north-south bands and are closely associated with granodiorite, monzonite, quartz monzonite, and granite intrusives. These bands
grossly correspond to two bands of andesite, a rock now believed by many to be derived from the melting of crustal rocks. The tungsten–andesite–quartz latite (quartz latite is the fine-grained equivalent of quartz monzonite) association is observable in the Silverton caldera deposits in Colorado’s San Juan Mountains. Mid-Tertiary San Juan field caldera deposits in Colorado’s San Juan Mountains with andesite. As crystallization proceeded with time, the volcanic products switched to explosive, highly volatile quartz latite ash flows and related intrusives. The hydrothermal activity associated with this late-stage volcanism produced rich mineral deposits containing huebnerite.

The tungsten–andesite relation is not always as easy to see and understand as it is at Silverton, Colorado. However, the close association of tungsten with granodiorite, monzonite, and granite is much more obvious. Hence, this association is an excellent exploration tool.

In terms of bulk, the least significant part of magmatic–hydrothermal process is the pegmatite and hydrothermal activity. This takes place at the end of magmatic activity. Following the crystallization of most of the magma, a residual fluid remains that consists of any material that could not be used in the crystallization of rock-forming minerals. This fluid usually is made up of excess silica and, depending on the original magma composition, minor amounts of the alkalis, alkaline earths, metal ions, and volatiles. For ore deposition, the most important components are metal ions and volatiles, such as water and halogen, sulfur, and carbon compounds. If a magma is low in water and other volatiles, the residual fluid will form barren zones of silicification, simple pegmatites, or quartz veins. If volatiles and metal ions are present, complex pegmatites, greisen, and “porphyry” copper deposits or hydrothermal vein deposits may form.

Tungsten owes its place in this residual fluid to its chemistry. The tungsten ion is the wrong size and charge for easy substitution for iron, magnesium, calcium, aluminum, or silicon, the major elements that fill the structures of the rock forming minerals. The same is true for the complex $\text{WO}_4^{2-}$. It cannot substitute for aluminum or silicon complexes. This allows any tungsten that might be in the original magma to be concentrated in the residual field as $\text{WO}_4^{2-}$.

Scheelite, huebnerite, wolframite, and ferberite all occur in pegmatites. The tungsten minerals often occur with cassiterite, molybdenite, chalcopryite, and pyrite. This association has a high-temperature genesis. Quartz, several feldspars, and micas always make up the bulk of any pegmatite. Common ore pegmatite accessories consist of tourmaline, garnet, topaz, and fluorite. Where scheelite occurs, a suite of calcium silicates may also occur.

Although the difference between hydrothermal and pegmatite systems is gradational, a division is made on temperature of formation and the products of the fluids involved. Pegmatites are formed above approximately 550°C. The hydrothermal temperature range starts approximately 550°C and continues down to approximately 50°C. Main products of the latter process are quartz and calcite with ore minerals where conditions are appropriate. The pegmatite process may be viewed as the last step in stripping the late-stage magmatic fluid of its aluminum silicate mineral components. Hence, the remaining hydrothermal fluid is greatly enriched in silica, metals, and volatiles. The metals and volatiles that
began as minute percentages in the parent magma and have been concentrated in successive crystallization processes are now in sufficient quantities to form the ore minerals.

As the name hydrothermal, or hot water, suggests, the water and other volatiles are of prime importance to this fluid. Many hydrothermal deposits have been formed at some distance from their source. This requires transport of the mineral components and, when changes in the physical chemistry of the system occur, deposition of the minerals. Several characteristics of hydrothermal mineral deposits indicate that volatiles carry out this transport and deposition. Transport appears to be controlled and carried out by complex ions. Which complex ions are involved has developed into a major controversy (Barnes, 1967). Although chlorine and sulfur ion complexes have attracted the most attention as ore mineral transport agents, the presence of water and carbonyl species may also be important.

The physical state of the hydrothermal fluid also adds an important dimension to the transport mechanism. Lately, the general hydrothermal model treats the physical state of the fluid as supercritical, that is to say, under such high pressures that the fluid is liquid even at source temperature of as high as 600°C (Barnes, 1967). However, sudden releases of pressure through the fracturing that often accompanies igneous intrusion would cause “boiling” and the release of vapor phase. This vapor phase would exist until the system pressure reached equilibrium with the new volume of space available. Pressure releases of this sort could happen in numerous steps, causing the formation of several vapor phases with the subsequent resolution of the vapor into the supercritical fluid formed at the new lower pressure. The final step in this process is the release of vapors from supercritical fluids into a 1-atm environment. This can be observed at any geothermal area.

The deposits formed from these instantaneous vapor phases are treated separately by many geologists, especially Europeans. The validity of the genesis of these “pneumatolytic deposits” is questioned by many American geologists on the basis of the inability of vapors to transport ore minerals and the questionable formation of a true vapor phase from a “boiling” supercritical fluid. Experimentation has shown that gas transport of metal ions is possible, and the second part of the argument concerning the phase is perhaps more a semantic problem. From a purely practical approach, those interested in tungsten must consider the pneumatolytic approach because many tungsten deposits have traditionally been classed as pneumatolytic deposits. These include some pegmatite, contact zone, and vein deposits.

Evidence for the transport method of tungsten is even more tenuous than that of other metals, and little research has been done along this line. Tungsten occurs with other metals, which demonstrates that it can be transported by the same mechanism. However, a manmade “hydrothermal” tungsten transport and deposition system has come to light that presents additional evidence to the mainstream of thought on hydrothermal transport. Fireclay bricks from the stack of the old ferrotungsten smelter at Boulder, Colorado have been found to contain high quantities of tungsten. Microscopic examination of the bricks revealed that the
Table 1.6. Decreasing Temperature Series of Major Economic Ores

<table>
<thead>
<tr>
<th>Element</th>
<th>Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>Cassiterite</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Wolframite, scheelite, huebnerite, and ferberite</td>
</tr>
<tr>
<td>Copper</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Zinc</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>Lead</td>
<td>Galena</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentite and silver sulfosalts</td>
</tr>
<tr>
<td>Gold</td>
<td>Gold and gold tellurides</td>
</tr>
<tr>
<td>Antimony</td>
<td>Stibnite</td>
</tr>
<tr>
<td>Mercury</td>
<td>Cinnabar</td>
</tr>
</tbody>
</table>

tungsten and associated minerals permeated and replaced the fireclay, creating a manmade “mineral deposit.” The smelter feed consisted mainly of ferberite and quartz from the ore with carbon and fluorine from cooling coal and fluorite flux. Probably some water was also present from feed-contained moisture. Vapors containing the volatile fluorine, sulfur, carbon, and water and transporting tungsten, iron, and silica left the smelted material at over 1000°C (1-atm pressure) and traveled up the stack.

The end result of this manmade gas transport mineral deposit is very much like the natural ores that fed the smelter. The natural ore consists of ferberite and quartz, with minor pyrite and marcasite filling fissure veins. Associated alteration silicified and sericitized the granodiorite wall rock. Ferberite, wolframite, quartz, and pyrite filled fissures, and silica, sericite, ferberite, and wolframite altered the granitoid wall rock.

Temperature has been cited as a main cause of mineral zoning since before the turn of the century. As with the rock-forming minerals, hydrothermal minerals form at certain temperatures. As the hydrothermal fluid travels away from the source, its temperature drops, and a series of minerals is precipitated. The general decreasing temperature series in terms of the major economic elements is given in Table 1.6. Note that tungsten’s place in this series is at the high-temperature end. This generally places tungsten in near source high-temperature deposits such as pegmatites, greisens, contact metasomatic bodies, and high-temperature veins.

1.3.2. Classification of Tungsten Deposits

Tungsten ore deposits as a group are probably more easily genetically classified than the deposits of many other metals. This is because all economic tungsten deposits can be related to the magmatic–hydrothermal process. Thus, different tungsten deposits can be placed in a classification system according to what specific physical–chemical changes occur as the hydrothermal fluid moves away from the source.

The tungsten-bearing hydrothermal fluid may stay with the intrusive body, in close proximity, or it may be tapped off. If it stays with the intrusive, the two
products of the magma—the final rock type and the remaining fluid—may be sufficiently different that the hydrothermal fluid alters and mineralizes the intrusive rock. The fluid may also permeate and convert the surrounding rocks to a composition similar to that of the altered intrusive. This is particularly the case when intruded rocks are similar in chemistry to the intruding rocks. The product of this type of hydrothermal alteration, known as a greisen, is a granitelike rock made up of quartz, mica, and topaz, with tourmaline, fluorite, rutile, cassiterite, and wolframite. The ore minerals occur as disseminations and in veins, and the ore bodies may be in any shape and size, depending on the solution access.

A variation on the above type of deposit occurs when the intruding magma and accompanying hydrothermal fluids invade limestone. The acid fluids react violently with the limestone as they percolate out into the fractures developed during intrusion. Huge volumes of limestone can be altered to a calcium silicate rock known as skarn or tactite. As with the greisen, the ore fluids remain in close proximity to the intrusion, hence, the name “contact metasomatic” is used to describe the deposit. Because of the excess calcium available from the limestone, the tungsten ore mineral deposited is scheelite. Mineralization is disseminated, but grade can become quite high in given areas.

As a magma intrudes, it creates certain fracture patterns in the surrounding rock. These fractured areas are generally under lower pressures than the volatile hydrothermal fluids that are carried with the magma. This pressure differential may be so great, particularly in the case of shallow intrusives, that the released fluids literally explode into the fractures. If the rock is sufficiently fractured by the intrusive or by earlier unrelated events, the hydrothermal fluids may travel great distances from the parent magma. Temperature and pressure generally change rapidly as the fluid moves away from the magma. This physical change along with the chemical changes created by dissolved or precipitated elements, causes the solution to precipitate a series of minerals. These minerals fill the fractures and become the vein ore bodies.

Since mineralization is usually restricted by the tabular shape of the fractures, the ore bodies are also tabular. Veins may also intersect, forming a pipelike ore body at the intersection. All four main tungsten minerals occur in veins. Generally, they are in high- or medium-temperature deposits.

Although the tungsten minerals have the high specific gravity necessary for gravity concentration, none of the four major ore minerals is resistant to abrasion. This property reduces the chances for placer concentration. Hence, the ideal conditions close to a source that are necessary for the formation of a tungsten placer are rather rare.

In the following, examples of each category are described under the specific headings.

1.3.2.1. Pegmatite Deposits

Tungsten production from pegmatite deposits has been minor, although the Oreana Mine, Nevada, is an exception. Production has been from a 610-m (2000-ft)-long pegmatite dike that contained several high-grade ore bodies. The
discovered ore body was 30.5 m (100 ft) long, 22.9 m (75 ft) deep, 0.6–9 m (2–30 ft) wide, and, in places, consisted of almost pure scheelite. The geology of the area is described by Kerr (1946).

Pre-ore deposition geology in the Oreana area consists of west-dipping Triassic limestones and shales and older volcanics. These strata have been intruded by diorite sills and dikes that have been recrystallized to schistose metadiorite.

Three further periods of igneous intrusion followed the diorite. The first of these produced a granite porphyry that crops out mainly to the southeast of Oreana along the crest of the Humbolt Range. The granite of the tungsten depositional period appears to have intruded this porphyry; hence, the porphyry is older. However, the entire group of granitoid intrusives are close in age, and they may all be products of the same magma. The intrusions of the second period consisted mainly of granite with quartz monzonite. It is the aplite and pegmatite bodies related to this period of activity that carry the tungsten. The third intrusive period produced diabase dikes that are controlled by basin and range structures. Hence, these dikes are much later Tertiary features and are not related to the tungsten deposition.

The tungsten-bearing igneous period, probably late Cretaceous in age, began with the intrusion of a granitic stock in the eastern part of the Oreana area. Parts of this stock are quartz monzonite, probably due to assimilation of limestone during intrusion. Deuteric alteration has occurred, attesting to the volatile content of the parent magma.

Following the placement of the granite, a series of pegmatite–aplite dikes invaded the margins of the stock and the sediments and diorite to the west. These dikes are products of the final stages of the magmatism that produced the granite. They contain the mineral products of the volatiles and late differentiates, including tungsten, concentrated during the crystallization of the magma. Aplite and pegmatite dikes both occur at Oreana. Often, along a single continuous dike, the rock type will vary between aplite and pegmatite, depending on the local escape of volatiles. The control of volatile content at Oreana is apparently a stratigraphic one. As large volumes of aplite–pegmatite fluids moved out away from the intrusive center, they first encountered sedimentary rocks. These rocks were too porous to maintain the volatiles even in the larger dikes, and aplites were formed. Farther to the west of the intrusive–sediment contact, the fluids encountered diorite sills, and here, even though fluid volume was reduced, some areas of the diorite maintained volatile pressure, and both pegmatites and aplites were formed. As pegmatite dikes pass through the diorite into limestone, they die out entirely, leaving a silicified limestone.

Tungsten occurs in bodies of sufficient size and grade to make ore only in the pegmatites and in the contact bodies. The ore mineral is exclusively scheelite, which is to be expected with the limestone in the vicinity. Small uneconomic quantities of scheelite are also disseminated in the aplites. No tungsten has been found in the quartz monzonite or granite associated with the pegmatite.

The mineralogy of the pegmatite ore bodies is highly variable. In places it is nearly pure scheelite, and 30% WO₃ concentrates have been shipped directly. However, the mineral content can change abruptly to nearly pure quartz or fluorite.
Suites of typical pegmatite minerals such as orthoclase, oligoclase, microline, albite, quartz, muscovite, phlogopite, beryl, fluorite, zoisite, and garnet, make up the bulk of the tungsten-bearing material. Scheelite occurs in this groundmass as euhedral to anhedral masses associated with oligoclase and phlogopite. The scheelite replaces the oligoclase and is roughly contemporaneous with the phlogopite of this mixture. The entire mix appears to be a late stage of crystallization within the pegmatite suite. This places the scheelite late in the overall depositional sequence.

The contact ore bodies have a somewhat different mineralogy in that they contain lime silicate minerals. This is to be expected, considering the interaction between the pegmatite fluids and the limrstone. Commonly, contact bodies contain garnet, epidote, idocrase, zoisite, clinzoisite, and tremolite. Scheelite occurs as disseminated grains. The grade of these bodies is generally about 5% WO₃.

A few other mining districts in the United States are also noted for small quantities of pegmatite tungsten production. In the Black Hills of South Dakota, pegmatites of the Nigger Hill and Harney Peak districts contain wolframite, scheelite, huebnerite, and minor ferberite associated with cassiterite. At Silver Hill, southeast of Spokane, Washington, pegmatite dikes and related quartz veins carry scheelite and wolframite associated with tin. The Dixon Mine in the Hansonburg district, New Mexico, has been considered a pegmatite occurrence of huebnerite.

1.3.2.2. Greisen Deposits

The greisen mechanism can be related in many respects to features of the so called “porphyry” copper systems of the Southwest. However, the true greisen must be associated with granite intrusives and it must contain a given suite of alteration minerals, particularly topaz, tourmaline, quartz, and sericite. While many “porphyry” copper deposits meet some of these requirements, they are sufficiently different to fall into a separate genetic category.

The Climax, Colorado deposit (Wallace et al., 1968) is an exceptionally complex ore body. Actually, it consists of four intrusives closely associated in time and space, each with its own alteration and mineralization. This complex was intruded during the Oligocene into Precambrian gneissose schists and various igneous rocks and a full complement of Cambrian through Cretaceous sediments. Of the pre-Climax geology in the area, the most important is the structure of the Mosquito fault, which strike N 10° E, dips 70° W, and has a displacement of 2743 m (9000 ft). This fault zone is a major north–south structure that has been active at least since the Mesozoic. Its style is similar to many Colorado structures that have been active well back into the Precambrian. The Climax ore body lies to the west of the fault and surrounded by Precambrian rocks. The fault is a major crustal feature and it most likely provided the structural access for the Climax intrusions.

Although the four intrusive bodies were severely altered, all are thought to have been essentially similar chemically and mineralogically. For each intrusion, displacement occurred through stoping and forceful injection. This created a fractured hood zone above the advancing magma that was permeated with late-
stage volatile magmatic fluids. When active intrusion ended, these altered hood zones became the greisen ore bodies.

Fortunately, penetration decreased with each successive pulse of the Climax stock. Hence, the hood-shaped mineralized zones associated with each pulse have been preserved. Erosion, mine workings, and drillings have exposed these nested hood zones sufficiently so as to provide extensive data on the size, shape, and general makeup of the system. The present known ore mineralization covers an elliptical 914 × 1219 m (3000 × 4000 ft) area. The ore body related to the earliest intrusive pulse, the Ceresco ore body, is vertically the highest in the sequence. It has been almost completely removed by erosion. Below the Ceresco ore body is the hood of the upper ore body. The greater portion is intact and the majority of Climax’s production has been from this body. Below the upper ore body is the lower ore body, which is related to the third intrusive pulse. This is the lowest commercial mineralization, hence, it completes the known 762-m (2500-ft) vertical extent of the ore mineralization. Below the lower ore body is the hood-zone mineralization associated with the last intrusive pulse. Although it contains molybdenum and tungsten, it is not economically mineable. The upper ore body tungsten occurs as disseminated grains of huebnerite and wolframite in veinlets throughout a distinct zone along the upper and outer edges of the ore body hood. Associated minerals are pyrite, quartz, sericite, topaz, and fluorite. Cassiterite is also found in very low quantities in this zone. This association of tungsten, tin, and fluorine (topaz and fluorite) is typical of greisen deposits. The portion of the tungsten zone at the outer edge of the ore body places it later than the molybdenum in the ore-forming paragenesis. This seems out of sequence, since molybdenum generally is deposited later than tungsten and tin. However, the minerals of the system as a whole are compatible. The late occurrence of tungsten in this case must be attributed to characteristics of the system other than temperature.

Tungsten is also a by-product of the tin greisen deposits of Cornwall, England. However, tungsten is not always the by-product. The greisen and associated mineralization of Tavoy, Burma, and Kangsi, China, are mainly tungsten deposits with lesser amounts of tin and molybdenum. The Mt. Pleasant, New Brunswick, Canada, greisen deposit now being developed will apparently also supply more tungsten than molybdenum and tin.

1.3.2.3. Contact Metasomatic Deposits

Contact metasomatic deposits have been responsible for the production of much of the world’s tungsten. In the United States, most of the major California and Nevada deposits are of this type. Contact deposits are usually large and, like greisen deposits, lend themselves to open-pit or other large-volume operations. The Bishop mining district of California, (Gary, 1968; Bateman, 1965) is a classic example of a contact metasomatic tungsten deposit.

The Bishop district lies on the east slope of the Sierra Nevadas about 201 km (125 miles) east of San Francisco. The local geology is typical of the complexly structured Sierras. Strongly folded Paleozoic and Mesozoic sedimentary and volcanic rocks have been intruded and metamorphosed by numerous Cretaceous and early
Tertiary igneous bodies. Quaternary volcanic activity and erosion were the final steps in the development of the terrain that is present today.

The most important occurrence of the pre-ore deposit geological history was the deposition of the Paleozoic limestones and various calcareous sediments. These rocks, now the low- to medium-grade metamorphic equivalents of marble and calcareous hornfels, are the host rocks for the tungsten ore bodies.

Invasion of these limestones by plutons began in the Cretaceous with the intrusion of gabbro and quartz diorite. This was followed by a second series of intrusions consisting of quartz monzonites and granodiorites. The latest of the second series of intrusions, the Tungsten Hills quartz monzonite, is the product of the tungsten-carrying magma. It is a light gray, medium-grained porphyritic quartz monzonite with phenocrysts of orthoclase and a groundmass of quartz, orthoclase, plagioclase, biotite, and hornblende. Wherever the Tungsten Hills quartz monzonite is in contact with limestone, scheelite-bearing tactite has been developed. The third and last group of intrusions, which consisted of alaskite and quartz monzonite thought to be related to the widespread cathedral peak granite, occurred following ore deposition.

A well-developed contact metamorphic zoning pattern occurs along the limestone–quartz monzonite contact that serves as an additional guide to ore. Barren marble lies farthest from the quartz monzonite. The original limestone bedding is preserved. A zone of calcisilicate rocks, ranging in recorded thickness from a few centimeters to 24.4 m (80 ft), lies between the marble and the tactite.

The major portion of the tactite, known as normal tactite, is composed of garnet, pyroxene, amphibole, quartz, and plagioclase with minor epidote, vesuvianite, fluorite, and apatite. The thickness of the tactite zone ranges over 15.2 m (50 ft). It is within this normal tactite that most of the scheelite occurs. Aside from the normal tactite, there are three minor tactite variations. The light-colored tactite occurs in pods near the marble–tactite contact, and it is notable for its high scheelite content [scheelite has been found in masses up to 203 mm (8 in.) across]. Amphibole tactite contains major amounts of hornblende and occurs in pods and as a narrow separating zone between the tactite and the quartz monzonite. This tactite contains the highest copper values as chalcopyrite and bornite. A thin zone of epidote tactite rims the amphibole tactite between it and the quartz monzonite. Epidote is the major constituent of this tactite. Minor amounts of molybdenite and chalcopyrite can be found, but scheelite is rare. Local ore traps occur in limestone roof pendants and remnant blocks in the quartz monzonite and in irregularities along the intrusive–limestone contact. These areas were subjected to more intense alteration because of the relatively high ore fluid volume to limestone volume ratio in a given area. Limestone purity also had an effect on deposition. High-purity limestone has been more completely replaced than argillaceous limestone. Good scheelite-grade material runs 0.5% WO3. Veinlet scheelite occurs with quartz in late pneumatolytic or early hydrothermal process that crosscut all tactite structure. Scheelite is almost always associated with quartz, fluorite, and apatite. Molybdenite and copper is usually present.

Other contact metasomatic deposits in the United States occur in Nevada, California, Montana, Idaho, Utah, New Mexico, and Arizona. The Mill City,
Nevada, deposits have had an especially large production. Outside the Sierra Nevada states, the largest contact metasomatic scheelite is in the Browns Lake area, west of Dillon, Montana. Mexico, Brazil, South Korea, and Southeast Asia all have considerable production from contact metasomatic deposits. In all cases, there is a standard genesis. Igneous bodies ranging in composition from granite to quartz diorite have intruded limestone, producing a contact metasomatic scheelite-bearing tactite.

1.3.2.4. Vein Deposits

Hydrothermal vein deposits of tungsten have been important producers in the past. During the peak demand years of World War I, the Boulder County, Colorado, vein deposits supplied most of the United States' tungsten needs. Because of the recent development of and need for low-cost open pit mining methods, the Boulder County and other high-grade vein deposits are dormant.

The Boulder County tungsten district, described by Lovering and Tweto (1953), lies along a belt 3.2 km (2 miles) wide and 19.3 m (12 miles) long centered about 12.9 km (8 miles) west of Boulder, Colorado. Several famous gold and silver mines lie around the fringes of the tungsten district. Although Paleozoic and Mesozoic sedimentary rocks lie nearby at Boulder to the east of the tungsten district, the mineralization is entirely in Precambrian igneous and metamorphic rocks. The most widespread country rock is the Boulder Creek granodiorite. At the west end of the district, the Idaho Springs schists underlie the area. These quartz–feldspar biotite–sillimanite schists are older than the Boulder Creek batholith. Both rock types have been invaded by numerous pegmatite and aplite dikes, which represent the late phases of the granodiorite. The youngest Precambrian rock type is the Silver Plume granite, which crops out as dikes and stocks throughout the district.

The ore deposits have been related to one of a series of early Tertiary dikes and stocks. These consist of gabbro, hornblende monzonite porphyry, hornblende latite porphyry, limburgite porphyry, trachyte porphyry, and biotite latite porphyry. The biotite latite porphyry, the last of the major Tertiary intrusive rock types carries traces of tungsten. This, along with field data that indicates that these intrusions just preceded ore deposition, has led to the conclusion that the ore-forming solutions were derived from the magma that produced the biotite latite porphyry.

Regional structure has an important role in ore deposit control. There are two major fracture trends in the tungsten district: northwest and northeast. Although there is no direct evidence that this set has been operative since the Precambrian, it is assumed that it is part of the dominating northwest–northeast pattern that is such an important part of the Precambrian to Recent Colorado structural style.

Late Cretaceous or early Tertiary activity along the northwest structural trend developed massive vertical fault breccia zones. These are known locally as breccia “reefs” because later silification has made them resistant to erosion. In the tungsten district, the “reefs” are 3.2–4.8 km (2–3 miles) apart, range from 3.05 to 15.3 m (10–50 ft) wide, and they can be traced for many kilometers across country. The reefs do not contain economic quantities of tungsten. Major minerals present in the siliceous matrix are quartz and hematite.
The northeast structural trend is represented by faults and fractures which may be complementary to the breccia "reefs" or, as some field evidence suggests, may have formed later than the silicification of the reefs. Faults along this trend are numerous. However, they are not as well developed as the breccia "reefs." Their strike will vary from east to north and their dip, although generally near vertical, can be as little as 30°. Both strike and dip are influenced by the foliation trends of the country rock. Widths range from a few centimeters to a few meters and lengths can rarely be traced for more than 1.6 km (1 mile).

The tungsten ore deposits are located in the northeast trending fractures. Almost invariably, the best deposits are found at or near the intersections of the northeast fracture with the breccia "reefs." Although there is some controversy about timing, it appears that the breccia "reefs" served as conduits for the ore solutions. As solutions moved out into cooler intersecting northeast fractures, the ore minerals were deposited. Ore was never deposited in the breccia "reefs," because the conduit was physically and chemically in phase with the solutions throughout the period of ore element transport. Along the northeast fractures, width and length of veins and ore shoots were controlled by fracture intersections and cymoid loops. (A cymoid loop is created where movement along a fracture of changing strike or dip produces an open space.) A good ore shoot may be 30.5 m (100 ft) long, equally as deep, and 0.6–0.9 m (2–3 ft) wide.

Ferberite, along with quartz and wall rock breccia make up better than 99% of the ore. Very minor amounts of wolframite, scheelite, pyrite, and marcasite also occur in the ore. Base and precious metal minerals are very rare. Ferberite usually occurs in the veins as cement for altered wall rock fault breccia, High-grade ore has a striking appearance with the black massive or crystalline ferberite enclosing the angular white breccia fragments. Numerous small, subrounded, peanut-sized breccia fragments are so common in some high-grade ore that it is known as peanut ore by the miners.

Usually, ferberite is mixed with quartz in varying quantities, ranging from 2 or 3% and up. Very fine ferberite grains in quartz are known as horn tungsten, and even though it may occasionally carry several percent WO₃, horn tungsten has yet to be milled profitably.

The source of the tungsten has been tied to the biotite latite; however, the conditions of deposition and other points concerning the genesis of the deposits are not well understood. The presence of low-temperature quartz and marcasite with the ferberite has been used to support the hypothesis that the deposits are low temperature. The spatial relation of normally low-temperature precious metal deposits situated around the normally high-temperature ferberite district has been used to formulate a zoning system for Boulder County. These two approaches could be reconciled with a xenothermal system or near-surface rapid discharge of, and deposition by, mineralizing fluids. However, many of the standard features of a xenothermal deposit, such as complex mineralization, are lacking.

One of the problems with the determination of the genesis of the Boulder County tungsten deposits is the lack of up-to-date comprehensive investigations. The last detailed work (Lovering and Tweto, 1953) was done over 20 years ago. Many of the conclusions concerning the physical chemistry of the genetic system
have been antiquated by the great volume of geological understanding developed during the intervening years. Another problem is the lack of an integrated study of all Boulder County mineral deposits. The spatial and structural relations are such that they must be considered together. Misinterpretation of old mine data has also hindered the understanding of the deposits. There is a published belief that all Boulder County deposits are shallow, generally less than 107 m (350 ft) deep. This idea is based on the fact that most of the mines are no deeper than that figure. Actually, the mines are shallow because the equipment available to the small miner at the time was incapable of mining deep deposits. Where large operations developed the deposits, many deeper ore bodies were worked.

Vein tungsten deposits of varying economic importance occur in every state west of the Rocky Mountains and in South Dakota. Major vein production has come from South Dakota, Colorado, Idaho, Nevada, and California. In the Black Hills of South Dakota, wolframite occurs in quartz veins. Following the Boulder County deposits in importance in Colorado are the Silverton district hubeberite deposits. Huebnerite with minor molybdenite and base metal sulfides occurs in quartz veins related to the Silverton volcanic caldera. At the Ima Mine, Lemhi County, Idaho, hubeberite is associated with molybdenite, pyrite, chalcopyrite, bornite, sphalerite, tetrahedrite, rhodochrosite, and fluorite.

While the wolframite group of tungsten minerals predominates in the Rocky Mountain states, scheelite is the main vein tungsten mineral in the Sierra Nevada states. The majority of the California and Nevada deposits are contact metasomatic. However, highly productive veins occur at Atolia, California, and Silver Dyke, Nevada. At Atolia, scheelite is found in quartz veins up to 3.05 m (10 ft) wide to a known depth of 366 m (1200 ft). The Silver Dyke deposits consist of scattered scheelite in a quartz vein system that can be traced for over 9.7 km (6 miles).

Except for the vein deposit of Henderson, North Carolina, tungsten occurrences in the eastern United States have been essentially only of academic interest. At Henderson, hubeberite with minor scheelite and sulfides occurs in quartz veins in and around a granodiorite intrusive. The source of the tungsten is considered to be the granodiorite. The granodiorite and associated metamorphism is Paleozoic rather than Tertiary. This, of course, is a reflection of the different ages of tectonism in the East and in the West. Furthermore, the granodiorite is thought by some to be partly or wholly metamorphic. If that is the case, it introduces an entirely different approach to the possible source of tungsten in ore deposits.

The great Chinese tungsten production has been mainly from veins, although all types of deposits are present (Li and Wang, 1955). The ore consists of wolframite and minor scheelite with quartz. Topaz, fluorite, bismuthinite, molybdenite, and other sulfides also occur. The veins are associated with granite intrusions into sediments. The Burmese deposits in Mawchi, Merguir, and Tavoy districts are similar. Both areas are thought to be high-temperature occurrences, with gradations between greisen, pegmatite, and vein deposits. In Bolivia, there are several mining districts in the tin belt where wolframite occurs with tin in quartz veins. The Beira Beixa, Portugal, deposits are famous for crystal specimens of wolframite from quartz veins.
1.3.2.5. Other Types of Deposits

Tungsten deposits can be classified into a few major types of occurrences. However, as with any element, there are subclassifications or unusual occurrences that must also be dealt with.

A. Pneumatolytic Deposits

The term “pneumatolytic” can apply to any deposit where gas transport of minerals has been a major mechanism in the genesis. Although tungsten minerals are generally deposited at high temperatures, a situation could arise where the late-stage volatile fluids of a magma were suddenly released through fracturing of overlying rock. Superheated gaseous mineralizing fluids would then escape and deposit as they encountered lower temperatures and pressures and changing chemistries. Irregular pods of scheelite in limestone with no connecting vein structure have been thought to result from this mechanism. The scheelite deposits of Olson Gulch, Silver Lake, and Georgetown Lake, Deer Lodge County, Montana, are of this type.

B. Replacement Deposits

Replacement ore bodies result from special circumstances encountered during transport and deposition of ore-forming fluids. The term is descriptive rather than genetic. It is generally used for massive replacement of country rock by ore minerals. However, replacement of barren rock by an assemblage of minerals including disseminated ore minerals can also be referred to as a replacement deposit. Massive replacement usually occurs when ore fluids traveling in fractures through nonreactive rock reach a reactive rock such as limestone. The chemical reaction between fluids and limestone results in the replacement of large areas of limestone with ore. The contact ore bodies at Oreana, Nevada, and the Deer Lodge County, Montana, pneumatolytic deposits described earlier are examples of replacement.

Disseminated replacement deposition can be said to occur in several types of deposits. The Climax greisen deposit and any contact metasomatic deposit can be called disseminated replacement bodies. While the use of the term “replacement” is redundant with these deposits, there are some cases where it is helpful. The Yellow Mine near Stibnite, Valley County, Idaho, is best described as a disseminated replacement in a shear zone. This deposit was apparently fed by fractures, and it might have remained a vein deposit had it not been for the fluids entering an intensely sheared fault zone. The wide area of fault gouge and breccia provided permeability for the fluids and a large material surface area for the reaction of the fluids with the country rock. The result is a disseminated replacement scheelite deposit in the shear zone.

C. Hot Spring Deposits

The hot spring is generally considered to be the low-temperature surface expression of the hydrothermal system. Since tungsten precipitates at higher
temperatures than those found in hot springs, it is not expected to reach the surface in solution. However, at Golconda, Nevada, deposits that are obviously of hot spring origin have produced considerable tungsten. The tungsten occurs in amorphous iron and manganese oxides interspersed with calcareous and siliceous hot spring deposits. The ore beds can run as high as 6\% WO₃. Chemical treatment is required to remove the tungsten. It is not known what physical–chemical conditions prevailed to keep the tungsten in solution until the fluids reached the surface.

D. Secondary Enrichment Deposits

Secondary enrichment of tungsten deposits is extremely rare. Although tungstite does occur as a weathering product of all the four main tungsten minerals, it is not normally a major mineral in economic deposits. The Boulder County, Colorado, ferberite mines often encountered pods of tungstite in weathered portions of the vein. However, these pods were only economic when they were mined with the primary ores.

Tungstite deposits at Easly and Juslee, east of La Paz, Bolivia, are the only known economic secondary tungsten mines. The primary minerals consisted of wolframite and ferberite in veins. Deep weathering of these veins converted the iron manganese tungstates to tungstite.

E. Placer Deposits

Minor tungsten production has come from placer deposits in many of the world's tungsten districts. Ferberite, wolframite, huebnerite, and scheelite, though easily broken down mechanically, are all heavy and chemically resistant. Hence, they will be concentrated by erosion and deposition. Scheelite gravels collected in sediments down slope from the Atolia, California, vein deposits have been mined successfully. Boulder County streams locally concentrated ferberite sufficiently to allow mining of the deposits.

1.4. MINING

1.4.1. General Information

1.4.1.1. Distribution and Scope

The estimation of tungsten concentration in the earth's crust ranges from 1 to 1.3 ppm (Hobbs and Elliot, 1973) and ranks about 18th among the metals and 26th among the elements in relative abundance.

Tungsten is mined in many countries; the five largest in order of importance for recent years were China, Russia, South Korea, United States, and Bolivia, with China possessing about 50\% of the world reserves (see Table 11.1). The tungsten mining industry worldwide is comprised of 20 or so substantial steady producers
<table>
<thead>
<tr>
<th>Country and name of mine</th>
<th>Tungsten mineral</th>
<th>Ore production (mtpd)</th>
<th>Average grade (%WO₃)</th>
<th>By-product</th>
<th>Mining method</th>
<th>1973 Production (mt contained tungsten)$^\text{a}$, Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine Creek</td>
<td>Scheelite</td>
<td>1800</td>
<td>0.6</td>
<td>Mo, Cu</td>
<td>Sublevel stoping</td>
<td>3202,</td>
</tr>
<tr>
<td>Canada</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canada Tungsten Mining Co.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Room-and-pillar and backfill</td>
<td>2084,</td>
</tr>
<tr>
<td>Australia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>King Island</td>
<td>Scheelite</td>
<td>450</td>
<td>1.6</td>
<td>Cu</td>
<td>Room-and-pillar and cut-and-fill</td>
<td>1156,</td>
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<td>South Korea</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sang Dong</td>
<td>Scheelite</td>
<td>900</td>
<td>0.5</td>
<td>Mo</td>
<td>Room-and-pillar and cut-and-fill</td>
<td>1250,</td>
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<td>Brazil</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Brejui</td>
<td>Scheelite</td>
<td>1620</td>
<td>0.7</td>
<td>Bi, Mo</td>
<td>Pillars and cut-and-fill</td>
<td>2000,</td>
</tr>
<tr>
<td>Portugal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Panaqueira</td>
<td>Wolframite</td>
<td>1600$^\text{b}$</td>
<td>0.26</td>
<td>Sn, Cu</td>
<td>Longwall</td>
<td>348, 995,</td>
</tr>
<tr>
<td>Bolivia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chojilla</td>
<td>Wolframite</td>
<td>1800$^\text{b}$</td>
<td>0.32</td>
<td>Sn</td>
<td>Underground</td>
<td>1502, 1502,</td>
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<td>Sweden</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yajoberg</td>
<td>Scheelite</td>
<td>500</td>
<td>0.3</td>
<td>Cs, fluor spar —</td>
<td>234$^c$</td>
<td>234$^c$, 234$^c$,</td>
</tr>
<tr>
<td>Russia</td>
<td>Scheelite</td>
<td>1200</td>
<td>0.3</td>
<td>Mo</td>
<td>Sublevel stoping</td>
<td>4619$^c$, 4619$^c$,</td>
</tr>
</tbody>
</table>

$^\text{b}$ Estimate.

[over 300 mtpd (metric tons per day)] and innumerable intermittent and smaller or short-lived operations. Generally, one or two mines dominate the tungsten output of each producing country (Table 1.7, Fig. 1.6). Small deposits, however, have made a significant impact on the market when prices are high. This response to the market is particularly pronounced in the United States where mobilization tends to be more rapid than in the other countries. Bolivia and Brazil, for instance, rely heavily upon increased hand labor in response to price incentives, and increased output is much slower.

Content of tungsten ores occasionally ranges up to several percent WO₃ content, but such rich ores are uncommon and represent small tonnages. Probably, the highest-grade ore body of important size (with the possible exception of mines in China) was the Canada Tungsten Mining Company deposit near the Yukon border. The initial ore body contained about 1,000,000 mt of ore at 2.47% WO₃. The Union Mine of Atolia, California, was reported to have averaged 4% WO₃ from 1909 to 1940. Little data on the content of China’s tungsten mines are available, but it is known that certain mines contain numerous wolframite veins with 2.5% or more WO₃. Bolivia has some deposits that are similar to those of China and range up to 2.5% WO₃ in veins with wolframite and tin. The largest mines in Australia, Portugal, South Korea, and Brazil have average WO₃ contents less than 1%. The average for the larger mines in the United States is about 0.6%; that in Brazil is
very close to that in the United States. The lower limit of WO₃ content of tungsten mines varies somewhat with the market and local cost factors. The approximate average lower limit of ore grade for mines in the United States is about 0.3% WO₃ (possible only with extensive mechanization during favorable economic periods).

Tungsten mines of the world are comparatively small and rarely produce more than 2000 mtpd of raw ore. The maximum size of tungsten operations is limited by the nature of tungsten ore bodies that do not occur in huge ore bodies mineable solely for tungsten. Few tungsten deposits are known in which it has been possible to block out more than a few million metric tons of ore at one time. Open pit methods have been used at a few mines, such as the King Island mine, Australia, and Canada tungsten, Northwest Territories, Canada, but these are exceptions and do not exceed about 1000 mtpd. Most open-pit tungsten operations are short lived and are soon converted to underground methods as the deposit is followed to greater depths.

Underground mining is almost always necessary, and the particular method is determined by the following factors: (1) size, shape, and attitude of ore body; (2) competence of ore zone and wall rocks; and (3) continuity and grade of ore body. Common methods of mining ore are open stoping, shrinkage, room and pillar, sublevel stoping, cut-and-fill, and square set. There are variations of each method and some mines use more than one method simultaneously; others progress from one method to another to improve efficiency.

Tungsten deposits occur universally in association with metamorphic rocks and granite igneous rocks. The most common metamorphic rocks are marble, gneiss, schist, skarn, hornfels, quartzite, and slate. Such rocks are always crystalline, usually dense, and commonly hard. From a mining standpoint, they are also generally considered competent when encountered in mine workings. Exceptions are found in deposits where there has been extensive shearing, fracturing, or wall rock alteration (see Sec. 1.4.2.6).

1.4.1.2. Brief History

Tungsten mining in the world became significant around 1900 with the rise of production in the United States, Bolivia, Australia, Spain, and Portugal. In 1905, world production rose to about 1720 mtpy (metric tons per year) of contained tungsten. Production increased to a maximum peak of 6820 mtpy before World War I and was marked by sharp increases during the periods of World Wars I and II and the Korean conflict. For more details and recent world production, the reader is referred to Sec. 11.2.1.

The discovery of tungsten in China in 1911, with the subsequent large supplies of concentrates placed on world markets, changed the pattern of trade and made China the potentially dominant factor in the world tungsten market after 1918. Among the current major producing countries (see Table 11.1), Canada, Brazil, and South Korea entered the tungsten mining industry only in recent years.

Tungsten mining began in the United States in a small way in 1898 in Connecticut, South Dakota, and Arizona (Hobbs and Elliot, 1973) and in 1899 in
Colorado. The Boulder District of Colorado became the first important producer, with an output of 20 mtpy of metal in 1900. A few years later, tungsten was discovered in the Atolia District of California, and by 1917, these two districts together reached peak outputs totaling about 2000 mtpy, equivalent to 76% of domestic tungsten production. Production followed from new districts in California, Nevada, Idaho, and Montana with the last new district found in North Carolina in 1942.

Tungsten mines almost invariably have their own mill located at the mine site. Mines, regardless of size, can justify their own mill more easily than they can justify haulage costs of raw ore over long distances. Custom mills for toll treatment of ores are uncommon, and they have therefore been unavailable to the vast majority of mines. A typical tungsten mine in the various districts of the world consists of an integrated mining and milling operation producing wolframite or scheelite concentrates customarily running from 60% to 75% WO₃. By-products occurring in some deposits with the tungsten and sold also as concentrates include tin, bismuth, molybdenum, and copper.

Transportation used in conjunction with the previously noted mining methods has been conventional track haulage with small 1½- to 5-ton electric or diesel locomotives, some hand tramming, hoisting with small skips or buckets (usually unbalanced), and scraping with air-driven or electric double-drum scrapers.

Except for a few large mines where long-range development may be justified, mining proceeds along with as much development work as is necessary to maintain immediate production requirements and with as many development headings as possible advanced in ore.

In the realm of mine safety and health, no problems have been presented that are peculiar to tungsten mining. Other than the universal problem of associated silica dust, tungsten minerals are not toxic, nor are its associated minerals toxic or radioactive, and the mines are not gassy. Likewise, in the realm of pollution, tungsten mines present no special problems since they are primarily small-tonnage underground operations.

1.4.2. United States

Important tungsten deposits lie essentially in two north–south zones in the western states (Li and Wang, 1955). The principal tungsten districts in the United States are shown in Fig. 1.7 (NMAB, 1973; Lemmon and Tweto, 1962). The available information of major individual mines in this country are described in the following sections in alphabetical order. For more detailed geological zones or deposits, the reader is referred to Lemmon and Tweto (1962).

1.4.2.1. Black Rock Mine

The mine is located 35.4 km (22 miles) northwest of Bishop, California, in the Benton Range, at an altitude of 2134 m (7000 ft).
Fig. 1.7. Principal tungsten districts in the United States (NMAB, 1973). Solid circles indicate production and resources more than 20,000 tons (9091 mt); open circles indicate other significant production or resources; double circles indicate tungsten in Searles Lake brines.

A. History and Production

1916 Discovered.
1928–1930 Operated by A. E. Beauregard on a small scale intermittently, with a 24 mtpd mill.
1931–1937 Inactive.
1937–1941 Tungsten Corporation of California formed and 135 mtpd gravity mill erected; 104,000 mt ore were mined until closure in 1941.
1942–1947 Property reverted to Beauregard, and 75,530 mt ore were mined during this period.
1948–1949 Property leased to Tungsten Corporation and 1820 mt ore were mined.
1950–1957 Leased and operated by Wah Chang Corporation, the mine was operated at a rate of 356–455 mtpd by 1955, with a total production for the mine about 273,000 mt ore rating 0.5% WO₃. The operation was halted in July 1957.

B. Geology

The Black Rock Mine is developed in a contact metamorphic deposit with tactite and calcareous rocks overlain by quartz-sericite hornfels. The formation has been intruded by a stock of Jurassic granite, but the contact is not exposed in the mine area. The mine lies at the crest of a north-plunging anticline in a large body
of tactite, which is the most abundant rock in the mine area. The tactite is interbedded with lenses of calcisilicate hornfels and marble and is in the form of elongated layers exposed mainly on the crest and west limb of the anticline (Rinehart and Ross, 1957). Scheelite is irregularly distributed through the tactite. The only obvious control of scheelite is the folding, since most of the ore occurs on the crest of the anticline, and on the gently dipping west limb of the fold.

The ore bodies have been exploited in six locations, and are irregular and unpredictable in size and shape.

C. Mining

In addition to three open pits, the mine was developed by five main levels at about 30-m intervals and included 10,000 m of drifts interconnected by raises, manways, and stopes. The deepest level was the 1980 m (above sea level) and all but the 2012-m level had an adit to the surface (Johnson and Fillips, 1959).

Underground mining practice was essentially open stope. The ore shoots were so erratic that they could not be blocked out by any consistent system in advance of mining, and ore was mined as it was developed.

Development drifts were driven along one wall of a zone, then test holes were drilled to the opposite wall and between levels. In low-dipping ore shoots (15° or so), double-drum scrapers were used to advance drifts up dip and were spaced on convenient centers. Diagonal headings were then run through the ore zone, leaving diamond-shaped pillars for support. Waste blocks were left as pillars in the stope. Slusher ramps were installed in the haulage drift and the ore was scraped directly into the cars. If the ore dip was over 30°, raises were used in the same manner and scrapers used only to pull ore into raises for loading into cars by chutes or mucking machines.

Thicker ore shoots were mined by a type of shrinkage operation where a slice of ore was first taken upward along the hanging wall and advanced up dip at an angle such that the broken ore would flow to drawpoints below. Mining progressed upward, and broken ore was drawn off below by gravity as required. Broken ore remaining on the foot wall when the sliced hanging wall reached the next level was drawn off by scrapers. The cycle was repeated with a similar cut below the first. Combinations of these methods were used in more fractured and soft oxidized sections of the ore shoots.

Transportation along the upper levels was by 1.8-mt (2-ton) locomotives pulling 0.57-m³ (20-ft³) rocker dump cars and 4.6-mt (5-ton) Granby-type cars pulled by a 5.5-mt (6-ton) locomotive on a 610-mm (24-in.) gauge for the 1980-m level. On the 2440-m level, ore was trammed by hand. Air operated arc gates mounted in steel-lined timber supports were used to load cars from the 6800-m and 6600-m ore passes. Ore hauled from the adits was placed on dumps and loaded into trucks by a skip loader. Drilling for blast holes was by conventional jackleg drills and stopers, and blasting was by 203 × 25 mm (8 × 1 in.) gel stick powder detonated by primers with black fuse and igniter cord. The total mine work force was about 28 men, and production per man shift was reported to be 15 mt in 1957.
1.4.2.2. Boulder District Mines

The mines are located at Boulder County, Colorado, 13 km west of Boulder, Colorado.

A. History and Production

1898–1917 Discovery of ferberite in 1898. Production commenced shortly afterward by numerous small operations.

1917–1955 Production rose to a peak of 147,420 mtu/year; decreased afterwards due to depletion of ore in known deposits and high cost of narrow deposits mining.

1955–1959 Production reached 16,000 mtu/year. Total production up to this time was about 1,500,000 mtu.

B. Geology

See Sec. 1.3.2.4.

C. Mining

The tungsten-bearing veins generally are narrow and irregular and have small ore shoots ranging from 10 cm to 2 m in thickness. Gouge, indicating faulting along the fracture is present in some veins, and wall rock alteration has permeated vein walls in places forming soft slabbing ground (Belsor, 1959).

Grade of ores in the Boulder District is difficult to determine, but the Good Friday mine was reported to be 2–4% WO₃. That the ore grade was comparatively high (over 1% in some mines) is attested to by the fact that some reworked dumps and backfills contained 1% WO₃.

General mining practice in the district was following the narrow veins and shoots with drifts and raises. Small shafts and winzes advanced on the vein, and then stoping proceeded mostly by open stopes, cut-and-fill, and shrinkage. Ore was essentially followed out by the simplest means and often required upgrading by hand sorting in the stopes or on sorting belts on the surface. The cut-and-fill practice was ideal for many of the narrow but rich veins. A vein only 15 cm wide could be mined out by first carefully blasting down the waste, then leveling and covering the muck with boards, rugs, or sheet iron. Then the vein remaining on the wall was blasted down and the ore shoveled down a cribbed raise to the level of loading.

Much hand work was done, including hand tramming and mucking, and even mules were used for haulage. Equipment used was makeshift, and special methods were improvised to cut costs and for solving special problems. Drilling and blasting was by conventional drifters and jacklegs using stick powder, fuse, and primers.

Two large mines of the district were the Cold Springs and Good Friday. Productive veins extended up to 800 m in length, 150 m deep, and varied in width from 0.5 to 4 m.
1.4.2.3. Climax Molybdenum Mines (Tungsten as By-Product)

A. History and Production

1918–1919 Owned and operated by Climax Molybdenum company; production of molybdenum began in 1918, but the mine shut down in March 1919 for lack of market.

1924–1977 The mine reopened in August 1924 and has been continuous operation ever since. In 1948, a by-product plant was built to treat the tailings from the rougher molybdenum circuit. Since then, about 8180 mt ofWO₃ have been produced, though the ore content is about 0.025% WO₃.

B. Geology

See Sec. 1.3.2.2.

C. Mining

Mining is done by a block-caving system, or more specifically, a panel-caving system using subdrift development. The ore body is undercut with sublevel drifts, and long-hole drilling is employed in between, then blasted. This fractures the rock and it is drawn off by finger raises. Fractures thus develop and the entire block subsides (EMJ, 1972). Since this operation is essentially mined for molybdenum, no more details will be given here.

1.4.2.4. Hamme Mine

The mine is located 25 km northwest of Henderson in Vance County, North Carolina.

A. History and Production


1943–1945 Development and limited production.


1968–1971 Bought by Ranchers Exploration and Development Corporation. Developed and rehabilitated for 550 mtpd. Closed 1971. Mine and mill have been maintained on a “stand-by” status since then.

B. Geology

The district is underlain by chloritic schist and granite, the contact of which
marks the west boundary of the district. The deposit occurs in granitic rocks along shear zones lying obliquely to the contact and the foliation.

The Hamme Mine is located along the strike of two shear zones. Ore occurrences consist of irregular discontinuous quartz veins or lenticular bodies controlled by the shear zones. The largest deposit has a strike length of 249 m with widths up to 12 m and has been proven over 210 m deep. In the main shear zones, the veins strike northeasterly and dip about 70° E. The ore mineral is huebnerite, but some scheelite is also present. The vein and wall rocks are minutely fractured but not heavy, and unsupported ground slabs off readily. Ore grade runs from 0.5 to 1% WO₃ (Bishop, 1948; Sweet, 1954).

C. Mining

Early mining practice was by the square set method until about 1960 and was converted to cut-and-fill, with some shrinkage used in places. The square set method consisted of establishing sill sets from hanging wall to footwall above the development drift sets. Chutes were placed on 4.5- to 7.5-m intervals, and mining floors were then advanced upward. Sets were 2.6 m high on 1.5-m centers using 20 × 20 cm oak timber (EMJ, 1970; Sweet, 1954; Malcolm, 1962). The operating expenses were excessively high, and up to 78% of the total operating costs were used in mining directly; 160 men were employed for a 240 mtpd rate. Timber costs were $1.00 per mt ore.

In 1960, the mine was developed for a cut-and-fill mining method, for which only raises and drifts needed to be timbered, while the stope walls could be supported by fill. The fill material was mill tailings brought in as a slurry. The first step was to drive a drift on the hanging wall of the vein (Fig. 1.8). The footwall position was then located by drilling jackleg holes to the limit of the ore. Next, finger raises for mucking

![Fig. 1.8. Installation of draw points and raises to silling sublevel, Hamme Mine (Malcolm, 1962). (1) Draw point. (2) Chute. (3) Manway and service. (4) Finger raises. (5) Manway. (6) Ore outline.](image)
machine draw points and manway raises were driven to the height of a sill floor (about 5.5 m above the rail). These were placed along the strike of the vein with a spacing determined by the expected tonnage to be passed. Then a sublevel drift was driven along the sill floor the length of the ore shoot. At this point, a raise for sand fill and ventilation began to join the level above. Next, the ore on the sill floor was slabbed out the width of the vein and slushed to the level below. A cross-cut was driven from the haulage drift to the footwall for loading from the finger raises. Manway raises were driven directly over the drift and through to the sill floor. Raise sets here were sealed to prevent sand spillage, and mining proceeded by blasting down the back of the stope, slushing down the chute raises, adding a section to the raise, and finally sand filling. Chute and manway raises were thus carried up through the sand fill while the previously driven raises to the level above were used for delivery of sand and fresh air to the working level. Dry mill tailings were trucked to a tank for mixing with water to a pulp density of 65%. The slurry was then pumped to the mine by rubber-lined pipes with a hose used for distribution to the stopes. The sand, 85% of +100 mesh, allowed blasting of ore onto the dewatered fill immediately after placement. Chutes were lined with burlap to prevent leakage of sand. A 50% reduction in the number of men employed had been achieved along with a savings of $1.15/mt in supply costs.

1.4.2.5. **Mill City Mines**

This deposit is developed by four mines, the Stark, Humboldt, Sutton 1, and Sutton 2. The mines are located 8 km north of Mill City, Pershing County, Nevada.

A. **History and Production**

1917–1928  Discovered in 1917. See Table 1.8 for production details.
1929–1934  Operated by Nevada Massachusetts Company; reached a rate of 182 mtpd.
1935–1943  Production increased to 236 mtpd; the mill was destroyed by fire in 1943.
1944–1945  A 900-mtpd mill was installed to retreat old tailings and then remodeled to handle mine ore at 320–360 mtpd. The total production up to this time was 899,499 mtu of WO₃.
1946–1958  Production increased to 500 mtpd in 1956, running 0.4% WO₃; production continued to 1958.

B. **Geology**

Tungsten ore bodies occur along beds of limestone interbedded with Triassic shale and sandstone altered to slate and hornfels, respectively. The sequence is intruded by granitic stocks that cut the limestone beds and are exposed in the mine area. Individual ore bodies are deposited in tectite and silicified limestone, both
formed as scheelite bearing shoots along the limestone beds. They occur along a 600-
m-long segment and have been mined over a vertical range of 540 m. Individual
shoots range in thickness from 1 m to a maximum of 6 m and vary from 30 to 35 m in
length. All beds dip westerly 70° (Tingley, 1975).

**C. Mining**

The Humboldt and Stark mines were developed along one vein, and Sutton 1
and 2 were on three separate veins. The Stark was developed by an inclined shaft to
410 m, the Sutton 1 to 105 m, and the Sutton 2 to 265 m from the end of an adit 210 m
long with an underground headframe. The Humboldt mine was also developed with
an inclined shaft that reached 555 m (Vanderburg, 1935).

Stopping at all mines is by the shrinkage method (Fig. 1.9). After drifting along
the ore to the end of the block, a ventilation raise is driven to to the level above in
conjunction with chute raises spaced along the drift at 4- to 6-m intervals. Next, a
manway raise is started 20–30 m from the ventilation raise. The chute raises are
belled out to connect with each other and then timber chutes are installed for direct
loading into cars. The manway and ventilation raises are timbered also, but the
manway raise progresses upward with the working level of the stope. Stopes are
mined by flatback cuts taken the length of the block between the mine raises. Cuts
are made with stoper or jackleg drills and are advanced from both ends of the blocks.
Excess broken ore built up over the chutes is carefully drawn off to allow a 2-m
working place between the rock face and the broken ore. The stope is carried to the
level above, leaving a 2-m pillar until all work on the level above is completed. Then,
all the ore is drawn off to the level below and the stope emptied.

Blasting in stopes is done by loading the small-diameter stoper or jackleg holes
with 35–50% gelatin stick powder and fired with conventional primers. Except
where hand tramming is done, haulage is by a storage-battery locomotive which
pulls rocker side-dump cars or 0.5-m³ end-dump cars.
1.4.2.6. **Nevada Scheelite Mine**

The mine is located 8 km east of Rawhide, Mineral County, Nevada.

A. **History and Production**

1938–1940  Discovered.
1940–1944  Production up to 1944 was 58,695 mt of ore yielding 46,062 mtu.
1944–1951  The mine operated almost continuously.
1951–1957  Kennametal acquired the property and operated at 90 mtpd, assaying 1.25% WO₃.

B. **Geology**

The Nevada Scheelite deposit is a contact metamorphic type in which scheelite occurs in tactite on a contact between granite and limestone. The country rock is metavolcanic, containing a limestone member deposited between two tuff beds. These rocks have been intruded by a granitic stock with numerous dikes and sills. Tactite bodies occur on the granite–limestone contacts.

Contrary to the occurrence of most tactite bound deposits where the ground is hard and needs no support, the Nevada Scheelite deposit requires much support, and the square-set system of mining has been used throughout. Faulting along the tactite beds and the presence of considerable amounts of sulfides are probably reasons for the bad ground conditions. The ore is a porous limonitic tactite composing minerals garnet, epidote, diopside, quartz, calcite, and scheelite. Pyrite and chalcopyrite are locally abundant. Tactite bodies up to 15 m thick, averaging less than 5 m thick, follow the contact, which is essentially vertical but locally flattens to low angles where granite forms a hanging wall (Geehan and Trangove, 1950).

C. **Mining**

The mine was serviced by a two-compartment vertical shaft plus a winze to 150 m with three levels and 600 m of drifts together with stopes and raises. The ore shoots were developed along these levels by following the granite–limestone contact plus a parallel drift in the hard limestone footwall. Stopes were started from the contact drifts with raises for a manway. Then separate raises were carried up from the parallel drift for ore passes. Square sets followed the ore upward, and ore was dropped to the footwall drift for scraper loading. Where the ground was unusually heavy, raises were driven into granite hanging wall for fill, but these stopes caved before they could be filled.

Square sets were 1.4 m in plan and 2 m high using 25 x 25 cm square timber. About 14 mt of ore would be removed from each set in a stope. The method, although expensive, allowed easy horizontal and vertical expansion by advancing one square set at a time safely through heavy ground.
1.4.2.7. Pine Creek Mine

The mine is located on the eastern crest of the Sierra Nevada Range, 34 km northwest of Bishop, California, at elevations between 2400 and 3600 m.

A. History and Production

1918–1935 Tungsten mining began at the surface of 3600-m elevation. Production was intermittent; reached 115 mtpd in 1924.

1936–1977 Union Carbide Corporation acquired the property, and production has been continuous ever since. Production rates were 230 mtpd in 1937, 300 mtpd in 1942, and reached 1800 mtpd in 1970. Total production to date about 10,000,000 mt ore, the largest producer in the Western Hemisphere.

B. Geology

The Pine Creek Mine and a number of smaller mines that comprise the deposits of the Bishop District are typical of the contact metamorphic type common in the western United States. The main ore mineral is scheelite, which occurs disseminated in large masses of tactite spanning a 900-m steeply dipping segment of the contact between marble of the Pine Creek pendant and quartz monzonite. The tactite zone is continuous along the contact, although its thickness varies from several centimeters to a few meters. The main intrusive contact is steeply dipping but contains irregularities, including flattening, troughs, and sometimes complete envelopment by monzonite of metamorphics. The tungsten ore bodies within the tactite masses reflect the form of the tactite, which, in turn, reflects the form and attitude of the intrusive contact (Bateman, 1956).

Individual ore shoots of commercial grade tungsten are 1.5–30 m thick, a few hundred meters in strike length, and ranging up to a few hundred meters on the dip. Two parent rock types make up the wall rocks of the deposits. One type is the quartz–monzonite intrusive and the other is marble, with tactite replacing some of the beds.

The valuable minerals nearly all occur in tactite, which can best be described as a brown to greenish rock containing various proportions of garnet and pyroxenes, subordinate amounts of quartz, calcite, fluorite, wollastonite, feldspar, scheelite, and various sulfides, such as molybdenite, chalcopryite, and bornite etc. The bulk of the ore as mined for tungsten also contains molybdenum averaging about 0.1–0.5%.

C. Mining

Mining proceeded from the outcrop downward in successive lifts and successively longer adits until the present and final lower haulageway was driven. The principal conditions which dictate the mining methods are: (1) stable ground conditions, allowing openings the full width of ore; (2) large, steep ore bodies with width up to 30 m; (3) continuity of mineralization and good continuity of ore between walls of the ore body.
Fig. 1.10. Longitudinal section through Pine Creek Mine. (Courtesy of Union Carbide Corporation.)
The Pine Creek Mine essentially employs two separate mining methods, namely, (1) sublevel blast hole stoping and (2) sublevel caving. A third method is shrinkage stoping, which is applied to ore bodies less than 6 m wide and to ore bodies irregular in dip (Gray, 1975; Wright, 1964; McKinley and Wright, 1957). Sublevel blast hole stoping (Figs. 1.10 and 1.11) is a method by which steeply dipping ore shoots are developed into horizontal slices by undercuts taken the full width of the ore. The undercuts (or sublevels) are driven one above the other on 14.5-m centers and advanced from inclined ramps or vertical manway raises and are further connected by a slot raise at the far end of the ore block. Ideally, an ore body would be developed completely from bottom to top in this manner, with access to the block being made from main haulageways and long service raises. Once an ore body is developed, it is mined from the bottom upward. In practice, the entire sequence of operations of sublevel drifting, blast hole drilling, loading, and blasting may be done simultaneously on one ore shoot with mining progressing upward as ore is being removed at the bottom.

In the initial development, drifts are driven from main levels along the strike to the end of the ore shoot. The blocks between main levels are then further divided vertically into 15-m-high blocks with undercuts. These are driven 3 m high for

Fig. 1.11. Vertical section through typical ore block at Pine Creek Mine showing sublevel stoping method. Scale: 0.5 cm represents 12 m.
Occurrence, Geology, Mining, and Beneficiation of Tungsten

clearance of airtracks and are advanced from the switch-back ends of the inclined haulage ramps. The ramps run at about 20% grade and provide rapid access by rubber-tired loaders to each undercut.

Bald raises are driven vertically through both ends of each ore shoot to serve as an ore pass and a free face for blasting. They may be widened into a slot raise spanning the full width of the ore. A pillar is retained between one slot raise and the ramp. The ore passes connect below into a loading chamber consisting of pillar raises or mill holes from which ore is loaded into cars from steel chutes. Ore removed from advancing the undercuts is hauled and dumped by LHD (load haul dump — front end loader) units down the previously driven bald ore passes. Raise boring equipment is presently being tested as an alternative for driving these raises.

After an undercut is completed and cleaned, it is then drilled out by airtrack with vertical parallel holes to the undercut below. An average of about 45 m is completed per shift.

Holes are placed on the floor of the undercut on a 1.2 × 2.4 m grid with the holes spaced 2.4 m apart in rows at right angles to strike and the rows spaced 1.2 m apart parallel to strike leaving about a 1.2-m burden against the walls. The holes are laid out by engineers using the results of the mapping of the undercuts. Ten to twelve rows are fired in each blast. Holes are loaded with stick powder and detonated electrically. In a single shot, 5,000–20,000 mt or more may be blasted. Broken ore falls to chutes connected to a lower level, where the ore is loaded directly into cars by means of steel chutes with hydraulically operated gates. From there, ore is loaded into 10-ton rotary-dump cars pulled by an electrically powered locomotive.

The inclined roadways or ramps are a key development in the mining methods at Pine Creek. They are 3.6 or 4.2 m wide by 3 m high and have a grade of 20%. They are run zigzag fashion to make access to each undercut and wide enough to have ample room for the Wagner ST-5 (5-yard) LHD units that are used to drive the undercuts and connecting ramps. A Gardner Denver diesel-driven jumbo using HPR 123 or 99 drills is used in conjunction with the ST-5 to drive drifts and undercuts.

The sublevel caving method is used in certain areas where the ground is fractured and caving of stope walls would be expected. The blocks are developed in a manner similar to sublevel stoping except that the ore is not undercut full width and parallel drifts have to be run in wide ore bodies, and the extraction proceeds from the top downward. Having once begun a cave section (as at the top of a fractured ore zone), undercuts are begun at about 13.7-m intervals, progressing downward, and are run through the block to its limit. In this method, drilling proceeds at the back or "roof" of the undercut with a pattern of holes angled upward to the overlying broken ore. Holes are advanced upward and are stopped the instant the bit reaches the broken ore. Blasting then proceeds at the far end of the block by loading a section of holes adjacent to the broken rock. As in the other method, the holes are placed by engineers (from core hole and mapping data) according to the shape of the ore and the position of the cave line. After a section of ground is shot, the ore is loaded from the broken face until waste appears in the broken material. The undercut is thus drilled and shot in sections retreating out toward the ramp entry. Successive cuts are taken one below the other as the waste–ore line moves downward.
The method allows fractured ore to be mined that can not be mined economically by other methods. Extraction, however, is not complete due to dilution, and the amount of rock blasted at one time is less than with the other method. For drilling up holes, an Atlas Copco YAK BBC-100F containing two drills capable of angle and vertical holes is used for the caving method, and Wagner ST-5 loaders are used for mucking.

For the shrinkage stoping method, conventional jackleg drills are used for blast holes, and a horizontal 3.5-m cut is taken along the back for the length of the ore body. The shrinkage stope is serviced by a bald raise from the top, and the broken ore is drawn out from a series of draws from the bottom.

1.4.2.8. Strawberry Mine

The mine is located 145 km northeast of Fresno, California, in Madera County. Granite Creek, a tributary of the San Joaquin River, flows through the mine property at elevation 2200 m.

A. History and Production

1941 Deposit discovered and claimed by J. A. McDougald and J. E. Cobb.
1943–1945 A 30-mtpd mill constructed and small-scale mining of near-surface ore was conducted.
1945–1950 Leased and operated by Fresno Mining Company. During this period, the mine was operated each year except 1946 and 1947; the mill capacity was increased to 70 mtpd.
1955–1969 Original lease and company sold to New Idria Mining and Chemical Company. This company operated the mine each season during this period except 1957, 1958, 1963, and 1964. Also, exploration and mine development was done, and the mill capacity was increased to 185 mtpd by 1965.
1969 Mine closed due to heavy snow, which damaged the mill and camp. New Idria removed all equipment and terminated lease.
1972–1977 Property leased by Teledyne Wah Chang Corporation. Extensive exploration by diamond drilling was done during 1972 and 1973. Substantial new ore reserves were defined.

B. Geology

Scheelite occurs in a folded pendant of metasediments of probable Paleozoic age that has been intruded by granite of the Sierra Batholith. The structure of the pendant consists of tight, steep-plunging folds, marked along the north edge by a highly irregular contact with the granite. The tungsten ore bodies are confined to strata of marble interbedded with hornfels and some schist. The mine is located on
one of the folds and consists of two main ore zones that lie in discontinuous marble beds cut by the granite intrusion and crossed by granitic dikes (Krauskopf, 1953).

Number 1 and 2 mines lie on the west flank of the main fold and at granite-limestone contacts. The number 4 mine is positioned similarly, but on the opposite flank 1000 m to the east. In addition, there are several other small ore deposits not yet developed that occur with similar geological conditions.

Ore bodies are well-defined beds of tactite formed by replacement of the marble near the contact with the granite intrusion. The tactite forms over twenty separate bands of ore that vary in length up to 90 m, are from 1 m to 7.5 m thick, and extend on the dip up to 120 m. Scheelite occurs in all known tactite bodies with an average grade of 1% WO₃. Molybdenite occurs in number 1 and 2 mines in nearly economic content, but has not been separated in past milling operations.

An important additional feature of the ore bodies at the number 4 mine are late scheelite-bearing quartz veins. A series of these veins varying up to 0.5 m thick dip about 30° to 40°, strike at right angles to the ore beds, and cut through the central part of deposit. The tactite becomes strongly enriched where the veins pass through the ore shoots. In many places, the quartz veins bear rich scheelite in normally barren wall rock and granite dikes. The veins are composed almost entirely of large scheelite crystals embedded in quartz.

C. Mining

The deposit was mined entirely underground and was developed by two shallow vertical shafts 20 m and 45 m deep at number 1 and number 4 mines, respectively. Number 1 mine had two levels (2287-m and 2255-m elevations) and number 4 mine had three levels (at elevations of 2255 m, 2271 m, and 2240 m) with a total for the mine of about 2000 m of level workings. The reserves were about evenly divided between the two deposits, but most of the past production was taken from number 4 mine. This came from large stopes located between the Burma Tunnel (2210 m) and the surface. The total vertical range of development was only about 76 m.

The workings were in hard rock and support was almost never required. Also, the tactite ore bodies had sharply defined walls between which the tactite was easily recognized and might normally be mined completely from wall to wall (Fig. 1.12). Because of these favorable characteristics, the shrinkage method was adopted and was used for all mining at Strawberry. There had been little waste work done at the mine since drift development and raising had been done mostly in ore along the many separate ore bodies.

After drifting along an ore body, a bald raise was run at each end of a stoping block through to the level above. Once mining had started, all entries were from the level above, including entry of service lines, ventilation, and ladderway. Draw holes spaced about 4.5–6 m apart were driven into the footwall side of the drift, raised into the ore, and belled out to connect with each other and to the service raises. Mining then proceeded by advancing a “flat back” cut the length of the block by drilling with stopers or jackleg machines. The original raises put through for service and ventilation could then be used for draw holes.
Fig. 1.12. Longitudinal and vertical sections through typical stoping block, Strawberry Mine.

Mining progressed upward while ore was drawn off evenly from the draw holes with air-driven mucking machines (Eimco 12B). Mucking machine draw points had proven efficient and had the advantage over timbered shoots in that large blocks would not plug the draw points and could be blasted safely if necessary. In order to allow passage of the train between draw points, round logs were placed in steel-pin brackets to retard the flow of rock into the drift. A 1.5-m pillar of ore was left between the stope and the level for safety and might be mined after the level below has been developed.

Drilling was mostly by heavy-duty jacklegs using Atlas Copco 2.22-cm-diameter integral steel. This proved to be the only type to hold up in the extremely hard rock. Blasting was with ammonium nitrate–fuel oil delivered to the hole with a special air gun and was detonated with a cap and stick of gel powder in the back of the hole and timed with black fuse and igniter cord.

1.4.2.9. Tempiate (Lincoln) Mine

The mine is located 136 km by road west of Caliente, Lincoln County, Nevada.

A. History and Production

1916    Discovery.
1916–1939 Minor production.
1941–1943 The mill treated 51,597 mt of ore and 3400 mt of tailings, containing 28,615 mtu of WO₃ (Tschanz and Pampeyan, 1970).
1943–1951 Intermittent operations, production unknown.
1953–1957 Continuous operations by Wah Chang.
1957 Closed due to end of tungsten subsidy program. Production up to this date was about 1,000,000 mt of ore that averaged 0.4% WO₃.
1970–1977 Leased to Union Carbide Corporation, active exploring of the property and planning of a new 1000-mtpd operation.

B. Geology

The tungsten deposits occur in thick bodies of tactite in the bedding of Paleozoic limestone. The formation was intruded by two stocks of younger granite, which formed three elongated bands of tactite along the west side of the south stock. The number 1 zone (Moody zone) of tactite extends for about 2000 m along the contact and is 5–30 m thick, averaging about 12 m thick in the Lincoln Mine. This zone has produced most of the ore. Scheelite occurs in three zones controlled by zoning and by the original composition of the limestone. The footwall zone against the granite is a pyrite–pyrrhotite-rich tactite zone 6–1 m thick, with spotty scheelite (low-grade ore) followed by a center zone of garnet averaging about 0.5% WO₃, 3 m thick, and an outer zone of calcite–chlorite–fluorite-bearing rock with sphalerite and containing up to 2.5% WO₃ and about 1.25% zinc. This outer, or hanging wall, zone is made up of ore shoots measuring 15 m on the dip 35 m on strike and 1.5–9 m thick. Overall, ore shoots in the Moody zone range from 18 m to 90 m long, up to 12 m thick, and 120 m on the dip, with an average grade of 0.45% WO₃.

The second zone is the Grubstake, which lies parallel to the Moody and is separated by about 45 m of hornfels. This zone is 600 m long, averages 10 m thick and consists of several shallow high-grade ore bodies.

Outside the various ore shoots, submarginal ore in tactite is relatively uniform in grade over a vertical range of 400 m and has a WO₃ content between 0.1 and 0.2% (Tschanz and Pampeyan, 1970; Binyon et al., 1950).

C. Mining

The Lincoln Mine was developed by more than 26,000 m of underground workings on six levels — the 30-m, 60-m, 90-m, 150-m 210-m, and 270-m levels — with adits on the 30-m, 90-m, and 210-m levels and an inclined shaft to the 270-m level. All mining is done by the shrinkage method, using draw-point loading at the haulage level. Eimco 12B rocker shovels are used to load ore into cars pulled by a battery-powered locomotive to a shaft pocket for hoisting or to a bin on the surface (Stanley, 1955).
The vein is divided into stoping blocks 30 m long, and a manway and service raise are driven through the ends of the block. Draw points are spaced on 6-m centers and are belled out and connected above the drift. Drilling is done with 1-R jackleg drills with four men to a stope. Blasting is done electrically using millisecond delays set off from a central control panel underground. Nongeel stick powder is used along with a gel primer stick to reduce missed holes.

1.4.2.10. Yellow Pine Mine

The mine is located on the east fork of the Salmon River, Idaho, 5.2 km north of Stibnite.

A. History and Production

1914 Discovered.
1938–1939 Acquired by Bradley Mining Company, antimony–gold ore produced from west quarry, 150 mtpd.
1939 Operations shifted to the east quarry; mill capacity was increased to 450 mtpd.
1941 Scheelite discovered between quarries and a shaft was sunk; underground mining began.
1941–1945 Underground and open pit mining. All open pit by 1943 at rate of 800 mtpd on tungsten ore body. The mill produced five concentrates. Production data are shown in Table 1.9. Tungsten ore body exhausted in 1945.

B. Geology

The ore deposits of gold, tungsten, antimony, and silver are replacement deposits found in wider shear zones in quartz monzonite, with quartz latite, aplite, and pegmatite dikes, in the Idaho Batholith. Scheelite is found beneath overburden

<table>
<thead>
<tr>
<th>Year</th>
<th>Ore production (mt)</th>
<th>Concentrate production (mt)</th>
<th>WO₃ production (mtu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1941</td>
<td>86,497ᵇ</td>
<td>5,262</td>
<td>25,380</td>
</tr>
<tr>
<td>1942</td>
<td>88,047</td>
<td>13,826</td>
<td>164,738</td>
</tr>
<tr>
<td>1943</td>
<td>162,481</td>
<td>20,713</td>
<td>275,883</td>
</tr>
<tr>
<td>1944</td>
<td>192,146ᶜ</td>
<td>12,215</td>
<td>212,401</td>
</tr>
<tr>
<td>1945</td>
<td>99,805</td>
<td>6,899</td>
<td>77,730</td>
</tr>
<tr>
<td>Total</td>
<td>628,976</td>
<td>58,915</td>
<td>756,132</td>
</tr>
</tbody>
</table>

ᵃ Cole and Bailey, 1948.
ᵇ Starting in August 1941.
ᶜ Including 878 mt of tailings retreated.
between two antimony–gold quarries located in opposite sides of a fork of the Salmon River. The tungsten ore occurs with antimony in a funnel-shaped ore body, with the tungsten deposited principally in the upper part. The ore body is located west of a quartz latite dike and between the Meadow Creek fault and the hanging wall shear zone. All the ore bodies are controlled by permeable fractured rock. The tungsten ore body is lying flat, 120 × 60 m, and extended to a depth of 55 m. The tungsten is unusually rich and yielded about 1.36% WO₃. The tungsten–antimony ore body is low in gold (about 2 g/mt), while the gold ore bodies contain only traces of tungsten and antimony (Cooper, 1951).

C. Mining

The mine workings consisted of the east and west quarries and abandoned underground workings (now destroyed by open pit mining). These consisted of a vertical shaft 55 m deep, an inclined shaft 50 m deep, 1200 m of drifts on three levels connected to the shafts, a 60-m winze on the third level, and a 1200-m drainage tunnel. Underground mining was done using square sets. A two-compartment raise was driven from the level to the surface, and then the operation began at the bottom by taking out a series of horizontal slices. Slushers were used for transferring and slushing ore directly into 0.51-m³ (18-ft³) end-dump cars. Stope sets measured 1.5 × 1.5 × 2.32 m. Stopes were back filled with glacial till via raises to the stope. Stope production per man shift was 6 mt. When mining was converted to open pit in 1943, 750,000 mt of glacial till was removed at a stripping ratio of 2:1. Stripping was done with five power shovels, ten tractors, twenty-five diesel trucks, and twenty-five gasoline trucks (Cole and Bailey, 1948).

Mining was done with eight benches, 9 × 9 m. Churn drills were used for 15-cm holes at the top of the benches and wagon drills for holes at the toe of the benches. Ten churn drill holes and about twenty-five wagon drill holes made up a typical blast. All holes were blasted simultaneously with Primacord. Power shovels were used to load trucks having a capacity from 7.6 to 19 m³.

1.4.3. Canada

1.4.3.1. Canada Tungsten Mine

The Canada Tungsten Mine in the Northwest Territories accounts for the majority of Canada’s tungsten output. This mine is located 320 km north of Watson Lake via a new road branching from the Alaskan Highway.

A. History and Production

1958 Discovered by the MacKenzie Syndicate.
1959–1962 Canada Tungsten Mining Company incorporated in 1959. Activity during this period was exploration, development, and testing. Drilling completed in 1960 outlined 1,200,000 mt of ore containing 3,000,000 mtu of WO₃.
1966  Mill totally destroyed by fire.
1967–1968  Mill rebuilt to 410 mtpd capacity (141,000 mtpy). Open pit operated 3½ months each year ending in October.
1968–1977  Operations reached 455 mtpd and mining converted to underground operation; new ore body.

B. Geology

The deposit of Canada Tungsten Mining Company is the result of contact metamorphism with the ore occurring in limestone and chert beds in contact with an intrusion of biotite quartz monzonite. The original sedimentary rocks are Cambrian limestone, argillite overlain by Ordovician slate and limestone.

The structure in the vicinity of the mine is tight folding with faulting. The ore is controlled by an overturned anticline and a strong fault. The original ore body (mined by open pit) is localized on the upper zone of the limb near the nose of the fold (east zone) and contains about 3,640,000 mt of ore at 1.63% WO3 and 0.2% copper (Cummings, 1975).

The ore bodies are in skarn zones replacing marble beds and in fractured chert. The ore body mined by open pit has been reported to contain 1,200,000 mt of ore at 2.47% WO3 (EMJ, 1963). This zone outcrops and measures 200 × 90 × 20 m, and dips at a low angle. The only tungsten mineral is scheelite and occurs with minor chalcopyrite, with massive pyrrhotite, and in quartz–calcite veinlets.

C. Mining

For open pit mining, 7.62-cm holes on 1.8-m centers were drilled (Air-trac drills). Conventional stick powder was detonated by Primacord, and about 4500 mt were broken with each shot. Trucks with 27-mt capacity were loaded with 1.9-m³ power shovels for haulage to the mill 5 km away (Ellerman, 1968). Underground mining commenced in 1975. The method is room and pillar, using trackless LHD equipment, to be followed by waste filling and pillar extraction.

1.4.4. Brazil and Bolivia

1.4.4.1. Brejui–Barra Verde Deposit (DNPMB, 1969)

This deposit is located 6 km south of Currais Novos, Rio Grande do Norte. The major mines and ownership are: (1) Brejui Mine, Mineração Tomaz Salustino; (2) Barra Verde Mine, Mineração Acauan; (3) Boca de Lage Mine, Tungstenio do Brasil; (4) Zangarelhas Mine, Mineração Zangarelhas. The two operating mines, the Brejui and Barra Verde accounted for 56% of the country’s output in 1971.

All four mines listed above are parts of a single, large tungsten deposit. From the original outcrop located at the Brejui mine the ore-bearing formation dips
about 10° to 15° southward and extends about 3.6 km at this inclination, for an overall vertical range of 760 m (Fig. 1.13).

A. History and Production

1. Brejui Mine

1943–1953 Scheelite was discovered on the farm of Tomaz Salustino in 1943, but mining was operated by Garimperos (lessees). Production during this period amounted to 4877 mt concentrates.

1953–1968 A mill installed. Production during this period was 5502 mt concentrates.

1968–1974 An estimated 3000 mt concentrates was produced during this period, which gives a total production up to 1974 about 13379 mt with an average WO$_3$ content of 73%.

1974–1977 Current production rate is 300 mtpd of as-mined ore.

2. Barra Verde Mine

1956–1963 Wah Chang Corporation leased the property and commenced operation in 1956. Production during this period amounted to 4624 mt concentrates.

1970–1975 Mineração Sertaneja secured the property and began operations with installation of a gravity mill. Production for this period, 3600 mt; total production to 1975, 8224 mt with an average WO$_3$ content of 75%.

1975–1977 Current rate of production is 400 mtpd of as-mined ore.

3. Boca de Lage Mine

This mine is operated by Union Carbide Corporation through Tungstenio do Brasil. Extensive exploration has been carried out since 1970 by diamond drilling and underground drifting. The ore zone is reached through a two-compartment, 200-m vertical shaft. Production plan includes a 300-mtpd gravity mill.

4. Zangarelas Mine

The property is jointly held by Teledyne Wah Chang Corporation and Mineração Zangarelas. Diamond drilling located mineable ore grade lenses at depths between about 400 and 620 m.
B. Geology

Precambrian rocks of the Brazilian shield are exposed in the Currais Novos area. The rocks in the vicinity of the Brejui–Barra Verde Mines consist of great thicknesses of schist interbedded with gneiss and contain the much thinner beds of limestone in which deposits of scheelite occur. These rocks are intruded by stocks of granite along with some thin pegmatite dikes. The sequence has been folded to various degrees and the limestone converted to tactite.

The ore zone is comprised of two marble beds averaging 20 m thick and separated by 20–60 m of quartz–biotite gneiss. Overlying the top bed is granite gneiss and biotite schist. The ore-bearing horizons lie in a remarkably persistent set of uniform plunging folds 150 m across overall and a plunge length over 3.6 km long, with the axis of the folds dipping 12° southward. Five separate tactite horizons are found within the marble beds occurring at or near the anticlinal or synclinal crests. The stratigraphic positions are the top, bottom, and center of both marble beds. The tactite zones may be nearly continuous throughout the known length of the zone, although it is not everywhere scheelite-bearing.

A granite intrusion lying to the west is not cut by the mine workings but seems to be related structurally to the ore zone. The bodies of tactite containing mineable scheelite taper from a maximum of 10 m to a thin bed and reach 100 m in length and about 30 m wide. Localization of ore is controlled by folding.

C. Mining

The Brejui Mine includes a small open pit and underground workings connected to a 45° inclined shaft. There are five main levels and about 3100 m of underground workings. Hoisting is done with two hoists operating through one shaft and one headframe, one each for ore and waste. The ore is picked up with a front-end loader and truck-hauled to a coarse-ore stockpile. From there it is pushed into a coarse-ore bin with a tractor.

The Barra Verde Mine exploits a continuation of the same ore body, and although workings are somewhat deeper than the Brejui, development and mining is similar. There are two vertical shafts with levels about 25 m apart with drifts totaling about 30,000 m.

Mining in both operating deposits is essentially by open stopes. The marble and tactite beds are hard and the hanging wall, which is normally gneiss, stands well. Artificial support in stopes is not required.

After ore is followed out by drifting on the levels (lenses are all curved due to folding) ore is blasted down on the level and drilling then proceeded by working off the top of the ore pile. Ore is then drawn off below as the deposit is followed upward. Sublevels are established and ore is moved to ore passes mostly by hand tramming or double-drum air slushers. A few small mucking machines and wood chutes are used for loading in some locations.

In exceptionally thick or steep ore shoots a modified shrinkage method is used.

The Brejui Mine, operating at 300 mtpd had a total work force of 550 men (including milling). Total operating costs, including mining and milling overhead, was $12.00 per mt of ore mined in 1972.
At the Boca de Lage Mine, development now in progress calls for balanced hoisting plus the use of small trackless LHD units for ore transportation and development on main levels.

1.4.4.2. Chojilla Mine

This mine is located northeast of La Paz, Bolivia. The tungsten output accounts for about one-half of Bolivia's total production. The Chojilla Mine is the largest producer in South America.

According to Li and Wang (1955), the principal deposits of the Chojilla Enramada and Santa Ana Mines in the Sur Yungas region are pegmatic quartz veins averaging 1 m in width, with wolframite and cassiterite. These occur in quartzites and metamorphosed slates with a general strike parallel to the beds but at right angles to the underlying granite. The main vein (number 4) has been developed over a length of 450 m and averages 1.25 m in width. The content has been reported as 0.44% tin and 0.32% WO₃.

1.4.5. Austria

1.4.5.1. Mittersill Mine

The mine is located 10 km south of the town of Mittersill, Salzburg, Austria.

A. History and Production

1967 Discovered.
1968–1970 The property is jointly owned by Metallgesellschaft AG., Frankfurt, Germany, Voest Alpine, Austria, and Teledyne Corp., United States. Exploration by surface and underground diamond drilling. Total drilling 6600 m with 53 holes.
1970–1977 Mine and mill development. Production started in 1976, projected at 150,000 mtpy and increasing to 250,000 mtpy of as-mined ore.

B. Geology

The tungsten mineralization at Mittersill occurs in a sequence of lower Paleozoic rocks consisting of beds of amphibolite schists, amphibolites, quartzites, quartz schists, and an albite gneiss of volcanic origin. The metamorphic sequence is folded, strikes northwesterly, and dips 25–45° northwest.

The scheelite deposit is not closely related to intrusive rocks, but instead is stratigraphically controlled, with enrichment of scheelite in quartz layers in metamorphic rocks. The ore shoots enclosed in the group are elongated, pitch northwesterly, and measure up to 150 × 50 × 10 m. The shoots have a lenticular shape with a maximum thickness in the center and thinning at the sides (Metallgesellschaft, 1973).
Deposits of residual material occur at Mittersill and constitute a significant share of the reserves. This is apparently broken vein material in residual alluvium closely associated with the underlying outcropping scheelite deposit. Reserves determined by drilling and sampling are 2,459,000 mt averaging 0.7% WO₃, based on a cutoff grade of 0.3% WO₃.

C. Mining

For the first 6 years, the deposit will be mined by open pit methods conducted 6–8 months yearly. The mine is at elevations between 2000 m and 2200 m above sea level and has occasional heavy snowfalls. Underground development will be done simultaneously, with the surface crew shifted to the underground during the winter. After about 8 years, all production will be underground. Mining in the open pit will be by trucks and shovels and inclined ramps using trackless LHD equipment for underground mining. The surface ores have an estimated content of 1% WO₃, and the underground ores range from 0.7 to 0.4% (Metallgesellschaft, 1974; Spross, 1975).

1.4.6. Portugal

1.4.6.1. Panasqueira Mine

The mine is situated near the center of Portugal near the town of Silvares in the Serra da Estrela, the highest mountain range in Portugal. The Panasqueira Mine is by far the largest and most important tungsten producer in Europe.

A. History and Production

1889 Discovery of wolframite in the property.
1910–1919 Production began by an English company in 1910; averaged about 182 mt (200 tons) per month (combined tin and tungsten) during this period.
1919–1934 Period of intermittent operation and low production.
1934–1943 Reorganization and expansion. Production reached 2246 mt per month wolframite and tin concentrates by 1941. Operation curtailed in 1943.
1943–1977 Expansion and development to current production of about 1954 mt per month of tin and tungsten concentrates; it is expected to reach 2400 mt per month (75% WO₃).

B. Geology

The area of the Panasqueira mine is underlaid by phyllite that has been intruded by granite, although no granite is in the immediate mine area. The total zone of mineralization lies in an area measuring 150 m thick, 600 m long, and 800 m down dip (Allan et al., 1946).
Ore bodies consist of a series of discontinuous lenses that make up a multiple-vein system. These are composed of quartz gangue with wolframite cassiterite filling thin low-dipping joint structures. Individual lenses of ore about 1.2 m thick extend down and dip to 100 m. In the old mine there are eight main lenses stacked one above the other, ranging from 5 to 20 m apart. Besides wolframite and cassiterite, other minerals present in the veins are, quartz, pyrite, arsenopyrite, and chalcopyrite.

C. Mining

Until the 1940s, no system was employed other than to follow the best ore and raising and placing support where necessary. Hand drilling, hand loading, and tramming by hand or with mules was done during this period.

In the early forties a more efficient system using main level cross-cuts, vertical single-compartment raises, sublevel drifts, and inclined raises was developed. The raises placed on 16-m centers were driven from the horizontal cross-cuts and extended through the vein. Drifts along strike were driven from the raises above and below the vein and were in turn connected to inclines; intermediate cross-cuts provided ore passes to the level below. This system provided flexibility and easy access to overlapping veins for ore removal and evolved into the present system of longwall mining (Allan et al., 1946).

1.4.7. Australia

1.4.7.1. King Island Mine

The mine is located at the southeast corner of King Island, Tasmania, Australia.

A. History and Production (Kidd, 1952; AM, 1974)

1917–1920 Small mining operation of 30mtpd during period conducted by King Island Development Company N.L. Closed in 1920 due to decrease in price.

1920–1937 Little or no activity.

1937–1943 King Island Scheelite N.L. formed and a 70-mtpd mill installed and operated, producing 30,481 mtpy.

1944–1946 New mill increased to 450 mtpd by 1946.


1960–1969 Reopened with limited output, which was finally increased to 320,000 mtpy by 1969.

1974–1977 Completion of open pit mining in 1974. Total open pit production to 1974 was 6,399,000 mt of ore assaying 0.58% WO₃. Presently the mine is operated underground at 320,000 mtpy; the ore is processed with a 1000-mtpd gravity–flotation mill.

B. Geology

The ore is a contact metamorphic deposit with bedded hornfels and volcanic and calcareous rocks intruded by granite. There are two main ore bodies: The Bold Head ore body, which consists of five major lenses, lies between a major fault to the east and a granite intrusive to the north. The Dolphin ore body mined by the original open cut consists of two major lenses bounded by faults to the north and east and a granite intrusion to the south. This ore body dips southeastward under the sea.

The Bold Head lenses vary in thickness from 0.1 to 30 m and dip 15 to 20 degrees to the southeast. The rocks are skarns, hornfels, and marbles. The Dolphin ore bodies (designated beds C and E) are skarn beds replacing marble and are 2 to 45 m thick and extend 400 and 500 m along the strike.

The bulk of the scheelite is finely disseminated from 2 mm down to micron sizes. Quartz veins occur also, but they are not regular or evenly distributed and vary from a few centimetres to several meters thick.

Estimated reserves of these mines are: Bold Head Mine, 2,600,000 mt at 0.8% WO₃; Dolphin Mine, 6,800,000 mt at 1.0% WO₃.

C. Mining

Underground development consists of truck inclines run at 10–15% grade. These are about 450 m long in the Bold Head and 360 m long in the Dolphin Mine. The inclines branch off to various levels and spiral downward at about a 14% grade. LHD units (Cat 980 B) are used for driving the inclines to about 450 m, then trucks are required. Kiruna K-250, 250-hp (187-kW) units are operating in the mines carrying about 27.3 mt (30 tons) per load. For drilling, three-boom Jumbos powered by diesel carriers are used. Also a Gardner Denver air track two-drill Jumbo is planned in addition for stoping (AM, 1974).

For ventilation, three 11.8-m-diameter bored raises will be used. For stoping, maximum use of mobile diesel equipment is employed. The mining method in the Bold Head is by pillar and stull stoping and shortwall slusher stopes. For this, drifts are driven along the strike and raises are run through to the levels up dip of the shallow angle ore bodies. In thin beds, slushers pull the ore down to the drifts for LHD access. These are essentially open stopes.

The Dolphin is being similarly developed by inclines and bored raises to mine the downward extension of the open pit. Development is still underway. The mining method is basically a room-and-pillar system combined with cut-and-fill practice. The pillars will have 8-m spans and 6-m² pillars in a grid pattern. The fill will progress upward in lifts as in conventional cut-and-fill practice. The operation employs 350 persons.
1.4.8. Asia

China has been the leading world producer since 1918 and the Soviet Union has been a major world producer since 1944. Information on production levels, however, is indirect and has for many years been known only from import data of other countries and scattered reports (see Chapter 11). Sources in the Soviet Union are North Caucasus, Transbaykal Far East, Central Asia, and Kazakhstan. One large producer is the Tyrnyauz Mine in the Kabardino-Balkar area, which produces scheelite with molybdenite from a large skarn-type deposit. Open pit and a sublevel drifting and caving system for underground mining is used. Production is 12,000 mtpd of ore containing 0.2% WO₃ plus 0.04% MoS₂.

In Thailand, Federation of Malaya, and Indonesia, tungsten is a by-product of tin mining. Thailand tungsten concentrate production for 1974 was 4276 mt, and for the first 5 months of 1975 was 1735 mt. The drop was due to the depletion of the country's largest tungsten deposit located in Nokhan S. Thammarot province. Details of other producing countries in Asia are described below.

1.4.8.1. China

In China, most of the tungsten comes from the Nanling Range of southern China, and 70% comes from the Kiangsi Province in the eastern part of the Nanling Range. The ore deposits were described in considerable detail by Li and Wang (1955), but individual mines were scarcely mentioned. Up to 1950, practically all production was believed to have come from the surface or from shallow underground workings. The deposits were principally high-grade wolframite veins, which outcropped in great numbers in many separate areas. The veins were steep, and many extended along the strike for hundreds of meters. These conditions were favorable for exploitation by individuals or small-scale operations. No development work was required, as the rich veins pay their way as they are followed downward.

However, in recent years Chinese exports decreased significantly (see Chapter 11). Theories were that much of the easily available reserves had been mined since the last reliable appraisals in 1948. The veins were narrow and steep and would be deepened considerably by the large extraction necessary to account for the annual production. At depths greater than a few hundred meters, continued hand labor become impractical and mechanization would have to be undertaken. The mechanization necessary to extract deeper reserves was probably incomplete, or the tungsten not accounted for was either stockpiled or taken up by increasing internal consumption.

1.4.8.2. Burma—Mawchi Mine

The Mawchi mine is located at Keren Hills area in the state of Karenni.

A. History and Production

Burma was a major tungsten producer that accounted for 17% of world production from 1913 to 1937. The production was 2200–2700 mt of metal
annually. In 1964, the Burma Corporation was nationalized and the production thereafter has been low. In 1970 the production was only 50 mt.

B. Geology

Veins containing wolframite, cassiterite, and scheelrite are found in a formation of argilite and fine sandstone intruded by granite (Li and Wang, 1955). The veins are of quartz, extending on strike for several hundred meters and are 1–2 m thick. The mine run ore is reported to be about 2.5% combined tin and tungsten.

1.4.8.3. South Korea — Sang Dong Mine

The Sang Dong Mine produces about 90% of the total tungsten of the country. The mine is located 160 km southeast of Seoul.

A. History and Production

1916–1945 Discovered and afterward the mine was taken over and operated by the Japanese until the end of World War II.

1945–1954 Korean Tungsten Mining Company, Ltd., took possession; modernization of mine and plant started. In 1953, 7456 mt of concentrates were produced. Total production to 1954 was about 15,000 mt.


B. Geology

The rocks at the Sang Dong Mine area are of the Myobong formation, consisting of hornfels, slate, phyllite, and limestone. The ore minerals are scheelite, bismuthinite, and molybdenite, which are deposited in tactite and quartz biotite lenses in association with the limestone. The beds strike N 70°–80° W and dip 20°–26°. There are seven known ore-bearing beds, three of which are mined and are described as a biotite quartz zone, a diopside hornblende zone, and a garnet diopside zone (Beall, 1969). The strike length of the main bed is 1500 m and has been mined down dip 1200 m and ranges from 4 to 6 m thick.

C. Mining

The deposit is developed by one inclined shaft from the surface, two inclined winzes (sunk from the 658- and 406-m levels), and one new circular concrete-lined vertical shaft. The new shaft is 4 m in diameter, 470 m deep, and is equipped with a modern Koepe friction hoist with a 600-hp (488-kW) motor and has automatic operation. There are 18 mining levels below the plant, which is at 658-m elevation.
The mining method is by a combination of room and pillar, followed by backfilling. Small air-driven mucking machines and slushers are used for loading and moving ores, and 4-ton (3.7-mt) Mancha locomotives are used for haulage along the levels. For drilling, Atlas Copco airleg drills are used with carbide-tipped integral steel, and dynamite is used for blasting. After removal of a slice of ore, openings are walled off and slurred mill tailings are placed for backfilling. The mine has 651 workers with an efficiency of 2.8 mt of ore per man shift.

1.5. BENEFICIATION OF TUNGSTEN ORES

In general, tungsten ores are beneficiated by crushing and grinding to liberation size of the tungsten minerals, followed by concentration and supplemented by leaching, roasting, magnetic, or high-tension separation when necessary.

Most tungsten deposits are of low grade (see Sec. 1.4.1), but international trade practice requires tungsten concentrates containing 60–70% WO₃. Prior to World War I, grinding of tungsten ore was largely by gravity stamps, which resulted in excessive sliming. The ground ore was then classified by screening and concentrated by vanners, shaking tables, and canvas-covered tables. The average recovery at these early mills was about 60% or even less.

Since 1910, stage crushing with size classification has been well developed, and flotation has been adopted for treating fines. With these developments, along with the improvement in gravity concentration in recent years, the recoveries for tungsten beneficiation to as high as 90% have been achieved.

1.5.1. Flowsheet Considerations

Certain generalities can be made concerning tungsten ore dressing, but in practice, each ore deposit requires a unique combination of unit processes to attain optimum treatment.

Variables that must be considered for the design of a concentrator include both chemical and physical characteristics of the minerals, such as specific gravity, friability, hardness, cleavage, and magnetic properties. For example, chemical processing to remove the molybdenum content is necessary if powellite is present in the ore. Rock characteristics such as liberation size, degree of locking, hardness and structure, should also be considered.

Due to the friability of tungsten minerals, a fundamental principle of concentrating ores is to recover concentrate as coarse as possible to minimize losses due to overgrinding. It follows that concentrates recovered at an early stage in the process will contain a middling product that requires further grinding and treatment to attain the desired grade. Many commercial operations include scalpers in the form of jigs or unit flotation cells in the circulating load of the grinding circuit to minimize losses due to sliming. The resulting bulk concentrates often receive separate special treatment, which can be justified because the value of the material is high and the scale is small, which allows much more attention to a high recovery. A tentative flowsheet can be developed by reference to Table 1.10, which shows
### Table 1.10. Mineral Separation Characteristics

<table>
<thead>
<tr>
<th>Specific gravity</th>
<th>Minerals floating with scheelite</th>
<th>Minerals that do not float</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnetic</td>
<td>Slightly magnetic</td>
</tr>
<tr>
<td>7.5</td>
<td>Wolframite</td>
<td>Cassiterite</td>
</tr>
<tr>
<td>7.0</td>
<td>Ferberite</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>Magnetite</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>Ilmenite</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>Pyrrhotite</td>
<td>Powellite</td>
</tr>
<tr>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>Kyanite</td>
</tr>
<tr>
<td>3.5</td>
<td>Apatite</td>
<td>Sillimanite</td>
</tr>
<tr>
<td>3.0</td>
<td></td>
<td>Fluorite</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Typical conditions using oleic acid, sodium silicate, and quebracho (tannin); pH 10.
*Depressed by cyanide.
*Flotation separation not complete.

### Table 1.11. Common Approaches to Mineral Separation

<table>
<thead>
<tr>
<th>Ore</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheelite, simple ore</td>
<td>Gravity, flotation, magnetic</td>
</tr>
<tr>
<td>Scheelite, sulfides</td>
<td>Gravity, sulfide flotation, roasting, magnetic</td>
</tr>
<tr>
<td>Scheelite–cassiterite concentrate</td>
<td>Electrostatic</td>
</tr>
<tr>
<td>Scheelite–calcite–apatite</td>
<td>Flotation, gravity, leaching</td>
</tr>
<tr>
<td>Scheelite–powellite concentrate</td>
<td>Chemical processing</td>
</tr>
<tr>
<td>Wolframite, simple ore</td>
<td>Gravity, flotation, magnetic</td>
</tr>
<tr>
<td>Wolframite–cassiterite ore</td>
<td>Gravity, flotation, magnetic</td>
</tr>
<tr>
<td>Wolframite–scheelite concentrate</td>
<td>Magnetic</td>
</tr>
<tr>
<td>Wolframite–sulfides</td>
<td>Sulfide flotation, gravity, magnetic</td>
</tr>
</tbody>
</table>
separation characteristics of minerals associated with scheelite. Common approaches to mineral separation for different kinds of tungsten ores are summarized in Table 1.11. However, even for the simplest ores, laboratory testing is required before selecting a flowsheet. Generally speaking, laboratory results can be used successfully to predict full-scale performance.

In many cases, the location of the deposit has bearing on the process selection. In developing countries, high energy cost and low labor costs allow manual operations such as panning and hand sorting as viable processes. Chemical processing in remote areas is often difficult due to the lack of trained personnel. Remoteness from markets places importance on concentrate grade in order to minimize shipping costs. Another important factor for flowsheet design is environmental consideration, especially in terms of suspended solids and reagent discharge to public waters. Tolerance for such discharges is location sensitive.

1.5.2. Characteristics of Tungsten Ores

The common economic tungsten occurrence in North America are scheelite-bearing contact metasomatic deposits where limestone is altered to calcium silicate rock called skarn or tactite. The physical characteristics of tactite are high density, hard, and abrasive. The country rock can be almost any type, but considering the origin of the ore, granite and metamorphic rocks would be expected.

The common occurrences of tungsten world wide are quartz vein deposits in which all four of the common tungsten minerals occur. Many of these deposits are composed of friable, coarsely crystalline tungsten minerals in vein quartz and breccia, which crush easily and are amenable to gravity concentration. Some of the deposits, however, consist of fine-grained ore mineral disseminated through fine-grained quartz, which requires fine grinding with excessive slaming. An example of this is the “horn ore” of the Boulder District, Colorado (see Sec. 1.4.2.2.).

1.5.3. Crushing and Grinding Equipment

Jaw crushing is the usual method of primary reduction because of the low tonnages and the large gape required for breakage of the blocky ore. A gyratory crusher capable of taking 75-cm feed would have a huge overcapacity for the typical tungsten mill. The common practice for second-stage crushing is to use jaw or cone crushers. Cone crushers are favored over gyratories because of greater throw and more clearance, allowing the crushed particles to fall free rapidly, minimizing overbreaking. These units can produce a closely sized product when staged and operated with a high circulating load with vibratory screens. Roll crushers were very popular in the past due to the characteristic low proportion of fines produced, but the low reduction rating and the high wear rates experienced offset any advantages over jaw and cone crushers. Impact crushers generally are considered inferior for tungsten applications because of the friability of the ore minerals, which results in excess slaming. Seyer (1958), however, reported a unique process that used these
characteristics to advantage by screening out the barren coarse rocks after primary crushing.

With the sliming problem always in mind, rod mills have been favored for reduction to liberation size. In ball mills, the balls are free to contact particles of varying size indiscriminately. In rod mills, adjacent rods are held apart by the largest particles, leaving gaps for the fines to be protected from grinding.

Capital costs and horsepower requirements for rod mills are approximately twice that for crushers of equal capacity. However, with abrasive tungsten ores, these higher costs are offset partially by the ease of replacing wear losses with rods without shutdown.

Ball mills are also used, but usually of grate discharge type with large balls. High hydraulic loading with closed circuit sizing is popular, the intention being to maintain short residence time in the mill, minimizing the amount of reduction per cycle.

1.5.4. Crushing and Grinding Circuits—Sizing

The standard practice for minimizing slime production is the design of circuits that use stage reduction, bypass undersize and recirculate the oversize fraction. Generally, two and sometimes three stages of crushing are used to keep the reduction ratio in each stage to minimize the amount of work done between sizing stages. Bypass grizzlies are normally employed at the feed point to the primary crushing, with vibrating screens being employed in closed circuit with the last stage of crushing. The same principles apply to grinding with even more importance as the rock particles approach liberation sizes. Size control in grinding circuits is more difficult and complex. Often the sizing circuits include scalpers to pull out concentrates as soon as they are liberated. Screening is the preferred method for sizing in grinding circuits where the liberation size is not too fine for screening to be impractical (Fig. 1.14) (Zdra, 1959; Banning, 1976; Belsor, 1959).

Mechanical classifiers such as the Dorr (rake type) or Akins (screw type) classifiers depend on settling rates for particle sizing. More recently, hydro-cyclones, which depend on settling rates at high g values, do the same job for equivalent operating costs but with considerably less capital and space requirements. A basic deficiency of classifiers and cyclones is that in addition to sizing, they tend to sort on the basis of specific gravity. In one particular grate discharge ball mill spiral classifier circuit, the circulating load for molybdenite is 370% while the circulating load for the heavier scheelite is 1290% (Carpenter, 1962; Moder and Dahlstrom, 1952).

While classification tends to contribute to tungsten sliming when used in closed circuit grinding, the disadvantages are often offset by the ease and low cost of operation when compared to screening. Scalpers in the circuit can essentially eliminate the problem by extracting the concentrate before regrinding (Fig. 1.14). The additional hutch water introduced by jigs requires provisions for the resulting low-density slurries, but the introduction of dry ore feed at the classifiers reduces the problem.
1.5.5. Gravity Concentration

All tungsten minerals have high specific gravities and therefore are amenable to gravity separation methods if liberation size permits. Consistent with the principle of early recovery between comminution stages, jigs are commonly placed in grinding circuits for use as scalpers to prevent overgrinding. Two types of jigs are used, depending on the particle size range to be recovered. For early stage recovery, the Harz-type jig is used to recover concentrates ranging from 6 to 25 mm in size. These concentrates usually require additional batch treatment such as crushing and rejigging on hutch-type jigs. The latter type of jig produces a hutch product from a ball or rod mill circuit. The compactness of the units and the small elevation differences required for pulp flow makes these units very useful.

Tabling is often the prime concentration method, commonly applied to the coarse fractions while flotation is used for the recovery of the slimes, — 200 mesh (74 µm). Shaking tables usually employed in tungsten mills are Wilfley, Deister, Holman, and Plat-O. Special types of tables with slime decks, corduroy surfaces, and cyclic-tilting tables have met with some success.

For optimum efficiency, table feed size control is exercised through the use of hydraulic classifiers, e.g., Fahrenwald type. Tables are adjustable, allowing close operator control for maximizing concentration grade. A drawback of tables is low throughput, (less than 20 mtpd per unit), but stacked multiple deck units are available for increasing capacity.

Humphreys spirals have been applied successfully for scavenging wolframite, cassiterite, and pyrite from high tonnages of sulfide flotation tailings at Climax (Burk, 1959). Pinched sluices and Reichart cones have found their way into similar applications elsewhere. These units are compact, passive, and inexpensive to operate.

The heavy-medium or sink–float process has found limited use in tungsten beneficiation. The process has value with some coarse ores as a preconcentration step that allows a smaller scale conventional mill. Essentially, it functions in a manner similar to that of the Harz jig but with the added feature of more selectivity by specific gravity of the concentrate. The most severe drawback for the process is the difficulty of separating the dense medium from the ore minerals, especially for fine particle sizes. An example of tungsten concentration by this process is at the Aberfoyle mill, Tasmania, Australia, where heavy-medium separation is accomplished using a ferrosilicon–magnetite medium with specific gravity of 2.62. The products are washed and screened and the medium is recovered by wet magnetic methods. The sink product, which amounts to 40% of the feed, consists of a mixed cassiterite–wolframite–sulfide concentrate that is treated further by standard methods.

1.5.6. Flotation

A majority of the large-scale scheelite producers in the world are using flotation to advantage. Scheelite ore bodies are generally of the contact metasomatic type, which characteristically have finer liberation size. Common collectors used for
Fig. 1.14. See legend on next page.
Fig. 1.14. Typical tungsten grinding circuits: (a) Wah Chang Lincoln Mill, (b) Mineral Engineering Company, (c) Boulder Tungsten Mill, (d) New Idria Strawberry Mill, (e) Zangarelhas Minerçãô.

Scheelite flotation are oleic acid, mixed oleic-linoleic acid, sodium oleate, tall oil, saponified tall oil, and mixtures of the above. Specific choices vary with the particular ore and modifying agents used, but in most cases, the differences in performance is minimal and often the choice is based on cost (Dean and Schack, 1963; Engel, 1952; Eigeles, 1947). Tall oil, the cheapest and probably the most popular collector, is a waste product of wood pulp treatment and is a mixture of oleic acid, linoleic acid, and resin acids with some saturated fatty acids (Pryor, 1965). Since paper is manufactured from many types of wood and by many processes, tall oil composition is highly variable, which means that testing is required before changing tall oil sources. Resin acids in the tall oil give an additional effect of frothing, while using fatty acids with a frother allows independent frothing control.
Some tanninlike bodies are also attributed to tall oil and may tend to depress some of the gangue minerals (Taggart, 1945).

In the absence of modifiers, all of the common collectors discussed above will readily float garnet, quartz, calcite, and essentially all of the common gangue minerals. Most of the collectors for scheelite are also frothers. While it is considered desirable to use single-function reagents to give independent control, it is impossible in scheelite flotation. Some froth control can be attained through mixing collectors of varying composition, such as soaps and acids. The pulp temperature is sometimes quite critical for froth control (McLeod, 1957). When frothers are desired, alcohols and cresylic acid are commonly used. Care must be taken to note the collecting properties of the frother, as some contain fatty acid impurities (Zadra, 1959).

Some control of the froth quality can be exercised by using wetting agents such as Aerosol OT to produce a lacy texture and cresylic acid to stiffen the froth. The selection and control of modifying and depressing agent are the most critical aspects of scheelite flotation. Because of the interactions and variability of these reagents, substantial laboratory testing is required to obtain optimum results.

The action of H\(^+\) and OH\(^-\) ions in flotation is a complex function of several effects, among which are the degree of dissociation of the collector, the electrokinetic potential of the mineral surface, and the presence of ions such as Ca\(^{2+}\), which can interact with the collector and depressants. In practice, the flotation pH is controlled to a tolerance of \(\pm 0.1\) pH unit, but the selected optimum pH for different ores varies from 9.0 to 10.5, depending on the minerals and reagents present in the system. The pH sensitivity can also be altered by the choice of collector (Purcell and Sun, 1963), conditioning temperature (Fig. 1.15), dispersants, and depressants.

Sodium silicate is used as a dispersant to prevent slime coatings, as it is an excellent peptizing agent for silicates and calcite, but low concentration can have the opposite activating effect on calcium minerals (Klassen and Mokrousov, 1963). The general formula for sodium silicate is \(nNa_2O \cdot mSiO_2\), with commercial sources having a modulus \(m/n\) between 2.2 and 3.0. In flotation, the low modulus reagent tends to alkalize the pulp and a modulus greater than 3 tends to produce hydrated silica. The selective action of sodium silicate is usually inadequate when used alone, but selectivity can be enhanced through the use of carbonate and polyvalent cations and elevated temperatures. Sodium carbonate and sodium hydroxide are used regularly as pH modifiers, but the carbonate exhibits effects independent of pH and dependent somewhat on the specific ore. Carbonate can be considered a depressant, but it also tends to reduce the depressing action of sodium silicate on certain calcium minerals (Klassen and Mokrousov, 1963). Polyvalent cations, especially Fe\(^{2+}\), have been demonstrated to be effective for depressing calcite when used with sodium silicate (Belash and Pugina, 1946).

If organic depressants such as quebracho or tannic acid are also in the system, the above cations should be avoided since they will complex with the organic, defeating the purpose of both. In fact, in some situations where heavy metal ions are in solution as a result of previous treatment for sulfide flotation, cyanide, phosphate, or sulfide should be used to complex the metal ions to prevent them from consuming excess organic modifiers.
Fig. 1.15. Sensitivity of scheelite recovery and grade to pH and temperature (using oleic acid as collector with NaOH and HCl) (Mitchell et al., 1951): (a) 26°C, (b) 58°C, (c) 80°C.

Tannin and quebracho, common modifiers, are used to depress calcite. The exact mechanism is not well understood, but it is believed that the tannin forms a preferential coating on the calcite that prevents action of the collector. Excess quebracho tends to depress scheelite and therefore requires accurate control to optimize grade without sacrificing recovery. Other organics find limited use in scheelite flotation, notably short-chain organic acids such as formic acid for depressing apatite and lactic acid for depressing mica.

Recent research at Union Carbide Corporation (Vazquez et al., 1976) has resulted in a new “lime process,” which produced excellent selectivity for scheelite in the presence of fluorite. Contrary to prevailing theory, the presence of lime in the system is beneficial if properly controlled. The process is simply the sequential addition of lime, which is believed to adsorb to the surface of fluorite, calcite, and quartz. This is then followed by the addition of sodium carbonate, which causes the selective formation of a calcium carbonate coating on the gangue mineral surface. Any excess lime is precipitated and thereby prevented from consuming the collector, which is added later. A selective depressant for calcite then is effective for depressing all minerals with the calcium carbonate coating (Fig 1.16).

In general, it may be said that increased selectivity through the addition of depressants will result in decreased recovery. The high value of scheelite and the
availability of inexpensive chemical processing requires a careful consideration of the level of selectivity required in the flotation process.

Flotation of the wolframite minerals is similar in practice to scheelite flotation, but the technique is not in common use for a variety of reasons. With notable exceptions, wolframite, huebnerite, and ferberite occur in vein-type deposits, where tungsten mineral grain size, associated minerals, and selective mining (sorting) make gravity and magnetic methods desirable. The pH sensitivity of the wolframite minerals is low and the process can be operated under acid as well as basic conditions. In the United States, flotation has been applied successfully to huebnerite (Dice, 1943) and to ferberite (Reck, 1970) in the “horn ores” of the Boulder, Colorado deposits.

Sulfide minerals almost always occur in tungsten deposits, and the approach to handling them is usually governed by their economic significance. When high sulfide
recovery is desirable, bulk sulfide flotation using xanthates usually precedes all other processing. The details of sulfide flotation are beyond the scope of this book. The effects of sulfide flotation on subsequent processing are generally minimal, but some tungsten will be lost to the sulfide as locked particles. If sulfide recovery is not critical, most of the sulfides can be depressed by cyanide during the standard tungsten flotation. In any case, some sulfides will be in the tungsten concentrates as impurities and can be removed by batch sulfide flotation as the last wet process in the mill. Concentrates destined for chemical processing to synthetic scheelite or ammonium paratungstate can contain small amounts of sulfides without penalty, and these small amounts need not be removed (see Chapter 2).

Reagent consumption for tungsten flotation depends on the specific ore. Table 1.12 gives typical reagent consumption employed in some companies in the United States (Zadra, 1959). Most studies have indicated that pulp concentration and temperature are not critical. Conditioning time, however, is reportedly more critical for concentrate grade. Froth spraying has been employed advantageously to increase grade by washing the entrained gangue minerals from the froth (Mitchell et al., 1951; Klassen and Mokrousov, 1963).

1.5.7. Magnetic Separation

Magnetic separators are frequently employed in tungsten beneficiation either for cleaning scheelite or for concentrating wolframite minerals. Table 1.10 includes the magnetic properties of the minerals commonly associated with tungsten deposits. It can be inferred that many simple separations are feasible, except that locked particles and iron coatings on normally low-magnetic or nonmagnetic minerals cause a problem. Traditionally, dry magnetic separators have been applied to scheelite concentrates for removing garnet, magnetite, and roasted pyrite. These units are also used to separate magnetic wolframite from cassiterite, unroasted pyrite, and other nonmagnetics.

There are two types of dry magnetic separators in use—the cross belt type (Witherill) and the induced roll type. The former is most selective for separating several different magnetic minerals, while the latter is favored for high-recovery simple separation. Among the disadvantages of the dry process are dusting, a drying step, and most important, difficulty in processing −100 mesh particles.

Recent advances have been made in wet magnetic separators by using pole boxes containing ferromagnetic packing to create a high field gradient (Jones separator). The feed slurry is introduced to the pole box with the magnetic field energized. The nonmagnetics are washed through, while the magnetic minerals stick to the packing. The field is interrupted either by switching off or by moving the box away from the magnetic poles, allowing the magnetics to be washed out of packing. The most common pole box configuration is in the form of a carousel, which allows continuous operation (Stone, 1964). The major advantages of the Jones separator are ready separation of fine sizes, single-stage process, and simple slurry feeding. Normally, the power requirement is less than 3 kW hr⁻¹ mt⁻¹ ore treated. The first commercial separator of this kind was installed in Tasmania, Australia, for removing garnet from scheelite.
## Table 1.12. Reagent Consumption of Primary Flotation for Some United States Companies

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Nevada Scheelite, Rawhide, Nevada</th>
<th>Gabbs Exploration, Gabbs, Nevada</th>
<th>Wah Chang Lincoln Div., Tempiute, Nevada</th>
<th>Wah Chang Benton Div., Bishop, California</th>
<th>Union Carbide, Bishop, California</th>
<th>Strawberry New Idria, Fresno, California</th>
<th>Minerals Engineering, Glen, Montana</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda ash</td>
<td>0.75</td>
<td>3.0–5.0</td>
<td>2.0–3.5</td>
<td>6.5</td>
<td>1.0–1.5</td>
<td>0.48</td>
<td>1.5–2.5</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>1.25</td>
<td>2.0</td>
<td>2.5</td>
<td>3.75</td>
<td>0.4c</td>
<td>—</td>
<td>1.0–1.5</td>
</tr>
<tr>
<td>Tannin</td>
<td>0.25b</td>
<td>0.1b</td>
<td>0.4c</td>
<td>0.25c</td>
<td>0.5–0.75</td>
<td>0.095c</td>
<td>0.05</td>
</tr>
<tr>
<td>Collector</td>
<td>Oleic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Others</td>
<td>0.3d</td>
<td>0.15</td>
<td>0.1</td>
<td>0.25</td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Frothers</td>
<td>0.025e</td>
<td>0.075e</td>
<td></td>
<td>0.075e</td>
<td>0.5–0.75e</td>
<td>0.315d</td>
<td>0.75f</td>
</tr>
<tr>
<td>Detergent</td>
<td>—</td>
<td>—</td>
<td>0.03f</td>
<td></td>
<td>0.085e</td>
<td>0.075–0.09a</td>
<td>—</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>0.15</td>
<td>0.05–0.1</td>
<td>0.2</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Zadra, 1959.  
+ Oleic acid + blown tail oil (1:1).  
&#8211; Palcolan.  
O Reagent 710.  
&#8211; Quebracho.  
^ Aliphat 44-E.  
* Emcol 4150.  
° Aerosol 18.  
* Pine oil.  
° Aliphat 44-E.  
* Emcol 4150.
1.5.8. High-Tension Separation

Electrodynamic and electrostatic separators are not commonly found in tungsten mills, except for the unique case of separating cassiterite from scheelite. Cassiterite is a conductor while scheelite is a nonconductor if not stained by a conductor. The surface condition and dryness of the feed to the machine is critical to good operation.

1.5.9. Current Industry Practice

1.5.9.1. Scheelite Ore Treatment at Minerals Engineering Company

The recently closed concentrator-chemical plant near Glen, Montana (Fig. 1.17) was typical of the world's major scheelite producers. The emphasis was on moderate concentration with high recovery followed by chemical processing to remove the contained molybdenum. Other producers that follow this flowsheet in a general way include the Pine Creek mill near Bishop, California, and the Sang Dong mill in Korea.

The Glen plant was designed for approximately 227 mtpd of ore from which 2270–2545 kg (5000–5600 lb) per day of pure ammonium paratungstate was produced (Banning, 1976). The crushing circuit had a capacity of approximately 45 tph of dry ore (<5% moisture). Simple open circuit crushing was practiced with a 406 × 762 mm (16 × 30 in.) Allis-Chalmers jaw crusher (set 76 mm or 3 in.) and a 914 mm (36 in.) Symonds standard cone crusher (set 22 mm or \( \frac{3}{8} \) in.) with a 22-mm (\( \frac{3}{8} \)-in.) screen between the crushers. Two small belt conveyors picked up leakage from the apron feeder in order to eliminate shutting down during a shift for cleaning under the feeder. All the undersize, 22-mm (\( \frac{3}{8} \)-in.) material was stored in a 1818-mt (2000-ton) stockpile situated over a chute for the ball mill feed belt. The crushed ore entered a 2.134-m diameter × 2.483-m (7-ft diameter × 8 ft) ball mill along with soda ash (2.5 kg mt\(^{-1}\)) and was ground at pH 10.0 with 60–65% solids. Rougher flotation was fed with essentially –48 mesh material from a Don-Oliver Rapine DSM (Dutch-State Mines) screen in closed circuit with the ball mill. The pulp was conditioned in a 1.829-m diameter × 1.829 m (6-ft diameter × 6 ft) Denver conditioner with sodium silicate, Dresinate TX, Emersol 221, and pine oil. Dresinate TX is a mixture of sodium oleate and sodium linoleate, whereas Emersol 221 is a low-titer oleic acid. The oleic acid was employed principally for froth control and recovery of scheelite in the coarse size fractions.

Rougher flotation was accomplished at approximately 35% solids and the concentrate was tailed. However, the concentrate from the first two cells of the rougher flotation could be drawn off, if desired, into the final concentrate stream, since at time the grade of the froth on these cells was sufficient to warrant such a step. Sodium silicate was added to the rougher concentrate prior to tabling in an effort to completely disperse the particulate material and, also, to further depress gangue minerals in the cleaning operation.

Five cleaning steps were involved in the acquisition of the final flotation concentrate. Successive additions of tannic acid were utilized throughout the cleaning operation for the depression of calcite. Tailings from the “cleaners” and
"recleaners" were tabled, and the table tailings were fed to scavenger flotation, along with the rougher flotation tailings. A regrinding step was used for the scavenger flotation feed, wherein a cyclone and a 914-mm diameter \( \times 1219 \text{ mm (3-ft diameter } \times 4 \text{ ft) conical ball mill were employed in an open circuit. Scavenger flotation produced the final tailing and a scavenger concentrate, which was tabled with the rougher concentrate.

The final concentrate was dewatered in a 6.096-m diameter (20-ft) Denver thickener and a 1.219-m (4-ft) disk filter. A monohearth furnace was used for drying. The concentrating circuit exhibited a recovery of 90–92%. Average assays were as
follows: feed, 1.0% WO₃; final concentrate, 45.0% WO₃; final tailing, 0.08% WO₃. The reagent consumptions are approximately as follows: soda ash, 2.5 kg mt⁻¹; sodium silicate, 2.5 kg mt⁻¹; Dresinate TX, 0.10 kg mt⁻¹; Emersol 221, 0.15 kg mt⁻¹; pine oil, 0.05 kg mt⁻¹; tannic acid, 0.05 kg mt⁻¹.

### 1.5.9.2. Scheelite–Fluorspar–Copper Concentration at Yxsjoberg

The Yxsjoberg Mill, Sweden, is a complex operation that utilizes practically every technique and principle applied to tungsten ores (Fig 1.18). The process consists basically of four concentrating stages—coarse scheelite tabling, sulfide flotation, fluorspar–scheelite flotation, an fluorspar–scheelite separation by tabling. Each of the stages contains examples of concentration at minimum liberation size with middling reground. Circulating loads between concentration stages are also used, so that all of the ore is eventually reduced to slimes by many stages of reduction and through a series of nested loops (MB, 1972).

The underground crushing station consists of a primary jaw crusheer followed by a gyratory, both in open circuit to a 545-mt (600-ton) underground bin, where the ore is hoisted to a headframe bin and then fed to a gyratory crusheer in closed circuit with a 25-mm (1-in.) screen. The undersize is conveyed to a 1454-mt (1600-ton) silo at the mill. From the silo, the fine ore passes open circuit through a rod mill for essentially a fourth crushing stage. The ore is sized into two fractions by 0.5-mm (0.020-in.) screens and passed over tables to scavenge the coarse liberated scheelite. The middlings from all tables are classified and the underflow ground in a separate rod mill and returned to the screens for another pass over the tables until the reduced middlings reported to the table tailings. Classifier overflow combines with the table tailings.

The table tailings enter a ball mill–cyclone circuit for fine grinding. Cyclone overflow feeds the copper scavenger flotation cells, and the sulfide concentrates undergo further ball milling and flotation to produce a 25% Cu concentrate.

Sulfide scavenger tailings enter the fluorspar roughing section, which also floats the fine scheelite. This is the last stage, which carries essentially the full feed tonnage, and all subsequent stages are treating concentrates. Fluorspar–scheelite rougher concentrates continue to cleaner cells with the concentrates from this step passing through two stages of tabling, which produce a scheelite concentrate, a middling, which returns to further grinding, and flotation, with ultimate return to the cleaner cells, and tailings, which are the fluorite concentrated product, 85–97% CaF₂.

The middling from the cleaner section is classified with the overflow passing over tilting tables, which produce a scheelite concentrate and waste tailings. The underflow passes over tables that produce a scheelite middling, which is ball milled and combined with the tailings for final flotation. The concentrate is returned to the fluorspar cleaner section.

Scheelite concentrates from the above three sources are dewatered and dried. Agglomerates from the dryer are milled, and the powder is passed through magnetic separators, with the magnetics returning to the tables. Two grades of scheelite concentrates are produced, 73% and 40% WO₃, respectively.
Fig. 1.18. Ore dressing at the Ysjoberg Mine (MB, 1972).
1.5.9.3. Wolframite Recovery at the Climax Molybdenum Plant

In terms of grade and tonnage, the Climax Molybdenum by-product plant operation is unique and possibly a harbinger of future practices in other large-tonnage mills which currently reject tungsten minerals in the tailings (Fig. 1.19). Although some improvements have been made in recent years (Sinisi, 1976), the following summary is based on the paper by Burk (1959) because it is the most complete study done to date.

Ore was crushed and ground to relatively fine sizes to liberate the primary value, molybdenite, which was floated, leaving 96% of the pulp to be further processed in the by-product plant. Fine liberation required for the molybdenite resulted in high slime content, which caused recovery problem in the gravity process that followed.

Flotation tailings from the primary concentrator were fed to five-turn Humphreys spirals, with about 7% middlings recycled. Feed rate per spiral was about 43.6 dry mt (48 tons) per day with a water consumption of 20 liters (5 gal) per minute. Cleaner spirals that followed were scheduled to be replaced by Reichart cones in late 1976; the cones were expected to consume less water, and increase recovery by 2–3%.

Spiral concentrates are dewatered in 254-mm (10-in.) 20° Krebs cyclones with a resulting underflow composition of 30% solids containing 0.6% WO₃ and 30% pyrite. Pyrite was floated using Z-3 ethyl xanthate at pH 5.0. Flotation tailings were distributed to a two-stage Deister slime table system, which rejected more light tailings. Monazite contained in the table concentrates was separated by amine flotation using Armac C at 38°C (100°F) and pH 1.2. Wolframite was selectively depressed by starch addition. The monazite concentrate was tabled to produce a low-grade WO₃ product. The flotation tailings were thickened and passed through a low-intensity wet magnetic separator to remove iron, after which the slurry was dewatered and dried. The final treatment was the three-stage dry magnetic separation, which produced high-grade wolframite, low-grade wolframite containing titanium minerals, and the nonmagnetic cassiterite, which contained residual pyrite, quartz, and rare earth minerals.

1.5.9.4. Scheelite Milling at Canadian Exploration, Ltd.

The Canadian Exploration, Ltd. Mill, Salmo, British Columbia, Canada, was a typical example of evolution from a small gravity plant to hybrid gravity–flotation plant (Fig. 1.20) with a capacity of 636 mtpd (700 tpd). Ore occurred in limestone and typical tactite, with a major difference being an extraordinary amount of pyrrhotite. Average feed assayed in 1956 was 0.7% WO₃ and 5 and 5% sulfur. Most of the scheelite was liberated at 65 mesh, but some locked scheelite was found in particles down to 200 mesh (scheelite tended to be finely disseminated in the pyrrhotite).

The high sulfide content of the ore was the major factor in choosing the milling scheme; there was ten to fifteen times as much sulfide as scheelite. The outline of the operation is as follows (Steane, 1957; McLeod, 1957):

1. Grinding to –200 mesh for 40% undersize.
Fig. 1.19. Climax by-product plant flowsheet (Burk, 1959): (1) D-41-5 slurry-type Hydroseal pumps, (2) D-6-5 slurry-type Hydroseal pumps, (3) 752 Humphreys spiral concentrators—five-turn model 24A, (4) Denver 5 x 5 in. (127 x 127 mm) SRL pumps, (5) Denver 6 x 6 in. (152 x 152 mm) SRL pumps, (6) Krebs D-
2. Flotation of sulfide minerals for removal of sulfur.
3. Separation of remaining feed into sand and slime fractions.
4. Hydraulic sizing of sand fraction into five sizes.
5. Tabling of sized fractions to recover scheelite of marketable grade.
6. Thickening and flotation of the combined table tailings and slime fraction to recover scheelite.
7. Leaching of scheelite flotation concentrate with hydrochloric acid to dissolve calcite and apatite.
8. Blending of table concentrate and leached concentrate by batches to give a reasonable uniform product to meet specifications.

In the grinding circuit, a rod mill fed a primary classifier, which overflowed a finished product and delivered sand to a ball mill which was in closed circuit with a second classifier. Approximately one-third of the feed left the circuit in the overflow of the primary classifier. A portion of this overflow was returned through the rod mill to facilitate the entrance of new feed and to assist the flow of coarse ore through the rods; this practice had increased the feed rate from 545 to 636 mt (600 to 700 tons) per day. Both mills were 1.8 m diameter × 3.7 m (6 ft diameter × 12 ft) Dominion overflow type, with combination scoop and drum feeders, and driven by 149 kW (200 hp) motors and speed reducers. The mills were lined with single-wave-type manganese steel. The rods were 76 mm diameter × 3400 mm (3-in. diameter × 11 ft 3 in.) in size and occupying 50% of the mill volume. Operating parameters were: rod mill discharge, 76–80% solids; ball mill discharge, 70% solids; primary and secondary classifier overflows, 45% solids. Size analyses of grinding circuit feed and discharge products are given in Table 1.13.

Feed to the sulfide flotation circuit assayed 4–7% sulfur. Flotation was carried out at 40% solids and pH 8.4, the natural pH of the ore pulp. Reagents used per metric ton of ore were: pentasol xanthate, 0.1 kg (0.22 lb); Aerofloat 25, 0.07 kg (0.15 lb); copper sulfate, 0.03 kg (0.05 lb); methyl amyl alcohol, 0.01 kg (0.02 lb).

Sulfuric acid up to 3 kg (6.6 lb) per metric ton was used for several years in the sulfide flotation to improve floatability of pyrrhotite, but sulfuric acid was suspected of lowering scheelite recovery in the subsequent scheelite flotation. Calcium sulfate thus formed increased the consumption of soda ash in scheelite flotation and at times made it impossible to obtain the desired pH of 10.2. Use of sulfuric acid was
discontinued in 1955. Reduced sulfide recovery was considered acceptable, and the small amount of residual sulfide in the scheelite table concentrate was removed in an auxiliary sulfide flotation circuit before reaching the cleaner tables.

Underflow from sulfide flotation was sized by two stages of Dorrclones with the overflow passing to the scheelite flotation feed thickener. Sands from the Dorrclone passed to a Dorrco (Fahrenwald type) hydraulic sizer to produce five size fractions for tabling. Tables were of No. 6 Deister Diagonal Deck type with the pitch
Table 1.13. Size Analyses of Grinding Circuit at Canadian Exploration Ltd., Mill

<table>
<thead>
<tr>
<th>Screen fraction</th>
<th>Mill feed</th>
<th>Rod mill discharge</th>
<th>Primary classification sand</th>
<th>Ball mill discharge</th>
<th>Secondary classification sand</th>
<th>Primary classification overflow</th>
<th>Secondary classification overflow</th>
<th>Combined classification overflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% on</td>
<td>% cum.</td>
<td>% on</td>
<td>% cum.</td>
<td>% on</td>
<td>% cum.</td>
<td>% on</td>
<td>% cum.</td>
</tr>
<tr>
<td>+18.8 mm</td>
<td>16.1</td>
<td>16.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-18.8 + 13.3 mm</td>
<td>24.9</td>
<td>41.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-13.3 + 9.4 mm</td>
<td>10.6</td>
<td>51.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-9.4 + 6.7 mm</td>
<td>8.8</td>
<td>60.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3 + 4 mesh</td>
<td>5.0</td>
<td>65.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4 + 6 mesh</td>
<td>4.8</td>
<td>70.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-6 + 8 mesh</td>
<td>2.4</td>
<td>72.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-8 + 10 mesh</td>
<td>2.7</td>
<td>75.3</td>
<td>6.4</td>
<td>6.4</td>
<td>11.2</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10 + 14 mesh</td>
<td>2.9</td>
<td>78.2</td>
<td>8.4</td>
<td>14.8</td>
<td>25.5</td>
<td>34.9</td>
<td>3.4</td>
<td>37.3</td>
</tr>
<tr>
<td>-14 + 20 mesh</td>
<td>2.2</td>
<td>80.4</td>
<td>10.8</td>
<td>25.6</td>
<td>43.7</td>
<td>74.1</td>
<td>3.4</td>
<td>77.5</td>
</tr>
<tr>
<td>-20 + 28 mesh</td>
<td>1.6</td>
<td>82.0</td>
<td>9.1</td>
<td>34.7</td>
<td>13.7</td>
<td>57.4</td>
<td>4.6</td>
<td>62.0</td>
</tr>
<tr>
<td>-28 + 35 mesh</td>
<td>1.9</td>
<td>83.9</td>
<td>8.9</td>
<td>43.6</td>
<td>12.2</td>
<td>69.6</td>
<td>10.4</td>
<td>80.0</td>
</tr>
<tr>
<td>-35 + 48 mesh</td>
<td>1.4</td>
<td>85.3</td>
<td>7.1</td>
<td>50.7</td>
<td>7.9</td>
<td>77.5</td>
<td>12.8</td>
<td>90.3</td>
</tr>
<tr>
<td>-48 + 65 mesh</td>
<td>1.3</td>
<td>86.6</td>
<td>6.3</td>
<td>57.0</td>
<td>5.1</td>
<td>82.6</td>
<td>14.5</td>
<td>97.1</td>
</tr>
<tr>
<td>-65 + 100 mesh</td>
<td>1.6</td>
<td>88.2</td>
<td>6.2</td>
<td>65.2</td>
<td>3.7</td>
<td>86.3</td>
<td>13.5</td>
<td>100.0</td>
</tr>
<tr>
<td>-100 + 150 mesh</td>
<td>1.8</td>
<td>89.4</td>
<td>5.1</td>
<td>68.3</td>
<td>2.5</td>
<td>88.8</td>
<td>9.4</td>
<td>100.0</td>
</tr>
<tr>
<td>-150 + 200 mesh</td>
<td>0.9</td>
<td>90.4</td>
<td>3.7</td>
<td>72.0</td>
<td>1.5</td>
<td>90.3</td>
<td>6.1</td>
<td>96.0</td>
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<tr>
<td>-200</td>
<td>9.6</td>
<td>100.0</td>
<td>28.0</td>
<td>100.0</td>
<td>9.7</td>
<td>100.0</td>
<td>25.3</td>
<td>100.0</td>
</tr>
<tr>
<td>Solids %</td>
<td></td>
<td>76.4</td>
<td>65.0</td>
<td>47.3</td>
<td>30</td>
<td></td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

Calculated proportion of mill feed (%)

* Steane, 1957.
adjusted according to the feed size. For the coarse fractions, the longitudinal pitch was 21 mm/m (0.25 in./ft), and transverse 94 mm/m (1.125 in./ft). The fine tables were pitched 10 and 62.5 mm/m (0.125 and 0.750 in./ft). Table speeds were \( \frac{3}{4} \) stroke/min with amplitudes running 9.5–19.1 mm (0.375–0.750 in.). There were 18 roughers, 4 middling tables, and 4 cleaner tables. Smaller hydraulic sizers were used to classify the middling and cleaner table feeds. Wet magnetic separation and auxiliary sulfide flotation were placed in the circuit ahead of the cleaner tables.

Two 12-m (40-ft) thickeners received all of the cyclone overflows and the table tailings. Either Separan 2610 or Aerofloc 3000, 0.0025 kg/mt (0.005 lb/ton) were used

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**Table 1.14. Elutriation of Tungsten Flotation Tailings, Canadian Exploration Ltd.**

*(Week's Composite July 16–22, 1956)*

<table>
<thead>
<tr>
<th>Size</th>
<th>Weight %</th>
<th>Assay (% WO₃)</th>
<th>Distribution of WO₃ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Progressive</td>
<td>Cumulative</td>
<td>Progressive</td>
</tr>
<tr>
<td>+48 mesh</td>
<td>10.4</td>
<td>10.4</td>
<td>0.10</td>
</tr>
<tr>
<td>-48 + 65 mesh</td>
<td>11.7</td>
<td>22.1</td>
<td>0.10</td>
</tr>
<tr>
<td>-65 + 100 mesh</td>
<td>13.5</td>
<td>35.6</td>
<td>0.08</td>
</tr>
<tr>
<td>-100 + 325 mesh</td>
<td>35.3</td>
<td>70.9</td>
<td>0.05</td>
</tr>
<tr>
<td>-325 + 26 μm</td>
<td>13.2</td>
<td>84.1</td>
<td>0.08</td>
</tr>
<tr>
<td>-26 + 13 μm</td>
<td>5.1</td>
<td>89.2</td>
<td>0.09</td>
</tr>
<tr>
<td>-13 μm</td>
<td>10.8</td>
<td>100.0</td>
<td>0.37</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Steane, 1957.

* 325 mesh aperture 42 μm. Elutriation sizes are for quartz.

---

**Table 1.15. Metallurgical Balance, Canadian Exploration, Ltd.**

*(September 1, 1955–May 31, 1956)*

<table>
<thead>
<tr>
<th>Process step</th>
<th>Ore</th>
<th>WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tons</td>
<td>% WO₃</td>
</tr>
<tr>
<td>Mill feed</td>
<td>150,125</td>
<td>136,464</td>
</tr>
<tr>
<td>Iron concentrate</td>
<td>12,294</td>
<td>11,175</td>
</tr>
<tr>
<td>Table concentrate</td>
<td>471</td>
<td>428</td>
</tr>
<tr>
<td>WO₃ flotation feed</td>
<td>137,360</td>
<td>124,860</td>
</tr>
<tr>
<td>Leached concentrate</td>
<td>823</td>
<td>748</td>
</tr>
<tr>
<td>Leaching loss</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Leach feed</td>
<td>1,998</td>
<td>1,817</td>
</tr>
<tr>
<td>WO₃ flotation tailings</td>
<td>135,362</td>
<td>123,044</td>
</tr>
<tr>
<td>Total tailings</td>
<td>148,831</td>
<td>135,288</td>
</tr>
<tr>
<td>Total recovery</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Steane, 1957.
Fig. 1.21. Canada Tungsten Mining Company mill flowsheet (EMJ, 1963. Copyright by McGraw-Hill, Inc., 1221 Avenue of the Americas, New York.): (1) 30 x 48 in. (762 x 1219 mm) Kennedy Van Saun jaw crushe, (2) 18 x 30 in. (457 x 762 mm) Allis-Chalmers jaw crushe, (3) 3-ft (914-mm) Symons standard cone crushe, (4) 7 x 10 ft (2.1 x 3.1 m) Hardinge rod mill, (5) Dorr-Oliver Dorrcelone, (6) Dorr-Oliver DSM screen classifiers, (7) No. 24 Denver cells, (8) Dorr-Oliver Dorrcelone, (9) Dorr-Oliver DSM screens, (10) triple-deck Concenco 666 Deister tables, (11) single-deck Deister tables, (12) 10-ton (9.2-mt) steel bins, (13) concentrate thicken, (14) eight-cell Denver No. 21 circuit, (15) five-stage cleaning takes place in a six-cell Denver No. 15.
to promote thickening. Thickener underflow at about 45% solids was conditioned for 16 min at pH 10.1–10.2, adjusted with soda ash at 16–20°C. The reagents consumed were: soda ash, 1.25 kg/mt; sodium silicate, 0.125 kg/mt; quebracho, 0.40 kg/mt; sodium cyanide, 0.075 kg/mt; oleic acid, 0.20 kg/mt. Typical flotation concentrate analyzed 30% WO₃, 0.24% sulfur, and 3.5% phosphorus. This concentrate was further upgraded by hydrochloric acid leaching to remove calcite and apatite. Typical data of flotation tailings are shown in Table 1.14 and metallurgical balance of the plant are shown in Table 1.15.

1.5.9.5. Milling of Tungsten Ores at the Canada Tungsten Mining Corporation

The flowsheet of the milling process for Canada Tungsten Mining Corporation, Canada, is shown in Fig. 1.21. The 273-mt (300-ton) capacity concentrating process involved crushing, grinding, tabling (+ 400 mesh), and flotation (− 400 mesh). The gravity concentrate was expected to analyze better than 72% WO₃, and the flotation concentrate about 70% WO₃. In both cases, molybdenum, bismuth, arsenic, lead, antimony, tin, and phosphorus impurities were to average less than 0.2%. A by-product recovery plant was to process copper and sulfides extracted from the flotation cells (EMJ, 1963).
Extractive Metallurgy of Tungsten

2.1. INTRODUCTION

Historically, the extractive metallurgy of tungsten has its origin in the initial isolation of the element from wolframite by Spanish brothers J. J. and F. de Elhujar in 1783 (Smithells, 1953). Three years later, they noted that tungsten forms a hard, brittle alloy with pig iron, and in the same year, H. I. Duhamel du Monceau suggested the possibility of using tungsten to harden steel. The earliest industrial application of tungsten was apparently in steel making, by J. Jacob and Koeller in France in 1855 (Li and Wang, 1955).

The first process for producing sodium tungstate and tungstic acid, from which high-purity tungsten can be made, was patented in Britain by Robert Oxland (1847). It is the basis of the modern alkali fusion process. Later C. M. Johnson (1910) introduced a process to decompose high-grade scheelite with hydrochloric acid. A more recently introduced method of decomposing tungsten ore was invented by I. M. Maslenitskii (1939). It is widely used today, since it may be applied efficiently to low-grade ores and works equally well with scheelite and some grades of wolframite.

In the last few years, chlorination as a step in tungsten extraction has been under investigation. Thus, Svanstrom and Ramqvist (1971) patented a method in which tungsten ore is converted to tungsten silicide by heating with silicon and then converted to tungsten hexachloride by chlorination at 800°C. The hexachloride can then be reduced to tungsten metal with hydrogen.

The term “extractive metallurgy” refers to those process steps that start with an ore concentrate and end with an intermediate compound that can be reduced to yield metallic tungsten of desired purity and metallurgical properties. The objective of the extractive process is thus to convert the tungsten value contained in the ore concentrate to the intermediate compound, usually tungstic acid or ammonium paratungstate. Generally, the ore concentrate is given a pretreatment to remove impurities that may be difficult or more expensive to eliminate at a later stage. The next step is the ore decomposition, in which the tungsten is isolated from other major constituents of the ore and converted to a form in which subsequent purification is feasible. Some purification is also accomplished during ore decomposition. Finally, the remaining impurities are removed, and the desired intermediate compound is obtained. Impurities that adversely affect the properties
of tungsten in some or all applications and that are apt to be present in ore concentrates, include alkali metals, alkaline earth metals, boron, aluminum, silicon, tin, lead, phosphorus, iron, cobalt, nickel, and copper. Contrary to the case of many other metals, little or no purification is effected during reduction of the intermediate compound to metallic tungsten. The reduction process will be treated in Chapter 3 separately.

The main primary sources of tungsten are the minerals scheelite and wolframite (see Sec. 1.2 for details). Table 2.1 lists analyses of a selection of scheelite and wolframite concentrates; this list may not be representative nor comprehensive but it illustrates the the range of Wo3 and impurity contents that can be encountered. It should be noted that even the highest-grade concentrates fall considerably short of the tungsten content of the pure compound, and that the lower-grade concentrates may contain less than 10% Wo3.

Due partly to the extremely high melting point of tungsten, its extraction is carried out by hydro- rather than pyrometallurgical processes. While a large number of schemes have been proposed for decomposing tungsten ores and purifying the resultant compounds, only a few have been adopted as the current industrial practices. Choice of the ore decomposition depends on both the type and the grade of the concentrate, and determines the options available for subsequent purification steps.

The methods of preliminary treatment of the ore concentrate are quite straightforward and involve either roasting in air or leaching with dilute acid. The former is used for wolframite contaminated with sulfur and arsenic and for low-grade scheelites, particularly those that may contain organic residues. The latter is applied for high-grade scheelites contaminated with phosphorus, partly ularly when present in the form of apatite.

Decomposition with hydrochloric acid is restricted to high-grade scheelite. The

<table>
<thead>
<tr>
<th>Source</th>
<th>WO3</th>
<th>CaO</th>
<th>Mg</th>
<th>B</th>
<th>Al</th>
<th>Si</th>
<th>Sn</th>
<th>Pb</th>
<th>P</th>
<th>As</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Scheelite</strong> (composition of pure calcium tungstate: 80.52% WO3, 19.48% CaO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sang Dong</td>
<td>71.4</td>
<td>20.3</td>
<td>0.3</td>
<td>—</td>
<td>2.0</td>
<td>0.77</td>
<td>0.01</td>
<td>&lt;0.025</td>
<td>0.016</td>
<td>—</td>
<td>0.010</td>
</tr>
<tr>
<td>South Korea</td>
<td>69.7</td>
<td>10.0</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.22</td>
<td>1.35</td>
<td>&lt;0.01</td>
<td>0.10</td>
<td>0.014</td>
<td>0.0066</td>
<td>0.010</td>
</tr>
<tr>
<td>Mexico</td>
<td>68.9</td>
<td>16.9</td>
<td>0.84</td>
<td>&lt;0.01</td>
<td>0.23</td>
<td>2.94</td>
<td>&lt;0.01</td>
<td>&lt;0.025</td>
<td>0.007</td>
<td>&lt;0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Canada</td>
<td>66.4</td>
<td>19.88</td>
<td>0.8</td>
<td>0.004</td>
<td>1.24</td>
<td>2.44</td>
<td>3.0</td>
<td>0.25</td>
<td>0.170</td>
<td>0.170</td>
<td>0.100</td>
</tr>
<tr>
<td>Thailand</td>
<td>72.0</td>
<td>20.3</td>
<td>0.25</td>
<td>&lt;0.001</td>
<td>1.0</td>
<td>0.60</td>
<td>0.04</td>
<td>0.02</td>
<td>0.008</td>
<td>&lt;0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Kings Island, Tasmania</td>
<td>31.4</td>
<td>13.9</td>
<td>2.4</td>
<td>&lt;0.0001</td>
<td>2.49</td>
<td>16.3</td>
<td>0.001</td>
<td>0.03</td>
<td>0.995</td>
<td>0.0002</td>
<td>&lt;0.0025</td>
</tr>
<tr>
<td>Minersville, Austria</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B. Wolframite</strong> (composition of pure FeWO4: 76.34%, WO3, 23.66% FeO; pure MnWO4: 76.57%, WO3, 23.43% MnO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>65.8</td>
<td>2.14</td>
<td>0.04</td>
<td>0.005</td>
<td>0.40</td>
<td>1.36</td>
<td>1.0</td>
<td>0.066</td>
<td>0.0137</td>
<td>0.058</td>
<td>0.045</td>
</tr>
<tr>
<td>Bolivia</td>
<td>60.5</td>
<td>2.30</td>
<td>—</td>
<td>—</td>
<td>1.17</td>
<td>2.73</td>
<td>—</td>
<td>0.220</td>
<td>1.0</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1. Analyses of Some Typical Tungsten
product tungstic acid is insoluble and is isolated by filtration. The technique is not applicable to low-grade scheelite, because the other components of the ore are either insoluble in hydrochloric acid and thus require a large amount of acid to make the slurry susceptible to agitation or are soluble and consume excessive amounts of the acid. Wolframite can also be decomposed by this method, but with quite poor efficiency. Further purification of tungstic acid is possible, but the amount of molybdenum removal is rather limited.

Decomposition with alkalis is more expensive than with hydrochloric acid but has the advantage that lower-grade concentrates can be decomposed efficiently, especially using the autoclave–soda process. Furthermore, either scheelite or low-manganese wolframite or mixtures thereof can be employed under identical conditions with sodium carbonate.

All of the alkali decomposition results in sodium tungstate solution as an intermediate product. Purification of sodium tungstate is more complicated than that of tungstic acid, but molybdenum removal can be accomplished much more efficiently. For almost all tungsten applications it is necessary to remove alkali metals to low levels (<25 ppm), and this has resulted recently in the almost universal adoption of a liquid–liquid (ion-exchange) extraction process using a high-molecular-weight amine as the extractant. This process extracts the tungsten from the sodium tungstate solution, leaving sodium in the aqueous phase. The tungsten is subsequently stripped from the amine using aqueous ammonia, and the intermediate product ammonium paratungstate (APT) is obtained by crystallization from the mother liquor.

In this chapter, the extractive metallurgy is described with special emphasis on unit operation technology; the relative merits of the process options will be discussed in detail. A considerable amount of laboratory data is presented, and the industrial practices are illustrated to show the trend of the recent development.

### Ore Concentrates from Various Sources

<table>
<thead>
<tr>
<th>Component content (wt %)</th>
<th>S</th>
<th>F</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mo</th>
<th>MnO</th>
<th>FeO</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
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<tr>
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<td></td>
</tr>
<tr>
<td>0.56</td>
<td></td>
<td>0.025</td>
<td>0.010</td>
<td>&lt;0.010</td>
<td>0.51</td>
<td>0.258</td>
<td>3.74</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>0.410</td>
<td></td>
<td>0.075</td>
<td>0.010</td>
<td>&lt;0.010</td>
<td>0.070</td>
<td>0.645</td>
<td>3.23</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.070</td>
<td>0.008</td>
<td>&lt;0.002</td>
<td>&lt;0.01</td>
<td>0.516</td>
<td>0.93</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.030</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>2.0</td>
<td>0.052</td>
<td>0.28</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td></td>
</tr>
<tr>
<td>0.062</td>
<td>0.135</td>
<td>0.060</td>
<td>0.005</td>
<td>0.008</td>
<td>0.157</td>
<td>1.37</td>
<td>&lt;0.001</td>
<td>0.0023</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.101</td>
<td>0.230</td>
<td>0.015</td>
<td>0.0075</td>
<td>&lt;0.003</td>
<td>10.8</td>
<td>13.2</td>
<td>0.050</td>
<td>0.010</td>
<td>0.750</td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.039</td>
</tr>
</tbody>
</table>
2.2. PRETREATMENT OF ORES

2.2.1. Scheelite

Scheelite frequently occurs in association with apatite minerals as well as sulfides and arsenides. Often these impurities are incompletely removed by the ore-dressing process and cause difficulties in tungsten purification process. These impurities can be removed from scheelite concentrates by hydrochloric acid leaching. Typically, acid leaching is accomplished in two stages: in the first stage, 140 kg of 28% hydrochloric acid is used for every metric ton of scheelite concentrate (50%, WO$_3$ and 6–7% water). Agitation is carried on for 1.5 hr at ambient temperature. In the second stage, 180 kg of 28% hydrochloric acid is used per metric ton of scheelite and with 10 min agitation at 30°C. This treatment reduces phosphorus to <200 ppm, arsenic to <100 ppm, and sulfur to <10000 ppm, provided these elements are in compounds liable to the acid attack. Since the long leaching period could result in dissolution of some scheelite, the processing conditions must be adjusted for different ores. It is also important to provide adequate fume control systems to handle the arsine and hydrogen sulfide evolved.

Roasting scheelite concentrate at high temperatures with excess air is often effective in removal of impurities such as sulfur, arsenic, and organic contaminants. The organic contaminants, which may be soil residues or ore-dressing reagents, frequently causes excessive foaming during the alkali leaching step. In the case of a low-grade scheelite such as that from Mittersill, Austria, roasting for 4 hr at 660°C in air completely eliminated organic carbon and caused reduction of arsenic from 300 ppm to 15 ppm.

2.2.2. Wolframite

Quite frequently, wolframite is found in association with sulfide and arsenides, and these are not removed efficiently by ore-dressing procedures. Roasting for 2–4 hr at 800°C in air causes significant removal of these contaminants. Table 2.2 gives data showing the extent of removal of these impurities from two Bolivian wolframites. Air roasting is conducted in a rotary furnace for both scheelite and

<table>
<thead>
<tr>
<th>Condition</th>
<th>Concentrate lot no. 1</th>
<th>Concentrate lot no. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfur (wt %)</td>
<td>Arsenic (wt %)</td>
</tr>
<tr>
<td>Before roasting</td>
<td>11.5</td>
<td>0.36</td>
</tr>
<tr>
<td>After roasting</td>
<td>0.021</td>
<td>0.043</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang, Albany, Oregon.
wolframite. Although this preliminary purification adds a process step, it is a considerable advantage to remove significant amounts of impurities so simply.

### 2.3. Decomposition of Ores

#### 2.3.1. Acid Leaching

Hydrochloric acid decomposes scheelite concentrate according to the reaction

$$\text{CaWO}_4 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{WO}_4$$  \hspace{1cm} (2.1)

Since CaCl$_2$ is soluble in aqueous hydrochloric acid, the precipitated tungstic acid can be isolated by filtration and washing. The equilibrium constant, $K = [\text{CaCl}_2]/[\text{HCl}]^2$, was found to be about $10^4$ by Meerson and Pavlyuk (1957a, b). With such a large equilibrium constant, the reaction should go to completion with the stoichiometric amount of acid. However, in practice, large amounts of excess HCl are required to complete the reaction. This is because of slow diffusion of HCl through the layer of H$_2$WO$_4$ that forms on CaWO$_4$ particles.

In order to increase the leaching rate, high HCl concentration, excess amount of the acid, high temperature, frequent agitation, and small particle size of ore concentrate are employed. For example, the Korean scheelite (Table 2.3) was ground to $-325$ mesh ($-44\,\mu$m) and excess amount of concentrated HCl was used. The relationship between the extent of decomposition as measured by calcium content and the reaction time for different amounts and initial concentration of HCl is shown in Fig. 2.1.

Some separation of molybdenum from tungsten occurs during the acid leach. This results from the grossly differing solubilities of molybdic and tungstic acids in HCl, which is probably due to the different tendency of the two elements to form chloro complexes in their +6 oxidation state (Canterford and Colton, 1968). The extent of molybdenum removal depends on the amount and concentration of HCl used and the efficiency of filtration and washing. Figure 2.2 shows the dependence of molybdenum removal on the quantity of 32% HCl used. The data were acquired using a Korean scheelite concentrate in which the ratio of molybdenum to tungsten was 2.04%. The improvement of molybdenum removal beyond 2.5 times the stoichiometric amount of HCl is small. Dependency of molybdenum removal on HCl concentration is shown in Fig. 2.3. Holding the excess amount of HCl constant, there is a substantial increase in efficiency on going from 32% to 38% of

### Table 2.3. Composition of the Korean Scheelite Used for Leaching Experiments at Teledyne Wah Chang Albany, Oregon

<table>
<thead>
<tr>
<th>Contents</th>
<th>WO$_3$</th>
<th>CaO</th>
<th>Mo</th>
<th>Si</th>
<th>P</th>
<th>As</th>
<th>Fe</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>71.4</td>
<td>20.3</td>
<td>1.15</td>
<td>0.89</td>
<td>0.016</td>
<td>0.012</td>
<td>0.17</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Fig. 2.1. Progress of the leaching reaction with various concentrations and various excess amounts of hydrochloric acid.

Fig. 2.2. Dependence of molybdenum removal on quantity of 32% HCl used; circles indicate single experiments, the bar indicates data spread of six experiments.
Fig. 2.3. Dependence of molybdenum removal on HCl concentration (4 hr, 80°C, amount of HCl 1.77 times stoichiometric).

the acid concentration; however, 32% acid is used in industry, because it is available at less expense commercially.

Filtration of tungstic acid slurry is of special importance in impurity removal and in material recovery. For example, filtration rate is reasonably fast at 90°C; cake thickness should be maintained so that no cracking occurs during filtration or washing. Washing with several displacements of 0.5% HCl at 70°C usually results in good-quality tungstic acid cake. When iron is present as an impurity, use of small amounts of nitrate or other oxidation reagent during digestion is recommended; this will oxidize the ferrous ions to ferric ions and facilitate filtration.

Acid leaching is effective in converting scheelite to tungstic acid with >99% efficiency under appropriate conditions. The process also can reduce molybdenum levels to below 10% of the original content in the ore concentrate. Iron and aluminum are also removed as soluble chlorides. Silicon is not removed by acid leaching, because its compounds are insoluble in HCl. Phosphorus and arsenic are difficult to remove, because they are converted to phosphoric and arsenic acids and precipitated with tungstic acid. Table 2.4 is a typical result of impurity removal after HCl leaching.

Ore decomposition by HCl leaching is often the process selected where high-purity scheelite concentrate is available and molybdenum level in the final product is not critical. For example, the Korean scheelite (Table 2.1) will yield ammonium paratungstate with less than 200 ppm of molybdenum after the acid leaching process is applied.
Table 2.4. Comparison of Impurities in the Ore Concentrate and Crude Tungstic Acid

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Sn</th>
<th>P</th>
<th>As</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Korean scheelite</td>
<td>3.6</td>
<td>2.0</td>
<td>2.7</td>
<td>0.18</td>
<td>0.05</td>
<td>0.018</td>
<td>0.019</td>
<td>0.20</td>
</tr>
<tr>
<td>Tungstic acid</td>
<td>0.07</td>
<td>0.23</td>
<td>1.8</td>
<td>0.07</td>
<td>0.05</td>
<td>0.014</td>
<td>0.013</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*Courtesy of Teledyne Wah Chang Albany, Oregon.*

2.3.2. Alkali Roasting Process

In the roasting processes, rotary kilns are used at a temperature of 800–900°C. For wolframite, the reactions are

\[ 2\text{FeWO}_4 + 2\text{Na}_2\text{CO}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Na}_2\text{WO}_4 + \text{Fe}_2\text{O}_3 + 2\text{CO}_2 \]  \hspace{1cm} (2.2)

\[ 3\text{MnWO}_4 + 3\text{Na}_2\text{CO}_3 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Na}_2\text{WO}_4 + \text{Mn}_3\text{O}_4 + 3\text{CO}_2 \]  \hspace{1cm} (2.3)

About 110–115% of the stoichiometrically required amount of sodium carbonate is used. Sometimes oxidizing agents, such as sodium nitrate, are added to the reaction mixture to the extent of 1–4% of the concentrate mass to accelerate formation of the higher oxides of iron and manganese. Contained tungsten is converted to sodium tungstate with an efficiency of ≈99.5%. Impurities such as silicon, phosphorus, and arsenic form soluble sodium salts under these conditions and so accompany the tungsten. Excess sodium carbonate reacts with ferric oxide to form sodium ferrite. Tin in the form SnO₂ does not react with sodium carbonate to a significant extent.

Decomposition of scheelite by roasting with sodium carbonate occurs according to

\[ \text{CaWO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{WO}_4 \]  \hspace{1cm} (2.4)

However, at higher temperatures, calcium carbonate decomposes:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  \hspace{1cm} (2.5)

and the calcium oxide formed reacts during the subsequent leaching to form calcium hydroxide, which reacts with sodium tungstate to form scheelite, reducing the efficiency of the process. Use of an excess of sodium carbonate suppresses this by precipitating calcium carbonate. The consumption of sodium carbonate can be reduced somewhat by addition of silica to the roasting charge. The silica converts the calcium oxide to silicate by the overall reaction

\[ \text{CaWO}_4 + \text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{Na}_2\text{WO}_4 + \text{CO}_2 \]  \hspace{1cm} (2.6)

Even with this improvement, efficient conversion of scheelite to calcium tungstate by
roasting requires 150–200% of the stoichiometric amount of sodium carbonate, based on reaction with scheelite alone.

The product of the roasting operation is leached with water at 80–90°C and then filtered. The sodium tungstate solution obtained contains 98–99% of the tungsten in the original concentrate and is contaminated with impurities such as phosphorus, arsenic, silicon, and molybdenum, which form soluble compounds under the roasting conditions. Techniques for removing these impurities will be discussed later.

Figure 2.4 shows a diagram of the plant installation for extraction of tungsten by the alkali roasting process (Zelikman and Meerson, 1973). The ore concentrate is ground in a continuous ball mill with air classifier and stored in a hopper from which it is dispensed by automatic scales to a screw conveyer–mixer. Sodium carbonate and nitrate are similarly weighed and placed in the conveyer–mixer, and the mixed charge is fed continuously to the rotary kiln. Typical dimensions for the kiln are 20 m long × 2 m I.D. (inside diameter). The kiln axis makes an angle of 3° with the horizontal and rotates about its axis once every 150 sec. Such a furnace will process about 1000 kg hr⁻¹ of charge. The kiln lining is made of high-density alumina. Corrosion is minimized by adjusting the temperature and composition of the charge so that it does not melt, but sinters to a doughlike consistency. Composition is controlled by adding leaching tails to the kiln feed in the amount of 20–22 wt% of the charge. This helps to prevent melt formation. After passage through the furnace, the treated charge is cooled and crushed to lumps about 2–5 cm (0.8–2 in.) in

![Diagram of plant installation for extraction of tungsten](image-url)
diameter. The lumps are then continuously wet ground, and the pulp is leached at 80–90°C in a three-stage continuous countercurrent process.

The alkali roasting process has the advantage that it permits high tungsten recovery with relatively modest expenditure of sodium carbonate, particularly when high-grade wolframite is used as the starting material. Its disadvantages are the high level of maintenance required for the rotary kiln, the extra processing steps involved in leaching the roasted material, the rapid increase of sodium carbonate consumption as lower-grade concentrates are used, and the virtually complete conversion of impurities such as arsenic, silicon, and phosphorus to soluble compounds that accompany the tungsten in the leaching step.

2.3.3. Caustic Leaching Process

Wolframite may be decomposed with production of sodium tungstate by reacting it with 40–50% sodium hydroxide solution at 110–130°C. Tungsten recovery of over 98% can be obtained if at least 150% of the stoichiometric quantity of alkali is used and the wolframite is ground to −44 μm (−325 mesh). The reaction is

\[ \text{MWO}_4 + 2\text{NaOH} \rightarrow \text{M(OH)}_2 + \text{Na}_2\text{WO}_4 \]  

(2.7)

where M indicates Fe or Mn. During processing, good agitation is essential. The reaction may be carried out in steel vessels sealed against the atmosphere to avoid formation of sodium carbonate. The reaction can be speeded and filtration of the resultant slurry rendered easier if a stream of air (free of CO₂) is introduced during leaching. This converts the metal hydroxides to the oxide, M₃O₄, form. The use of abrading agents such as milling balls speeds the reaction and affects some economies in alkali consumption.

The aqueous caustic leaching process is not generally applicable, because scheelite is unattacked by the leaching solution, and lower-grade or highly contaminated wolframites yield highly impure solutions. The presence of silica in any quantity is especially troublesome during filtration, because it is converted to sodium silicate under the leaching conditions. Industrial practice in this technique has changed little in recent years; for a complete account of it, earlier works may be consulted (Smithells, 1953; Li and Wang, 1955).

2.3.4. Autoclave–Soda Process

A more generally applicable method for decomposing tungsten ores is the autoclave–soda process, developed in the Soviet Union before World War II (Maslenitskii, 1939). This process as originally developed used sodium carbonate solution to decompose scheelite

\[ \text{NaCO}_3 + \text{CaWO}_4 \rightarrow \text{Na}_2\text{WO}_4 + \text{CaCO}_3 \]  

(2.8)

As practiced in industry, the process is run with −44 to −90 μm (−325 to −150
Extractive Metallurgy of Tungsten

mesh) concentrates at 190–225°C for 1½–4 hr using 10–18% sodium carbonate solution at 250–450% of the stoichiometric quantity, depending on the grade of concentrate used. The temperature employed results in pressures of 12–26 bars (174–377 psi), and the reaction is thus carried out in mild steel or alloy steel autoclaves. The process is simple and effective; its advantages are that high- or low-grade concentrates of either scheelite or low-manganese (MnWO₄ < 50 mole %) wolframite may be used; and that the maintenance cost is relatively low. A frequent criticism of the process is that a large amount in excess of sodium carbonate is necessary to obtain an acceptable recovery.

The autoclave–soda process has received considerable attention by researchers in institutes and industries, resulting in some important improvements lately. In the following, some of the investigations will be reviewed, and the current practice discussed. Following the pioneering work of I. M. Maslenitskii (1939), further work was done by N. N. Maslenitskii and Perlov (1960). The experimental work reported dealt exclusively with leaching of scheelite. For synthetic calcium tungstate of size –74 μm (200 mesh), it was found that 200% of the stoichiometrically required amount of sodium carbonate produced complete decomposition at 225°C, but that 250% was required at 200°C, and that equilibrium was established in 2 hr after operating temperature was reached. The time required to decompose 90% of the scheelite was 30 min. Equilibrium concentrations of reactants and products were measured for experiments at several temperatures in which the stoichiometric ratio of starting materials was used. The equilibrium constant, expressed as

\[ K = \frac{[WO_4^{2-}]}{[CO_3^{2-}]} \]  

(2.9)

ranged from 1.21 at 175°C to 1.85 at 250°C. K was found to decrease as the concentration of sodium carbonate increased. For example, at 200°C, K decreased from 1.45 to 0.96 when the quantity of sodium carbonate was increased from one to two times the stoichiometric amount.

Variation of the initial sodium carbonate concentration from 30 to 230 g/liter had no effect on tungsten recovery, but above 230 g/liter, recovery dropped sharply. This was found to be due to formation of the insoluble compounds Na₂CO₃ CaCO₃ and Na₂CO₃·2CaCO₃. The effect of this reaction was to remove sodium carbonate from the solution, where it could not interact with scheelite, and to coat the scheelite grains with an insoluble layer (Maslenitskii and Perlov, 1960; Queneau, 1967). This discovery is important because it imposes a limit on the amount of concentrate that can be charged to an autoclave of given size.

Maslenitskii and Perlov (1960) and later Queneau (1967) investigated the rate of scheelite leaching by sodium carbonate solution. By careful measurement of leaching rate on scheelite specimens of known and constant surface area, Queneau (1967) was able to narrow to two possible rate-determining processes. In either case, inhibition of mass transport of the carbonate ion through the calcite layer is crucial. The two possible processes are differentiated by whether the formation of calcium carbonate takes place at the film–scheelite interface or elsewhere within the film. In the former case, diffusion of carbonate ion is the only rate-determining
process; in the latter, rate determination involves both diffusion of carbonate ion and of a species containing calcium. A different conclusion, that the leaching/reaction rate is controlled by the rate of the chemical reaction, was reached by Zelikman and Meerson (1973). They stated that the temperature dependence of the reaction rate implied an activation energy of 20 kcal mole\(^{-1}\), which is very high compared with the value of 4 kcal mole\(^{-1}\) typical of diffusion of a solute in water. In fact, Queneau showed that the carbonate film was coherent, and the activation energy found is not inconsistent with values observed for diffusion through solids.

The consequence of Queneau’s findings is that better efficiency should accrue from a leaching process that incorporates a method for removing the calcite film from the scheelite particles. That it does was demonstrated by Maslenitskii and Perlov (1960), who showed that 99.5% of the contained tungsten could be recovered by use of a ball-mill autoclave at 200°C using twice the stoichiometric amount of sodium carbonate; whereas in absence of attrition, 25 times the stoichiometric amount of reagent was necessary. Other means of producing mechanical stimulation, such as with ultrasonic vibrations, are mentioned by Zelikman and Meerson (1973), who claim that sodium carbonate expenditure can be decreased to 1.8 to 2 times the stoichiometric amount.

Maslenitskii and Perlov (1960) and Zelikman and Meerson (1973) allude to the use of countercurrent leaching schemes to reduce sodium carbonate consumption. This may also be accomplished by using higher temperature, but this necessitates sturdier (and more expensive) autoclaves because of the higher pressure generated, and results in greater dissolution of objectionable materials present in the ore concentrate, for example, silica, phosphorus, arsenic, and fluoride.

Leaching studies of Korean and Austrian scheelites at Teledyne Wah Chang Albany (composition given in Table 2.3) showed that tungsten recovery was over 98% with the ore concentrate ground to \(-44 \mu m\ (-325\ mesh)\) using 3.25 times the stoichiometric amount of sodium carbonate (calculated on the basis of the tungsten content) as a solution of initial concentration 16.7% at 210°C for 1\(\frac{1}{2}\) hr. If the sodium carbonate concentration was increased beyond about 20% or the amount decreased below about three times that demanded by stoichiometry, the recovery fell. According to Maslenitskii and Perlov (1960), complete decomposition of calcium tungstate should be accomplished with 2.5 times the stoichiometric amount of sodium carbonate at 200°C. The extraneous materials present in the Korean concentrate — silica, fluoride, and molybdenum — account at least partially for the discrepancy.

Leaching of wolframite has not been studied as intensely as that of scheelite. However, Maslenitskii and Perlov (1960) and Zelikman and Meerson (1973) indicated that decomposition of the manganese and iron carbonate that were formed during the reaction led to the buildup of bicarbonate ion in the leach liquor and inhibition of leaching. The reaction was thought to be

\[
\text{Mn}_x\text{Fe}_{1-x}\text{WO}_4 + \text{Na}_2\text{CO}_3 \rightarrow x\text{MnCO}_3 + (1-x)\text{FeCO}_3 + \text{Na}_2\text{WO}_4
\] (2.10)
Maslenitskii and Perlov alluded to use of calcium hydroxide to suppress bicarbonate formation, while the Zelikman and Meerson referred to venting the autoclave so that carbon dioxide could escape, thus permitting bicarbonate to decompose. Investigations at Teledyne Wah Chang Albany, have shown, however, that low-manganese (MnWO₄ <50 mole %) wolframites could be leached efficiently with sodium carbonate alone. The conditions are 210°C for 3 hr, with 16.7% sodium carbonate solution at 3.3 times the stoichiometric amount (calculated on the basis of the tungsten present) and ore concentrate ground to -44 µm (-325 mesh). Recovery averaged 99% from a range of wolframites, the analyses of which were given in Table 2.1. The lowest recovery was 96%, from the lower-grade Bolivian wolframite. Analysis of the residues revealed the presence of manganese carbonate in the case of the wolframite with the higher manganese content. No ferrous carbonate was found in any residue, although magnetite was ubiquitous. Thus, it appears that ferrous carbonate is less stable than manganese carbonate. The carbonate content of the residues was always less than calculated on the basis of the amount of tungsten leached; the carbonate absent from the residue was accounted for as bicarbonate in the leach liquor. Further study showed that wolframite and scheelite could be leached with 98% or better recovery when mixed together, provided that the conditions found successful for leaching them separately were used.

The extent to which impurities present in the concentrate are rendered soluble by the leaching process is important. Experiments at Teledyne Wah Chang Albany, have shown that arsenic and phosphorus are less completely leached than tungsten, so the ratios of As/W and P/W are reduced, sometimes as much as tenfold. They are usually present in the leach liquor in sufficient quantity that subsequent purification is necessary, however. Tin remains virtually unattacked by the autoclave–soda process.

The concentration of silicon dioxide in the leach liquor ranges from 1g/liter or less to over 15 g/liter. It precipitates partially on cooling. The extent of silica solubility depends on the form and quantity in which it is present in the concentrate and on the state of division. When such silica occurs in the leach liquor special methods must be used for its removal.

Filtration of the leach liquor to remove the gangue material is relatively easy with both scheelite and wolframite concentrates. The amount of gangue material depends on the grade of concentrate used as feed. For example, leaching of a scheelite concentrate containing 30% WO₃ gave a slurry containing 25% by weight of solids. This was filtered on a straight-line belt filter at a rate of 540 liter/m² hr and the cake washed in three countercurrent washes with a water flow rate of 50% of that of the slurry. This resulted in a cake of 6 mm thickness containing 62% by weight of solids.
2.3.5. Chlorination

Scheelite and wolframite can be reacted with chlorine and carbon to form volatile tungsten oxychlorides. Recovered tungsten oxychlorides can either be dissolved in water to form tungstic acid or be chlorinated again to form tungsten hexachloride. Tungsten hexachloride can be fractionally distilled to remove other impurity chlorides, especially molybdenum chlorides, and then reduced to very fine tungsten metal powder. Tungstic acid obtained from oxychlorides can be digested with ammonia to produce ammonium paratungstate.

The chlorination process as means of cracking tungsten ores looks attractive because of its simplicity and the possibility of direct reduction of hexachloride to form very fine metal particles. However, there are some difficulties to overcome as seen in the following reactions:

At 600°C: \[ 2\text{CaWO}_4 + 3\text{C} + 6\text{Cl}_2 \rightarrow 2\text{CaCl}_2 + 2\text{WOCl}_4 + 3\text{CO}_2 \] (2.15)

At 300°C: \[ 2\text{Fe(Mn)}\text{WO}_4 + 3\text{C} + 7\text{Cl}_2 \rightarrow 2\text{Fe(Mn)}\text{Cl}_3 + 2\text{WOCl}_4 + 3\text{CO}_2 \] (2.16)

Scheelite is reacted with chlorine to produce tungsten oxychloride and calcium chloride. At the reaction temperature, calcium chloride is liquid and causes difficult reactor design problems. Chlorination of wolframite produces ferric (manganese) chloride and tungsten oxychloride. In the meantime, small amounts of ferrous chloride may also form, causing difficulties similar to those caused by calcium chloride mentioned above. Numerous investigations have been conducted using different chlorinating agents. Some of these studies are listed on Table 2.5.

Impurity removal is effected during the chlorination reaction and condensation. Nonvolatile chlorides such as CaCl₂ are easily separated from volatile tungsten oxychlorides, and part of the molybdenum oxychloride can be removed as a volatile compound during condensation of tungsten oxychlorides. However, impurity removal from tungsten oxychloride to satisfy final product quality is not practical. Ultimate purification must be performed with tungsten hexachloride.

When tungsten ores or oxides are chlorinated, oxychloride compounds are

| Table 2.5. Reacting Reagents Used for Tungsten Ore Chlorination Experiments |
|-----------------------------------------------|-----------------|------------------|
| Raw material                      | Reacting reagents                      | Reference           |
| Scheelite                         | C + Cl₂                                      | Henderson et al., 1965 |
| Scheelite-Wolframite             | SO₂ + Cl₂ and CaF₂ additions             | Henderson et al., 1965 |
| Scheelite                         | C + Cl₂, and fly-ash additions           | Hilgert and Moebius, 1969 |
| Wolframite                        | Cl₂-C + Cl₂ or HCl-H₂ + Cl₂              | Pokorny, 1960 |
| Wolframite (low grade)           | C + Cl₂                                     | Gokhale and Bhat, 1967 |
| Tungsten ores                     | Sulfur chlorides                          | Fridman and Bogoraz, 1946 |
formed in addition to the hexachloride. These oxychloride compounds are undesirable in the subsequent conversion to metal, because they form water vapor during hydrogen reduction or oxides when metallic reductants are employed. In addition, the instability of the mixed chlorides causes handling and metering problems during purification and reduction operations.

The laboratory apparatus used for conversion of WOCl₄ to WCl₆ is shown schematically in Fig. 2.5 (Henderson et al., 1968). A Vycor reaction column, 25.4 mm

---

**Fig. 2.5.**: Apparatus for converting WOCl₄ to WCl₆ (Henderson et al., 1968).
(1 in.) in diameter by 635 mm (25 in.) long, is heated by a resistance furnace mounted in a vertical position. Carbon is positioned slightly above the midpoint of the tube. A reservoir of WOCl₄ is connected to the lower end of the reaction tube by a ball joint. The reservoir is heated by electric resistance heaters, and a small tube extending from the side of this reservoir serves as an inlet for the chlorinating gas. This tube is also used to preheat the gas to 500°C. Phosgene and chlorine are introduced directly from compressed gas cylinders. Carbon tetrachloride is introduced in measured amount by vaporizing the liquid from a graduated cylinder that is heated in a water bath at 35–45°C. All parts of the apparatus are jointed at the top with standard taper connections. The reaction column is connected to a graphite block heated by electrical resistors. A hollow nickel plug is machined to fit a taper inside this block. This plug valve is used to direct the hexachloride vapors into either of two Pyrex condensers.

Before starting a typical run, the temperature of the apparatus is adjusted while chlorine or phosgene is swept through the reactor. When the desired temperature is obtained in the vertical reaction zone, the WOCl₄ reservoir is heated slowly to 200–240°C. After chlorine and WOCl₄ have been allowed to flow through all parts of the apparatus to remove all traces of residual air and water, the nickel plug is turned to direct the mixed chloride vapors into the bypass condenser C. Condensers are then adjusted to 200 and 250°C, respectively, to allow WCl₆ and WOCl₄ to be fractionated by selective condensation. When steady-state conditions have been established, the nickel plug is turned to direct the gases into condensers A and B. After the reaction has proceeded for 20 min, the valve is again turned to divert the volatile chlorides into bypass condenser C.

The operation is terminated by cooling the WOCl₄ reservoir while raising the reactor temperature to 800°C for an additional half hour to sweep out tungsten compounds absorbed in the tube. The system is purged with chlorine during this time to prepare the apparatus for the next run.

The conversion of WOCl₄ to WCl₆ was found to be dependent upon the reaction temperature (Fig. 2.6), the form of carbon, and the type of gaseous chlorinating agent used (Fig. 2.7). COCl₂ and chlorine are unreacted when employed without carbon. CCl₄ will react with WOCl₄ without addition of carbon (Fig. 2.8); however, carbon is required if conversions greater than 90% are desired at 500–700°C. Conversions greater than 90% can also be achieved when chlorine and phosgene are used as chlorinating agents with carbon, but a reaction temperature of 800°C is required. By-product CO₂ and CO affect the equilibrium of these chlorination reactions as the temperature is varied. CO₂ will oxidize WCl₆ to WOCl₄ in the higher temperature range, but the presence of carbon favors the formation of WCl₆ and CO. Carbon having high specific surface areas was found to yield higher degrees of conversion of WOCl₄ to WCl₆.

A pilot-scale chlorination of tungsten oxide to tungsten hexachloride has been operated at Teledyne Wah Chang Albany. The tungstic oxide was prepared by leaching scheelite with HCl followed by calcining. The mixture of WO₃ and carbon formed the fluidized bed in a 152-mm (6-in.) reactor with chlorine passing from the bottom. Temperature was maintained at 700–800°C by resistance heating, and the reaction rapidly proceeded to a mixture of WOCl and WCl₆. The vapor mixture was
Fig. 2.6. Effect of temperature on converting WOCl$_4$ to WCl$_6$ with chlorine over carbon (Henderson et al., 1968).

Fig. 2.7. Effect of temperature and CO$_2$ on converting WOCl$_4$ to WCl$_6$ over carbon (Henderson et al., 1968).
then fed to the "afterburner," where WOCl₄ was converted to WCl₆. The afterburner was a reactor packed with activated carbon with the temperature maintained at 900–1000°C. Both reactors were made of quartz tubes. The chlorination was efficient and required little labor. Scale-up of the system can be employed by replacing quartz tubes with graphite ones and using induction heating.

Another chlorination process involves a pretreatment of the ore. Tungsten ore, scheelite or wolframite, may be treated with one of several reducing agents, preferably silicon or aluminum, to form a lower-melting alloy. A phase diagram for the reducing agent and tungsten is used to select a suitable temperature and a suitable alloy composition. In the case of silicon, the content of silicon in the alloy should be at least 8% by weight and preferably 9–20%. The reduction is carried out in an electric arc furnace consisting of a graphite crucible and a graphite electrode. The furnace is heated to an operating temperature of 1800–2200°C. Ore mixed with reducing agent is continuously added. Tungsten silicide alloy settles to the bottom of the crucible and forms a slab or solid ingot. The slab usually contains about 45 mole % silicon and about 55 mole % tungsten. The liquidus point of a silicide with this composition lies at about 2350°C. The slag generally contains about 0.4% tungsten.

After cooling, the slab is removed from the crucible, the slag chiseled off, and the slab is crushed to provide particulate material with the size of hazel nuts. These chunks are then chlorinated at 800°C in a vertical-shaft chlorinator to produce tungsten hexachloride and silicon tetrachloride (Fig. 2.9). The reaction is exothermic after the initiation and can be maintained without external heat input. Tungsten hexachloride condenses in the primary condenser at the temperature of 75–150°C. Silicon tetrachloride can be recovered by cooling the gas to low temperatures in a tube-type condenser or by quenching the gas with cold silicon tetrachloride in a countercurrent gas–liquid absorber (Svanstrom and Ramqvist, 1972).

![Graph](image-url)

**Fig. 2.8.** Effect of temperature and carbon on converting WOCl₄ to WCl₆ with CCl₄ (Henderson et al., 1968).
Fig. 2.9. Tungsten silicide chlorinator (courtesy of Teledyne Wah Chang Albany, Oregon); (1) feed hopper, (2) feed valve, (3) igniter, (4) chlorine inlet, (5) cooling coil, (6) charge, (7) support, (8) transfer line, (9) primary condenser, (10) product outlet valve, (11) SiCl₄ condenser, (12) tube cutaway, (13) silicon tetrachloride reservoir, (14) recycle pump, (15) product valve, (16) recycle valve, (17) recycle line.

2.4. PURIFICATION OF INTERMEDIATE TUNGSTEN COMPOUNDS

2.4.1. Ammonium Tungstate Solution and Ammonium Paratungstate Crystallization

Preparation of pure ammonium paratungstate (APT) from crude tungstic acid involves three steps—digestion of the tungstic acid in aqueous ammonia, filtration of the ammonium tungstate solution, and crystallization of APT. In aqueous ammonia, removal of phosphorus and arsenic may be accomplished by addition of a little magnesium oxide, which forms insoluble magnesium ammonium phosphate and arsenate under these conditions. Iron and similar metals form colloidal hydroxides and their removal together with silica, which is also colloidal, is accomplished by addition of a small amount of activated carbon and by digesting for 1 or 2 hr. Filtration is rather slow but can be efficiently accomplished by the use of a pressure filter with filter aids.
Table 2.6. Effect of Amount of Ammonia for Digestion on the Removal of Silicon

<table>
<thead>
<tr>
<th>Amount of ammonia times stoichiometric quantity for (NH₄)₂WO₄</th>
<th>Si/W wt % in filtered (NH₄)₂WO₄ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>0.40</td>
</tr>
<tr>
<td>1.72</td>
<td>0.17</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Albany, Oregon.

APT crystals are obtained by evaporating the purified ammonium tungstate solution, and the amount of crystals formed depends upon the extent of evaporation. During the crystallization process, partial impurity removal is accomplished. Removal of molybdenum is especially noticeable. Usually, 80–90% of the input tungsten can be recovered as ammonium paratungstate of acceptable purity. The mother liquor from the crystallization is either recycled after appropriate impurity removal or is directly crystallized to yield impure APT for use in an application where a relatively high molybdenum content is not objectionable.

Experiments at Teledyne Wah Chang Albany, showed that suppression of dissolved silica is effected by increasing the amount of ammonia used to dissolve the tungstic acid (Table 2.6). However, digestion time beyond that necessary to dissolve the tungstic acid did not affect the impurity level. The effect of temperature on the removal of silica is shown in Table 2.7.

The material in the tungsten acid that does not dissolve in ammonia solution consists mainly of undissolved ore, gangue materials from the concentrate, and colloidal silica. All these materials are fine and readily blind filtration media. Thus, the use of filter aids and precoat materials are preferable. In the laboratory at Teledyne Wah Chang Albany, an optimum performance was obtained using a 1.6-mm (1/16-in.) layer of the cellulose as precoat on filter cloth, while using 0.02 kg activated carbon per kilogram of WO₃ as body mix. Diatomaceous earth causes silica contamination, while cellulose as a body mix did not improve filtration.

The digestion procedure for preparing the ammonium tungstate solution consists of the following: Tungstic acid is slurried with water to have a slurry density

Table 2.7. Effect of Digestion Temperature on the Removal of Silicon

<table>
<thead>
<tr>
<th>Digestion temperature (°C)</th>
<th>Si/W wt % in filtered (NH₄)₂WO₄ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.15</td>
</tr>
<tr>
<td>80</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Albany, Oregon.
1.35 kg/liter (0.385 kg/liter of WO₃). For every kilogram of WO₃ in the slurry, 1 liter of 28% ammonia and 0.02 kg of Nuchar K.D. activated carbon is added. The mixture is agitated and heated to 60°C. Digestion is complete in 2 hr. The system generates a pressure of approximately 0.422 kg/cm² (6 psi) so that the vessel must be closed to avoid loss of ammonia. The digestion of tungstic acid with ammonia can be done continuously. In a test run at Teledyne Wah Chang Albany, tungstic acid slurry and ammonia prepared as above, were fed into a reactor that was held at 60°C with a reflux condenser. Residence time ranging from 1 to 3 hr were found to produce sufficiently pure ammonium tungstate solution.

Filtration of the digested liquor separates the undissolved ore, gangue, and silica from the ammonium paratungstate solution. The solids removed by filtration after calcination amounted to about 4.6% of the weight of the tungsten trioxide processed and contained about 11% WO₃. This amounted to approximately 0.5% of the tungsten originally present in the ore concentrate and was the amount that escaped attack by the hydrochloric acid. The residue also contained a substantial fraction of the silicon, arsenic, phosphorus, and titanium present in the original ore concentrate. Average composition for such residue, which obtained from the treatment of Korean scheelite, is given in Table 2.8.

Tungsten is recovered as pure APT by evaporation of the ammonium tungstate solution. The APT occurs as the pentahydrate if the solution is evaporated by boiling under atmospheric pressure and as the dodecahydrate at lower temperatures. The pentahydrate is the usual product and has the formula 5(NH₄)₂O·12WO₃·5H₂O and contains 88.81% WO₃.

Impurities are partitioned preferentially to the mother liquor when APT crystallizes. The extent of crystallization is therefore determined by the desired purity of APT. Separation of molybdenum and tungsten during crystallization of APT has been known for some time (Smithells, 1953). Little is published about the dependence of the separation on such factors as the tungsten concentration and molybdenum to tungsten ratio in the initial ammonium tungstate solution. Data presented by Smithells (1953) are reproduced in Fig. 2.10. Unfortunately, information such as original tungsten concentration and original molybdenum-to-tungsten ratio in the ammonium tungstate solution are not available.

In prior discussion, Smithells reports that the specific gravity of ammonium tungstate solution used as feed to APT crystallizers is 1.12; this implies a WO₃

<table>
<thead>
<tr>
<th>Table 2.8. Average Composition of APT Filtration Residue vs. Original Analyses of Korean Scheelite*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Korean scheelite</td>
</tr>
<tr>
<td>APT filtration residue</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Albany, Oregon.
concentration near 130 g/liter as seen from Fig. 2.11, which gives dependence of specific gravity of stoichiometric ammonium tungstate solution on WO₃ concentration. No hints are available to allow estimation of the original molybdenum-to-tungsten ratio or concentration of ammonia.

Experiments were performed at Teledyne Wah Chang Albany to acquire more usable data. Ammonium tungstate solution containing 250—260 g/liter WO₃ and having a molybdenum-to-tungsten ratio of 0.14% was prepared using 1.42 times the stoichiometric amount of ammonia necessary to form (NH₄)₂WO₄. This solution had a specific gravity of 1.22. Samples were evaporated to different extents, and the percentages of molybdenum and tungsten that crystallized were determined. These were expressed in terms of a fraction of the original solution volume and were plotted in Fig. 2.12.

The data of Figs. 2.10 and 2.12 may be compared by plotting percent molybdenum crystallized versus percent tungsten crystallized, as in Fig. 2.13. The two sets of data show discrepancies in separation behavior and thus demonstrate
that, in addition to the amount of tungsten crystallized, the degree of separation also depends at least on the initial metal concentration. The fact that it may also depend on the initial molybdenum-to-tungsten ratio is seen from the results of Shapiro et al. (1965). Unfortunately, these authors varied so many parameters, that their data are not amenable to detailed analysis.

The extent to which crystallization of ammonium paratungstate is carried out depends on the impurity level in ammonium tungstate solution and the acceptable purity of the APT to be produced. Table 2.9 shows typical impurities of ammonium
Table 2.9. Typical Impurity Contents of Ammonium Tungstate, APT, and APT Mother Liquor

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>Mo</th>
<th>Na</th>
<th>Si</th>
<th>Ti</th>
<th>P</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium tungstate</td>
<td></td>
<td></td>
<td>0.10-0.18</td>
<td>0.10-0.20</td>
<td>0.007-0.015</td>
<td>0.002-0.004</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APT</td>
<td></td>
<td></td>
<td>0.03-0.07</td>
<td>&lt;0.001</td>
<td>0.002-0.005</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APT mother liquor</td>
<td>0.004</td>
<td>0.004</td>
<td>0.27</td>
<td>1.10</td>
<td>0.10</td>
<td>0.70</td>
<td>0.50</td>
<td>0.020</td>
<td>0.025</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Albany, Oregon.

tungstate solution and crystallized APT, with a recovery of 90%. Phosphorus levels can be reduced below 10 ppm by digesting tungstic acid with ammonia in the presence of 0.005 kg MgO per kilogram of WO₃ processed.

It is usual to wash the ammonium paratungstate crystals after their separation from the mother liquor by filtration to remove impurities. Such washing can cause loss of high-purity APT, because contrary to the literature (e.g., Smithells, 1953), APT has substantial solubility in water, as shown in Fig. 2.14, and this results in wash solutions containing WO₃ at the level of 10–20 g/liter, depending somewhat on the temperature of the wash water. As little as 0.1 kg water per kilogram of APT was adequate for washing at 20°C, provided the water was applied as a spray and the thickness of the cake was no more than 1 cm (0.4 in.). The displacement, expressed as the fraction of the total liquor that remains in the wet cake, is 6%. The necessary wash volume corresponds then to about 1.1 displacements.

The wash and the liquor are combined and contain about 10% of the tungsten introduced into the process as concentrate. The alternatives are to evaporate the solution to dryness and pyrolyze the crude APT to tungstic oxide, whereupon it can be sold to steel factories, or to recycle it through the process. Typical impurity contents, expressed as a fraction of the contained tungsten, are also given in Table 2.9.

The impurities present in the mother liquor and to be further removed are titanium, phosphorus, and arsenic. All others are present at tolerable con-

Fig. 2.14. Solubility of APT vs. temperature. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
centrations and need not be removed before recycling to the acid leaching stage. A simple scheme for such a recycle is to make the solution basic to pH 10–10.5 by addition of sodium carbonate and to add 0.1 kg magnesium sulfate per kilogram of WO₃ and digest for 1 hr. Phosphorus and arsenic are precipitated as the magnesium ammonium phosphate and arsenate complexes, which are sparingly soluble, and colloidal silica and titania are coprecipitated with the magnesium carbonate. Filtration removes these impurities, whereupon tungsten is precipitated as synthetic scheelite by addition of aqueous calcium chloride. The scheelite is recovered by filtration, dried, and recycled to the acid leaching stage.

2.4.2. Purification of Sodium Tungstate Solution

Sodium tungstate solution generated by decomposition of tungsten ore concentrates contains some of the impurities present in the raw material, and these must be reduced to acceptable levels before the intermediate compound is prepared. The most frequently encountered contaminants are silica, phosphorus, arsenic, and molybdenum. If the silica level is above 2–5 g/liter, a preliminary silica removal step is required. Prior to filtration to remove the unreacted gangue, aluminum sulfate, Al₂(SO₄)₃·18 H₂O and magnesium sulfate, MgSO₄·7 H₂O are added in quantities 0.08 kg and 0.03 kg per kilogram of WO₃, respectively. The solution is stirred for 1 hr at 70–80°C and then filtered using drum filters, as is usual in removal of gangue. This procedure decreases the silica level to 2 g/liter or below. This solution combined with original sodium tungstate solution containing silica less than 2 g/liter is further treated by a secondary silica removal step.

The preliminary silica removal and secondary silica removal steps are essentially the same. Both steps are conducted at pH 9–9.5. However, during the secondary silica removal step, filtration requires a filter aid such as cellulose. After the second silica removal, the silica level is in the range of 0.03–0.06 g/liter. Tungsten loss during this process is about 1% of the total tungsten value.

Molybdenum removal is accomplished by precipitation as molybdenum trisulfide. The first step is formation of the thiomolybdate ion by the reaction

\[ \text{MoO}_4^{2-} + 4\text{S}^2^- + 4\text{H}_2\text{O} \rightarrow \text{MoS}_3^{2-} + 8\text{OH}^- \]  

(2.17)

The sulfide is added as sodium sulfide or sodium hydrogen sulfide at pH 10. Conversion of thiomolybdate is complete in 1 hr at 80–85°C. In industrial practice, the sulfide reagent is added the same time as the reagents for silica removal. The amount of sulfide required for acceptable molybdenum removal depends upon the ratio of Mo/W and upon the concentration of tungsten. For the solution produced by a typical autoclave–soda process, the WO₃ concentration is near 100 g/liter and the Mo/W ratio is near 1–2%. In such cases, three times the amount of sulfide required stoichiometrically is sufficient. A lower Mo/W ratio requires progressively higher sulfide addition. A detailed study of the efficiency of molybdenum removal by this method was reported by Maslenitskii and Perlov (1960).

Following formation of the thiomolybdate complex, molybdenum is precipitated as trisulfide by acidifying to pH 2.5–3 while agitating the solution at
80°C over a period of 7–9 hr. The reaction is

$$\text{MoS}_4^{2-} + 2\text{H}_3\text{O}^+ \rightarrow \text{MoS}_3 + \text{H}_2\text{S} + \text{H}_2\text{O} \quad (2.18)$$

The molybdenum trisulfide is removed by filtration using plate and frame filters or other pressure filters. The fraction of solids in the slurry is usually near 0.12%; filtration rates of about 650 liter/m² hr are practicable. The cake thickness is about 45 mm (1.77 in.), and the cake contains about 30% solids by weight. It is then washed with approximately four displacements of water to minimize tungsten loss. During pH adjustment, maximum hydrogen sulfide evolution occurs near pH 6–7, and detectable amounts are evolved over the entire pH range.

The molybdenum removal step reduces the molybdenum level to less than 10 mg/liter (Mo/W 100 ppm). Tungsten loss in this step is about 1% of the throughput. In the course of silica and molybdenum removal, phosphorus and arsenic are reduced to less than 20 mg/liter and less than 3 mg/liter, respectively.

### 2.4.3. Liquid Ion Exchange Extraction (LIX)

The purpose of LIX is to extract tungsten-containing ions from sodium tungstate solution. It should be noted that impurities such as molybdenum, silicon, phosphorus, and arsenic are also extracted, and therefore no separation of these impurities is obtained in the LIX process. The extractant can be one of several high-molecular-weight amines dissolved in an inert hydrocarbon solvent such as kerosene. Tricaprylamine is a frequent choice, and this compound is available in sufficient purity from General Mills, Inc., under the name Alamine 336. Other amines, such as Adogen 283 from Ashland Oil Company in the United States and Hostarex A-327 from Farwarwe Hoechst A.G. in Europe, may also be used.

The extractant is used as a 5–10% (by volume) solution in kerosene with 5–10% (by volume) of decanol or similar alcohol as phase conditioner. A typical formula is 7% Alamine 336, 7–10% decanol, and 86% kerosene by volume. When such a solution is mixed with sodium tungstate solution under pH 1–7, tungstate ions transfer to the organic phase. The distribution coefficient is pH dependent and is sufficiently high in the range of 1–3.

For equilibrium between aqueous and organic phase in a system containing tungstate and sulfate, one has (Kim et al., 1968)

$$[\frac{1}{2}(\text{R}_3\text{NH} \cdot \text{HSO}_4)_2]_{\text{org}} + [(\text{W}_x\text{O}_y\text{H}_z)^n^-]_{\text{aq}}$$

$$\leftrightarrow [(\text{R}_3\text{NH})_n \cdot \text{W}_x\text{O}_y\text{H}_z]_{\text{org}} + [n(\text{HSO}_4^-)]_{\text{aq}} \quad (2.19)$$

The equilibrium constant $K$ can be expressed in terms of concentration as

$$K = \frac{[\frac{1}{2}(\text{R}_3\text{NH})_n \cdot \text{W}_x\text{O}_y\text{H}_z]_{\text{org}}[\text{HSO}_4^-]^n_{\text{aq}}}{[(\text{R}_3\text{NH} \cdot \text{HSO}_4)_2]^{n/2}_{\text{org}}[(\text{W}_x\text{O}_y\text{H}_z)^n^-]_{\text{aq}}} \quad (2.20)$$

The distribution coefficient $K_d$ is defined as
\[ K_d = \frac{[(R_3NH)_n \cdot W_5O_7H_2]_{\text{org}}}{[W_5O_7H_2^{n-}]_{\text{aq}}} \]  \hspace{1cm} (2.21)

or

\[ K_d = \frac{K[(R_3NH \cdot HSO_4)]^{n/2}_{\text{org}}}{[HSO_4^n]_{\text{aq}}} \]  \hspace{1cm} (2.22)

The tungsten species present in the pH range used for the commercial extraction are probably \( W_{12}O_{40}H_2^{5-} \), \( W_6O_{21}H^{5-} \), and \( W_{12}O_{39}^2- \) (Kim et al., 1968). However, under different conditions, different species may exist. Plant stoichiometry indicates \( Na_6W_{12}O_{39} \) in solvent extraction feed at pH of 2.5.

For purpose of plant design, it is essential to know the equilibrium concentrations of tungsten in the aqueous and organic phases over a range of values and under conditions pertinent to the actual process. The data of Fig. 2.15 were acquired using an organic phase made up by mixing of 7 volumes each of Alamine 336 and decanol with 86 volumes of kerosene, an operating temperature of 50°C, and an aqueous pH maintained at 2.5.

It is apparent that above aqueous tungsten concentration of 5 g/liter the organic phase is saturated at a concentration near 50 g/liter. Figure 2.15 may be used to estimate plant operating parameters such as organic-to-aqueous flow ratio, number of stages required for given tungsten recovery, and given concentration of feed. Since the equilibrium highly favors the transfer of tungsten to the organic phase, it is possible to obtain >99.9% extraction with only two stages. The other factor affecting extraction is the time of mixing in the mixer-settler operation. This can be appreciated from the kinetic data as shown in Table 2.10.

In practice the organic loading is generally controlled in the range of 20–40 g/liter of \( WO_3 \). The loading above 40 g/liter can result in the formation of a third

![Equilibrium concentration of tungsten in organic vs. aqueous phases. (Courtesy of Teledyne Wah Chang Albany, Oregon.)](image-url)
Table 2.10. Kinetic Experiments for Liquid Ion Exchange Extraction

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Before extraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tungsten feed (g WO$_3$/liter)</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>pH at 50°C</td>
<td>2.0</td>
<td>2.0</td>
<td>2.3</td>
<td>2.3</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Stirring time (sec)</td>
<td>8</td>
<td>600</td>
<td>8</td>
<td>600</td>
<td>8</td>
<td>600</td>
</tr>
<tr>
<td>After extraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous phase (raffinate) (g WO$_3$/liter)</td>
<td>42</td>
<td>28</td>
<td>42</td>
<td>34</td>
<td>0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>pH at (50°C)</td>
<td>2.35</td>
<td>2.4</td>
<td>3.0</td>
<td>3.6</td>
<td>3.05</td>
<td>3.1</td>
</tr>
<tr>
<td>Organic phase (g WO$_3$/liter)</td>
<td>56.7</td>
<td>68.3</td>
<td>56.7</td>
<td>63.2</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Huntsville, Alabama. The conditions used are as follows: stirring experiment in vessel at 50°C, 1000 rpm; alamine solution pH 2.5 at 50°C, 1.2 parts; tungsten feed, 1.0 part.

phase, which is insoluble in the organic and can cause difficulty in phase separation. Organic overloading is aggravated by impurities such as fluoride and silica in the aqueous feed.

The concentration of aqueous feed is 40–150 g/liter WO$_3$, and the ratio of organic to aqueous flow is maintained at 1.2 : 1 in the mixers. This organic-to-aqueous ratio ensures approximately equal proportions of the two phases and that the organic phase is continuous in the mixer, and this leads to efficient extraction. Because the concentration of feed is usually high, more organic than aqueous is needed overall, and the preferred ratio in the mixer is accomplished by adjusting the amount of aqueous phase recycled from the settler. Usually extraction and phase separation is satisfactory at 50°C.

The flow diagram of a typical continuous mixer–settler system is shown in Fig. 2.16. It is customary to convert the amine in the organic phase to the bisulfate form before it is admitted to the extraction section. However, there is nothing essential about this procedure. The important point is that the pH of the aqueous phase must be kept below about 3.0, because above this value the distribution coefficient becomes unacceptably low and recovery decreases. Since the combined amine removes both tungsten and hydrogen ion from the aqueous phase,

$$nR_3N + W_xO_yH_2^{+} + nH^+ \rightarrow (R_3NH)_nW_xO_yH_2$$  \hspace{1cm} (2.23)

it is necessary to add acid to compensate for the loss of hydrogen ion. This is done by first converting the amine to the bisulfate form in a separate mixer–settler. Precautions should be taken to avoid addition of more than the necessary amount of acid in order to minimize the amount of sulfate that transfers to the organic phase, because such sulfate later transfers to the ammonium tungstate solution during stripping. For normally encountered values of the pH of the aqueous feed (about 2.5), 0.25–0.5 moles of H$_2$SO$_4$ per mole of WO$_3$ in the feed is sufficient to ensure sulfate concentration of under 8 g/liter in the ammonium tungstate solution.
Fig. 2.16. Flow sheet of LIx process with some detailed data. (Courtesy of Teledyne Wah Chang Albany, Oregon. *All flows are in liters per minute. Aqueous feed (solid line): 100 g WO₃/liter, pH: 2.5; organic feed (broken line): 6 vol % Alamine 336, 6 vol % decanol; 86 vol % kerosene.)
The organic phase leaving the extraction section generally contains 20–40 g/liter of WO_3 as mentioned before. It also contains entrained aqueous solution from which it must be separated to avoid, in particular, contamination of the product with sodium. The extract is washed with deionized water in two mixer–settlers operating in countercurrent mode. The water flow rate is about 15–20% of the organic flow rate, and the volume ratio of organic to aqueous phase in the mixers is again 1.2 : 1. This is accomplished by recycling the aqueous phase from the settlers. Washing is normally done near 50°C, with mixer residence time double that used in extraction.

The washed organic phase is then stripped of the contained tungsten by contacting it with dilute aqueous ammonia solution containing some ammonium tungstate. The ammonia concentration used is based on the stoichiometrical calculation to form ammonium tungstate and 1 to 2 M free ammonia in the solution. A 100 g/liter WO_3 ammonium tungstate solution containing 2 M free ammonia requires a stripping solution of 5% NH_3 concentration. The free ammonia present in the solution reduces the possibility of APT precipitation in the stripping circuit as will be discussed later. The precipitate, which contains 80–85% WO_3, reduces ammonium tungstate content in the solution and therefore is undesirable. Since the ratio of organic to aqueous input volumes to the stripping section is about 5 : 1 and the preferred ratio in the strippers is 1.2 : 1, recycling of the aqueous phase from the settler to the mixing unit is again necessary.

The design of the stripping section differs from that of extraction and washing sections in that there are two mixers in series, operating in concurrent mode, and only one settler. The reason is that the reaction to form APT is relatively fast, but the reaction of APT with ammonia to form ammonium tungstate is slow. Sufficient resident time and free ammonia must be allowed for complete reaction. If the organic phase containing tungsten is allowed to remain in contact with aqueous ammonia in absence of agitation, the concentration of ammonia near the interface will fall and APT precipitation will also occur. Once precipitated particles have grown to any size, they are redissolved only with difficulty. Therefore, it is best to avoid any precipitation at all by ensuring sufficient mixing time and ammonia supply and by keeping the temperature of the solutions near 60°C. Concurrent stripping is described in detail by Chiola and Liedtke (1968). The stripped organic phase is recirculated to the extraction stage, and the ammonium tungstate solution is taken to the APT crystallizer.

2.4.4. Purification of Tungsten Chlorides

For the product of the chlorination process, molybdentum can be removed from tungsten oxychloride by selective absorption of the oxychloride on activated carbon (Peterson et al., 1968). Typically, scheelite ore is leached with hydrochloric acid to produce soluble calcium chloride and tungstic acid precipitate. The tungsten acid is recovered by filtration and calcined at 400°C. The product contains approximately 91.5% WO_3 and 0.57% Mo.

A chlorination feed prepared by mixing 7.5 parts by weight lampblack per 100 parts calcined tungstic acid is fed into a chamber heated to 600°C at a rate of 0.24
g/min. A chlorination agent is continuously passed through the feed and the metal oxychloride gases produced are passed through an activated carbon column 20 cm (7.874 in.) in height. Fresh activated carbon is added continuously at the top of the bed and spent carbon is removed from the bottom at a rate of 0.11 g/min.

Peterson et al. (1968) reported some experimental data by using different chlorinating agents. These were chlorine fed at a rate of 50 cm³/min or carbon tetrachloride fed at a rate of 0.5 g/min with a carrier gas of air, nitrogen, or carbon dioxide alternatively, each fed at a rate of 50 cm³/min. Samples of chloride product were taken at 30-min intervals during all runs. The resulting sample analyses are shown in Table 2.11, which indicates that oxygen has a severe detrimental effect on separation efficiency and should be excluded.

For further purification, fractional distillation of tungsten hexachloride is found to be effective. Molybdenum, iron, nickel, copper, magnesium, and manganese are reduced to a level at less than 10 ppm each (Skirvin et al., 1967; Nisel'son and Nikolaev, 1969). The distillation equipment is shown schematically in Fig 2.17 (Skirvin et al., 1967). A typical production process is as follows: The boiler is charged with 1400 g of tungsten hexachloride in an argon-filled glove box. The charged boiler is then attached to the distillation column. The boiler is heated to 339°C, the boiling point of tungsten hexachloride. A low overhead rate, ~2 g condensate per hour, is used initially to enhance the removal of impurities more volatile than tungsten hexachloride. This rate is continued for approximately 37 hr or until the analysis of the material in the exhaust tube indicates that molybdenum is no longer present in the overhead fraction. After an additional 41 hr, or until molybdenum is not detected in the overhead, a new condenser is installed. A typical analysis of the condensed material collected up to this time is listed in Table 2.12 as fraction 1. The overhead rate is increased to 85 g/hr after the second condenser is installed. The run is terminated about 14 hr later. A typical analysis of the material collected in the new condenser is shown in Table 2.12 as fraction 2.

Jonsson and Svanstrom (1970) patented a process in which tungsten

### Table 2.11. Molybdenum Content in Product Stream at Time Intervals of Operation

<table>
<thead>
<tr>
<th>Hours of operation</th>
<th>CCL₄ + air</th>
<th>CCL₄ + N₂</th>
<th>CCL₄ + CO₂</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.007</td>
<td>0.005</td>
<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td>1.0</td>
<td>0.010</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>1.5</td>
<td>0.130</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>2.0</td>
<td>0.120</td>
<td>0.004</td>
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<td>0.001</td>
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<tr>
<td>2.5</td>
<td>0.250</td>
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<td>0.006</td>
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<tr>
<td>3.0</td>
<td>1.900</td>
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<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>3.5</td>
<td>0.400</td>
<td>0.003</td>
<td>0.020</td>
<td>0.001</td>
</tr>
<tr>
<td>4.0</td>
<td>—</td>
<td>0.002</td>
<td>—</td>
<td>0.001</td>
</tr>
<tr>
<td>4.5</td>
<td>—</td>
<td>0.004</td>
<td>—</td>
<td>0.001</td>
</tr>
</tbody>
</table>

*Peterson et al. (1968).*
hexachlorides obtained from the chlorination process are purified by fractional distillation in a chlorine atmosphere in order to simultaneously chlorinate tungsten pentachloride to tungsten hexachloride. Fused salt scrubbing is also found to be effective in purifying tungsten hexachloride (Skirvin et al., 1967). Tungsten hexachloride is treated with a lithium chloride–potassium chloride eutectic (44% LiCl and 56% KCl) at 530°C in the apparatus shown in Fig. 2.18. An argon flow is used as the sweeping carrier gas. Condensers are replaced hourly and fractions of tungsten hexachloride are collected and analyzed. Typical analyses of the products from a 50-g charge are listed in Table 2.13. Molybdenum pentachloride, major volatile impurity, is stripped from the salt bath by purging with argon for 10 hr.
Table 2.12. Tungsten Chloride Fractional Distillation Process
Data and Analyses

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Boiler charge</th>
<th>Distillate</th>
<th>Boiler residue and column holdup</th>
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</thead>
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<tr>
<td></td>
<td>ppm^b</td>
<td>Fraction 1</td>
<td>Fraction 2</td>
</tr>
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</tr>
<tr>
<td>Co</td>
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<td>&lt;1^c</td>
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<td>Cr</td>
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<td>&lt;1^c</td>
<td>&lt;1^c</td>
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<tr>
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<td>0.5</td>
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<tr>
<td>Fe</td>
<td>&lt;5^e</td>
<td>&lt;5^e</td>
<td>&lt;5^e</td>
</tr>
<tr>
<td>Mg</td>
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<td>&lt;1^e</td>
<td>&lt;1^e</td>
</tr>
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<td>Weight (g)</td>
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<tr>
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<tr>
<td></td>
<td>Fraction of vaporizer charge (%)</td>
<td>12</td>
<td>85</td>
</tr>
</tbody>
</table>

* Skirvin et al., 1967.

^b All values are ±30% on a metal-to-metal basis.

^c Not detected at the level indicated.

2.4.5. Electrolysis of Tungsten

High-purity tungsten metal has been reproducibly obtained in laboratory scale by the electrolysis of various molten salts containing tungsten oxides or halides, (Gomes et al., 1964, 1966a,b, 1968, 1970, 1971; Gomes and Wong, 1969). These electrowinning processes show promise as an inexpensive method of producing tungsten metal and tungsten carbide directly from wolframite and scheelite ores. To date, however, there have been no large-scale pilot plant efforts to develop tungsten electrowinning. This is due principally to the particle size of the metal deposit (i.e., 20–200 μm), which is not compatible with the standard press and sinter consolidation techniques presently used in conjunction with the standard hydrogen-reduced powders.

Successful commercial electrowinning processes that employ molten salt baths, such as in the aluminum and magnesium industries, have several features in common.

1. They electrowin metals in the liquid phase, which can be tapped from the cell without occluding electrolyte from the cell.
Fig. 2.18. Fused-salt scrubbing apparatus (Skirvin et al., 1967).

Table 2.13. Typical Fused-Salt (44% LiCl–56% KCl) Scrubbing Analyses

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Vaporizer charge</th>
<th>Overhead fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial 15–20%</td>
</tr>
<tr>
<td>Al</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cu</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Fa</td>
<td>&lt;5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;5&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mo</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>&lt;1&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Si</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>V</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

* Skirvin et al., 1967.
* All values are ± 30% on a metal-to-metal basis.
* Not detected at the level indicated.
2. The cell current flowing through the molten electrolyte is used to resistively heat the cells internally.
3. Electrowinning cells are physically large and must be periodically maintained or rebuilt and therefore must be inexpensive and simply constructed.

The electrowinning of tungsten must be carried out in cells from which the atmosphere is carefully excluded. The material of construction for tungsten electrowinning cells is typically graphite, for which fabrication techniques have been developed in an aluminum industry.

The principal development problem in scale-up of tungsten electrowinning processes is the manipulation of solid, typically dendritic, cathode deposit, which must be periodically harvested and which occlude the molten salt phase from the cell (i.e., “drag out”). The salt drag out is typically equal in weight to the electrowon tungsten, and is subsequently leached from the deposit.

There are no existing large-scale commercial molten salt electrowinning operations that have solid cathode deposits, but the titanium electrowinning process has a cathode deposit like that of tungsten and has been fully developed by Titanium Corporation of America and is on the verge of commercial use. Solid zinc, copper, and lead deposits are electrowon from aqueous solutions on a large scale.

The cell reactions that occur during the electrowinning of tungsten from molten salt baths are

\[
\text{Cathode: } \quad \text{WO}_3 + 6e^- \rightarrow W + 3O^{2-} \quad (2.24)
\]
\[
\text{Anode: } \quad (3 + x)C + 3O^{2-} - 6e^- \rightarrow (3 - x)CO_2 + 2xCO \quad (2.25)
\]
\[
\text{Overall cell reaction: } \quad \text{WO}_3 + (3 + x)C \rightarrow W + (3 + x)CO_2 + 2xCO \quad (2.26)
\]

The cathode current density for the successful laboratory-size cells run 0.5–1 A/cm². On industrial-size cells, the anode–cathode gap width is adjusted so that the cell is heated by the passage of current through the resistance of the molten salt. For a 30,000-A cell, the gap would be of the order of 76.2 mm (3 in.). Typical current efficiencies for tungsten electrowinning cells are 75%, which implies that 0.64 g of tungsten will be won per ampere-hour of current used.

Winning tungsten by electrolysis offers several advantages when compared to the present method of hydrogen reduction:

(a) Electrowinning is a good purification technique. Those impurities that are less electroactive than tungsten (including molybdenum and iron) can be removed by a preelectrolysis step in which a small amount of tungsten is won at low current density onto a “gettering cathode,” which selectively reduces, and the less electroactive elements are removed from the bath. The more electroactive species will remain in the melt during the subsequent electrolysis of tungsten.

(b) Electrowinning baths have been developed that utilize scheelite and wolframite directly, and would reduce the number of steps that are necessary in the hydrogen-reduction flowsheet.
(c) Electricity and carbon are less expensive than hydrogen for use as a tungsten reductant.

There are, however, several disadvantages that have prevented the commercialization of this technique:

(a) The electrowon tungsten has a large particle size (>10 μm). The large particle size gives a relatively porous (70%) product when consolidated by ordinary pressing and sintering techniques, which precludes the possibility of further fabrication (see Chapter 5). To obtain a satisfactory wrought product from electrowon powder, special fabrication techniques must be used, such as high-energy extrusion of the powder sheathed in molybdenum for extrusion and forging.

(b) Although a relatively high current density can be used in tungsten electrowinning cells, which together with the high equivalent weight of tungsten gives a relatively large yield per cell, electrowinning operations are large and require a large capital cost and must demonstrate a clear economic advantage before they will be developed. Since the tungsten industry is still small compared to the established electrowinning operations (e.g., aluminum, magnesium), economics favor low capital cost systems.

(c) The electrowinning of tungsten has not, to date, been demonstrated on a reasonably sized pilot-plant scale. This step must be taken before serious consideration of a full-scale process.

Even though large-scale industrial electrowinning of tungsten appears to be in an early stage of development, several less ambitious uses of electrochemical processes in the tungsten industry may show more immediate promise. Deposits of tungsten alloyed with various metals (particularly iron, chromium, and nickel), as opposed to pure tungsten deposits, can be electroplated from aqueous solutions. Electroplated alloy coatings have proved to be useful as corrosion-resistant coatings. On the other hand, dense coatings of pure tungsten can be electroplated from molten salt solutions.

Electrolysis of tungsten can yield large, very pure crystals. Since these crystals cannot be formed by hydrogen reduction, an electrolytic tungsten industry could result if a need for these types of crystals develops.

Tungsten carbide has been electrowon directly from molten salt baths. Since the market for tungsten carbide is comparable to the tungsten metal market, a tungsten carbide industry based on electrolysis could be developed. Unlike tungsten metal, the tungsten carbide product is friable and can be ground in a tungsten carbide-lined ball or rod mill to yield micron-size material. Tungsten can be purified from carbon by electrorefining tungsten carbide. The electrorefining of tungsten removes most of the other impurities as well. Therefore, scrap reprocessing may utilize an electrochemical process.

2.5. ILLUSTRATION OF INDUSTRIAL PROCESSES

So far in this chapter, the topics that include treatment and decomposition of tungsten ores, impurity removal, and crystallization of APT have been discussed. With given ore, one can select proper treatment steps and integrate the selected steps
into a smooth process flow. The art of economical process synthesis is dependent upon many factors, such as the quality of ore, desired product, labor cost, chemical cost, and availability of capital. It should be specially noted that material yield in the tungsten extraction process is especially critical, because the price of tungsten ore is much higher than conversion cost to APT.

2.5.1. Classical APT Process

This process is the oldest industrial process used in the production of APT. The raw material for the process is either natural or synthetic scheelite. Acid leaching is used as the ore decomposition method, and the tungstic acid is dissolved and digested in ammonia solution. APT is obtained from the crystallization of ammonium tungstate solution. The process is exemplified by that used by Wah Chang Corporation at Glen Cove, New York, and the flowsheet is shown in Fig. 2.19. The process is described as follows: Ten ton lots of scheelite (60–75% WO₃) with particle size of -200 mesh (-74 μm) are charged to a digester vessel consisting of a steel shell lined with brick. Commercial HCl (20 Be) is added at a rate of 1.5 kg per kilogram of contained calcium tungstate in the ore. This corresponds to twice the amount of HCl required by the stoichiometry of the leaching reaction. Fifty kilograms of sodium nitrate is added as an oxidizing agent, and the total mixture is agitated and maintained at 70°C for 12 hr by steam sparge.

The slurry is then diluted and allowed to settle. Nine washes are performed by settling and decantation in wooden tanks, the first seven at 70°C and the last two at ambient temperature. The third through seventh washes are done with 1% HCl solution. The washed tungstic acid slurry is then ready for conversion to APT.

Variations of acid leaching include the excess of HCl used, which may be from 1.5 to 3 times the stoichiometric amount, the acid concentration, and the oxidizing agent used. The agent may be nitric acid or manganese dioxide instead of sodium nitrate. Other variations are the temperature and digestion time, which depend upon particle size of ore, acid concentration, and degree of agitation.

After washing, the slurry of tungstic acid is then sampled for specific gravity or WO₃ concentration as g/liter. The amount of 28% NH₃ solution required to form ammonium tungstate with approximately 100% excess ammonia is calculated. If the specific gravity of the slurry is greater than 1.50, extra water should be added so that the specific gravity of the resultant ammonium tungstate solution is kept below about 1.26. The process is conducted in batches of about 5500 liters.

When the slurry is dissolved, the solution is tested for calcium, and if it is present, a calculated amount of oxalic acid is added. Sixty kilograms of activated carbon, which acts as a filter aid, is then added, and the solution is pumped through a filter _en route_ to the crystallization tank. Crystallization is done batchwise, and the charge to the crystallizer is 10,000 liter. The operation is effected by evaporating the solution with agitation to a bulk while evaporation continues until the specific gravity of the solution falls to the range 1.05–1.07. At this point, crystallization is complete. The crystals are allowed to settle and the mother liquor decanted. The crystallized APT is washed twice with 7200 liters of water, each time using the settling–decantation method, and then dried at 120–138°C.
Fig. 2.19. Scheelite acid leaching — APT process flowsheet, Wah Chang Glen Cove.
The mother liquor, with a tungsten content near 80–90 g/literWO₃, is combined with the wash water and stirred prior to precipitation of synthetic scheelite. This is accomplished by placing the liquor in a 38,000-liter tank and adding a little over the stoichiometric amount of sodium hydroxide to convert to Na₂WO₄ and heating to 70°C for ammonia removal. The pH of the solution is then adjusted to 10.5–11.0 by adding sodium bicarbonate and hydrogen sulfide in order to complex molybdenum. The solution is then agitated for 1 hr at 70°C while adding calcium chloride solution. This results in precipitation of calcium tungstate while leaving molybdenum in the solution. When the synthetic scheelite has settled, the mother liquor is decanted and the scheelite is washed four times at 70°C by decantation. The slurry of synthetic scheelite is dried in a rotary calciner and then recycled to the acid leaching step.

In the Glen Cove plant, the process was batchwise, which was labor intensive. For example, the settling–decantation method could be replaced by a more efficient method of filtration and washing, and most of the process steps could also be incorporated in a continuous process with labor-saving instrumentation and automation. Any scheelite with high molybdenum content could not be used because there was no separate molybdenum removal step in the process.

A modified process with continuous leaching system was used by Ugine Carbone, France. The overall process flowsheet is shown in Fig. 2.20. Feed to the plant is natural scheelite concentrate, averaging 70%WO₃ and with a molybdenum content up to 2%. The ore is ground to −44 μm (−325 mesh) in a hammer mill with a built in air classifier and conveyed to a storage hopper. The ground ore is dispensed by a weighing hopper and mixed with a little water to make a pumpable slurry, heated to 70°C, and transferred to the leaching reactors. The continuous back-mix reactor system consists of four small agitated reactors in cascade. Hydrochloric acid, 32%, is charged to the first reactor at 100–150% excess over the stoichiometrically required amount. The reactors are made of carbon steel lined with rubber. The temperature is maintained at 60°C in the first reactor, 75°C in the second, 90°C in the third, and 100°C in the fourth. The heat is supplied by means of graphite heating elements in the transfer lines to and between the reactors. The system is run at a pressure slightly below atmospheric to avoid escape of fumes. Retention time is 2 hr per reactor.

The reacted slurry is discharged to one of ten settling tanks, where the leach liquor is siphoned off. Washing and decanting are then repeated three times; the whole operation requires 12 hr. The leach liquor and washings are neutralized in a lime pit. The washed tungstic acid is then pumped to one of three digesters equipped with agitators, where it is mixed with aqueous ammonia, specific gravity 0.93, in quantity doubling the amount required stoichiometrically to form ammonium tungstate. After agitation for another 30 min. with the temperature maintained at 60°C, the mixture is then filtered through a plate and frame filter, which is precoated with a cellulose filter aid. The filtrate, with a specific gravity of 1.15–1.20, is pumped to one of three crystallizers, each of which is equipped with a steam jacket. The solution is evaporated to the extent, depending on the Mo/W ratio, that 84–90% of the contained tungsten is crystallized as APT. It is then separated from the mother liquor on a pressure Nutsche filter and washed with water. The crystallized APT is
then dried at 80°C in a screw-fed drier, screened, and stored.

The mother liquor is either further crystallized to produce a low-grade APT containing 0.5–1.5% molybdenum or is treated to recover tungsten as synthetic scheelite, as described above. The consumption of materials for the Ugine Carbone process is given in Table 2.14, in terms of kg/mtu (kilogram per metric ton unit) of WO₃ processed.
Table 2.14. Materials Used for APT Production at Ugine Carbone

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity kg/mtu WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>24.6</td>
</tr>
<tr>
<td>Aqueous ammonia, specific gravity 0.93</td>
<td>1.7</td>
</tr>
<tr>
<td>Calcium hydroxide for spent acid neutralization</td>
<td>8.0</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1.1</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* Courtesy of Ugine Carbone, Grenoble, France.

If a steady supply of scheelite concentrate with low molybdenum content (Mo/WO₂ < 2%) is assured and there is no demand for APT with extremely low molybdenum, the classical APT process can be used with a minimum of capital and operating costs. However, the Ugine Carbone process could be further improved by incorporating completely into a continuous process with modern instrumentation and control valves and by adding pollution control devices for HCl and NH₃ recovery.

The classical APT process with its best design still has some disadvantages. The starting ore must be high-grade scheelite with low molybdenum content. Although the process is rather simple as compared to other industrial practices as mentioned below, the design of equipment material is difficult because of severe corrosion problems with hot HCl and CaCl₂ solutions.

2.5.2. LIX Process

The LIX process was first used commercially by Union Carbide for the production of APT with high purity. The plant was built near Bishop Mine, California and has been in operation over 20 years. At the present time, the LIX process is the most popular commercial process in the industry. Sylvania, Inc. and Korean Tungsten Mining Company each built a LIX plant in recent years. Last year (1976) Mittersill and Teledyne Wah Chang jointly built a modern plant using the LIX process in Austria.

Typical LIX process flowsheets are shown in Fig. 2.21 and 2.22. The Sylvania plant deviates somewhat from the process in that high-grade ore concentrates are digested in NaOH. Other plants can use low-grade scheelite concentrates (< 30% WO₃) because they utilize the autoclave–soda process for ore decomposition. The low-grade scheelite usually needs a pretreatment to remove impurities such as organic material, sulfur, phosphorus, and arsenic. Details have been discussed in Sec. 2.2.1.

Since the reaction rate in the autoclave is strongly affected by the particle size of the ore concentrate, ball milling is usually employed, with the resulting feed size ranging from -20 mesh to -325 mesh. A weighed amount of ore concentrate is fed
Fig. 2.21. Flowsheet of autoclave-soda process. (Courtesy of Teledyne Wah Chang Huntsville, Alabama.)
Fig. 2.22. Flowsheet of LIX process. (Courtesy of Teledyne Wah Chang Huntsville Alabama.) *This step is needed if APT precipitates; broken line indicates organic flow, solid line indicates aqueous or gaseous flow.
to a charge tank where a slurry of sodium carbonate is introduced in the amount of 250–480% of the stoichiometric quantity.

The batch autoclave is constructed with carbon steel for operating pressure of 14.1–24.6 kg/cm² (200–350 psia) and for temperature of 200–250°C. The temperature is maintained with live steam sparge during operation. To increase reaction rate, steel balls can be charged to the autoclave. When the digestion is complete in 4–6 hr, the charge is released to a flash tank where a portion of steam is recovered and the charge is cooled somewhat.

The digested slurry is filtered and washed. Two to three stages of vacuum drum filters are used with countercurrent washes. Steam blowback is found to be better for cake discharge. The filtered sodium tungstate solution is treated chemically to remove silica, phosphorus, arsenic, and molybdenum as described in Sec. 2.4.2. Usually, pressure filters such as plate and frame are used to remove the impurities. Tungsten loss during the filtration can be significant unless proper operating procedures, including temperatures, amount of chemical additions, digestion time, and filter aids, are followed. The purified sodium tungstate solution is then stored in storage tanks, where pH and temperature can be adjusted for ideal extraction conditions.

During and after the molybdenum removal step, pH value decreases and corrosion problem can be significant. In one plant, stainless steel was corroded by fluoride ions so severely that process vessels, pumps, and valves had to be replaced by proper fiberglass equipment. The LIX extraction circuit, as shown in Fig. 2.22, consists of two stages of each extraction, washing, stripping, and sulfonation of the solvent. Like any other solvent extraction circuit, the process system is effected by numerous recycle streams. Therefore, understanding of the entire process interaction and controlling important operating variables are critical. The operating variables are listed in Table 2.15 and typical plant data are shown in Table 2.16.

### Table 2.15. Operating Variables in LIX Circuit

<table>
<thead>
<tr>
<th>Equipment operating or stage</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractors</td>
<td>a. Flow rate of feed to extractor</td>
</tr>
<tr>
<td></td>
<td>b. Concentration of feed to first extractor</td>
</tr>
<tr>
<td></td>
<td>c. Feed temperature</td>
</tr>
<tr>
<td></td>
<td>d. Feed pH</td>
</tr>
<tr>
<td></td>
<td>e. Flow rate of organic</td>
</tr>
<tr>
<td></td>
<td>f. Flow ratio of organic to aqueous in mixers</td>
</tr>
<tr>
<td></td>
<td>g. Concentration of organic phase (WO₃ g/liter)</td>
</tr>
<tr>
<td></td>
<td>h. Speed of agitation</td>
</tr>
<tr>
<td>Strippers</td>
<td>a. Flow rate of ammonia</td>
</tr>
<tr>
<td></td>
<td>b. Concentration of ammonia</td>
</tr>
<tr>
<td></td>
<td>c. Flow ratio of organic to aqueous in mixers</td>
</tr>
<tr>
<td></td>
<td>d. Speed of agitation</td>
</tr>
<tr>
<td>Solvent washing stages</td>
<td>a. Flow rate of water</td>
</tr>
<tr>
<td></td>
<td>b. Flow ratio of aqueous to organic in the mixers</td>
</tr>
<tr>
<td>Sulfonation</td>
<td>a. Flow rate of sulfuric acid</td>
</tr>
<tr>
<td></td>
<td>b. Flow ratio of aqueous to organic in the mixers</td>
</tr>
</tbody>
</table>
Table 2.16. Typical LIX Extraction Plant Operating Data

A. Feeds
Extraction input
- Quantity ........................................ 240 kg/hr WO_3
- Loading .......................................... 100 (40–120) g/liter WO_3
- Rate ............................................. 40 liter/min
- Acid (5% H_2SO_4) rate.......................... 10 liter/min
- Wash water rate .................................. 27 liter/min
- Stripping (5% NH_3) rate....................... 40 liter/min

B. Organic
Composition ........................................ 7:7:86 vol % (Alamine 336:decanol:kerosene)
- Loading .......................................... 25 g/liter WO_3
- Rate ............................................. 160 liter/min

C. Strip solution
- Loading .......................................... 100 g/liter WO_3
- Rate ............................................. 40 liter/min

D. Equipment design
- Mixers (all except wash) ...................... 0.614 m^3
- Mixers (wash) ................................... 1.225 m^3
- Settlers, surface area (all) ................... 7.2 m^2
- Settler weirs (height)
  - Organic ....................................... 0.7 m
  - Aqueous ....................................... 0.5 m

E. Operating data

<table>
<thead>
<tr>
<th>Flow design</th>
<th>Flow rates (liter/min)</th>
<th>Organic aqueous ratio</th>
<th>Organic Input</th>
<th>Recycle</th>
<th>Total</th>
<th>Mixer residence time (min)</th>
<th>Settler (liter/min-m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid 1</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>10</td>
<td>123.3</td>
<td>293.3</td>
<td>2.09</td>
</tr>
<tr>
<td>Sulfuric acid 2</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>10</td>
<td>123.3</td>
<td>293.3</td>
<td>2.09</td>
</tr>
<tr>
<td>Extract 1</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>40</td>
<td>93.3</td>
<td>293.3</td>
<td>2.09</td>
</tr>
<tr>
<td>Extract 2</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>40</td>
<td>93.3</td>
<td>293.3</td>
<td>2.09</td>
</tr>
<tr>
<td>Wash 1</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>27</td>
<td>106.3</td>
<td>293.3</td>
<td>4.18</td>
</tr>
<tr>
<td>Wash 2</td>
<td>Organic</td>
<td>1:2:1</td>
<td>160</td>
<td>27</td>
<td>106.3</td>
<td>293.3</td>
<td>4.18</td>
</tr>
<tr>
<td>Strip 1</td>
<td>Aqueous</td>
<td>1:1:2</td>
<td>160</td>
<td>40</td>
<td>152</td>
<td>352</td>
<td>3.49</td>
</tr>
<tr>
<td>Strip 2</td>
<td>Aqueous</td>
<td>1:1:2</td>
<td>160</td>
<td>40</td>
<td>152</td>
<td>352</td>
<td>3.49</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Huntsville, Alabama.

Crystallization of APT is done in a typical evaporative crystallizer made of stainless steel 316. APT slurry is filtered using a vacuum belt filter and washed. The crystallized APT is dried in a steam-heated dryers and calcined to produce blue oxide. A typical chemical consumption in an operating plant is shown in Table 2.17.
Table 2.17. Typical Consumption of Chemicals in an Autoclave–Soda LIX Extraction Plant, 1.6 × 10^6 kg (3.5 × 10^6 lb) Tungsten per Year

<table>
<thead>
<tr>
<th>Material</th>
<th>Rate of consumption (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃ contained in ore</td>
<td>225</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>309</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>18</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>6.75</td>
</tr>
<tr>
<td>Na₂S</td>
<td>12</td>
</tr>
<tr>
<td>H₂SO₄, concentrated</td>
<td>315</td>
</tr>
<tr>
<td>Organic</td>
<td></td>
</tr>
<tr>
<td>Alamine 336</td>
<td>1.92</td>
</tr>
<tr>
<td>Decanel</td>
<td>2.04</td>
</tr>
<tr>
<td>Kerosene</td>
<td>2.11</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>27</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang. Huntsville, Alabama.

The LIX process has many advantages over classical APT processes among which the major ones are:

1. Lower-grade ore can be used. Therefore, a plant can be built near the mining operation to save expenditure in ore concentration.

2. The process is basically continuous. Labor requirement is not high, yield is over 98%, and product quality is uniform.

3. Since it has separate steps for impurity removal, a wide range of ore quality can be used to produce high-purity APT. Ore purchasing is flexible.

2.5.3. Tungsten Hexachloride Distillation Process

In the Sandvik Company, Sweden, a distillation process based on the patent of Jonsson et al. (1970) was developed to a commercial-scale plant. Crude tungsten hexachloride is produced by chlorination of scrap metal. The original process concept, which uses tungsten–silicon alloy as the raw material, has never been realized. The crude tungsten hexachloride containing molybdenum and other metal chlorides is purified in a multistage fractional column. The purified tungsten hexachloride, containing less than 100 ppm molybdenum, can be reduced to metal powder with extremely fine particle size. In this process, a continuous fluidized bed can be utilized.

The fractional distillation system is continuous, requiring low labor costs and essentially no chemicals. The throughput is rather high. Even though this process has a great potential, much research and development effort should be made before it is widely accepted. One of the difficulties to be overcome is oxygen contamination in the final product and the other is the poor yield.
2.6. RECYCLING OF TUNGSTEN

2.6.1. General Remarks

There are two broad categories of materials that constitute tungsten scrap. These are residues from fabricating tungsten or other tungsten-containing materials and worn, used, or spent materials containing tungsten. Among the former are included ends of sintered bars, floor sweepings from areas where carbides are prepared and handled, grinding sludge, metal scale, and machine chips; among the latter, used tungsten carbide tool bits and spent catalysts. Scrap is usually segregated according to type and quality, and the way in which it is recycled is dependent on the type of scrap. Generally, an application is chosen for the scrap such that it can be used with minimum pretreatment. Expensive options, such as chemical reprocessing, are avoided if possible. High-grade tungsten metal scrap, such as ends of sintered bars, is thus used directly in making superalloys and alloy steels. Scrap sintered tungsten carbide parts likewise are not often recycled chemically, but are comminuted in one of several ways and resintered. Tungsten powder and tungsten carbide powder recovered as floor sweepings usually contaminated with iron, nickel, etc., can be used successfully in preparation of tungsten carbide for hard facing, in which case, high purity of the material is not required. Scrap thoriated tungsten can be used in addition to alloy steel; however, it can only be used in limited quantities, because the presence of thorium is objectionable in large amounts in steels. Alloy steels containing tungsten are recycled in melting new batches of metal.

Chemical recycling is used only where substantial purification is necessary before the tungsten values can be reused. Contrary to the case of scrap that can be used directly, scrap that requires chemical reprocessing usually has a value similar to an ore concentrate.

2.6.2. Processes for Recycling Cemented Tungsten Carbide

Three processes are currently in use for recycling tungsten carbide. These are the coldstream process, the zinc process, and the leach–milling process. The coldstream process employs a high-velocity stream of air in which approximately 6-mesh (3.4-mm) fragments of cemented carbide are entrained, then impinged at a velocity near mach 2 on a massive stationary target, suitably cooled. The impact partially shatters the carbide, and the product is then air-classified and the oversize recycled to the impingement stage. The fines are then resintered. Limitations of the coldstream process are that it does not work very well with grades of cemented carbide high in binder because of higher ductility and that it produces some oxygen contamination (from the air) and some iron contamination (from the target). Oxygen contamination can be removed by sintering in hydrogen, but this tends to produce a product deficient in carbon. The difficulties with cemented carbide of high binder content can be mitigated by heating the material to approximately 1800°C, then quenching rapidly, which causes embrittlement. Scrap is segregated into straight WC–Co grades and those high in TiC and TaC before comminution. The process thus produces two kinds of powder. Cost of the service is $2.25/kg ($1.02/lb) with 90% recovery.
The zinc process relies on the principle that molten zinc forms an alloy system with cobalt and disrupts the integrity of the cemented carbide. The zinc can then be removed by distillation, leaving a crumbly mass of tungsten carbide and cobalt that is readily ground and resintered. Limitations of the process are that large pieces of carbide must be treated more than once and that adequate zinc removal requires two distillation treatments, the second of which is done in the presence of hydrogen, which tends to produce a carbon deficiency. Historically, the process has its origins in a patent awarded to Powder Alloys Ltd. (Trent, 1946). This patent discloses the fact that molten zinc will rapidly alloy with and embrittles the cobalt binder of cemented carbide. However, as mentioned in this patent, both the zinc and the cobalt were removed by treatment with hydrochloric acid, and only the tungsten carbide was reused directly. Removal of the zinc by distillation was invented by Barnard et al. (1971). When this is done, the product contains all of the original cobalt and may be resintered without further treatment after grinding.

The zinc process is usually operated batchwise. Graphite crucibles are loaded with 13.6–22.7 kg (30–50 lb) of scrap cemented carbide and zinc in the amount 1 to 1.3 times the weight of carbide. Twelve crucibles are stacked in the furnace in such a way as to allow free circulation around them. The furnace is then flushed with nitrogen or argon and the temperature raised to 900°C, at which temperature it is held for 12 hr; then the zinc is distilled off by reducing the pressure. Adequate zinc removal requires that the pressure be held at 50–200 Torr for at least 5 hr, with the temperature at 900°C. Distillation of the zinc from the product requires a total of 15 hr. Figure 2.23 is a schematic diagram of the retort in which the process is carried out.

The third method, leach–milling, relies on the fact that mineral acids will dissolve the binder metals from cemented tungsten carbide. The process is conducted in a rotating rubber-lined mill. It is a lengthy process, since the cobalt binder dissolves slowly. The recovered tungsten carbide usually has a high oxygen content.

2.6.3. Recycling by Chemical Methods

Recycling methods that use chemical processing are applicable to a diversity of materials, but are more expensive and troublesome than those that recycle materials more directly. Chlorination to recover tungsten values from scrap has been suggested. In the case of alloys, this reduces to the problem of separating the various chlorides produced. Usually this can be done by fractional distillation; the subject has been treated more fully in Sec. 2.4.4, especially in connection with removal of molybdenum. The method is applicable to carbide scrap (Jonsson, 1968). In this case, difficulties may be encountered due to layers of carbon building up on the carbide grains. This problem can be solved by purging the reactor periodically with carbon dioxide, whereby the carbon is converted to carbon monoxide. In the case of heavy alloy scrap, Gokhale and Gupta (1973) found 100% conversion of the tungsten to WCl₆ at 750°C.

Chlorination has been suggested as one step in recycling tungsten and other metals present in certain spent catalyst materials. These catalysts, used in quantity
by the petroleum industry, contain up to 10% tungsten, molybdenum, or vanadium, the remaining material being alumina or silica supports. According to Erikson et al. (1970), the material is sulfided at 400–800°C with hydrogen sulfide or carbon bisulfide then chlorinated with chlorine or carbon tetrachloride at 290–370°C. The resulting tungsten hexachloride and molybdenum and vanadium chlorides are then condensed and separated by distillation. Tungsten hexachloride may be used to make tungsten powder by vapor-phase reduction with hydrogen (see Chapter 3).

Electrolytic methods for recovering tungsten have been investigated. According to patents issued by the General Electric Company (1960a, 1961), tungsten scrap such as heavy alloys, thoriated tungsten, and tungsten carbide may be electrolytically oxidized by making it the anode in an electrochemical cell. The electrolyte may be sodium, potassium, or ammonium hydroxide. The process results in a tungstate solution as product. If the scrap is pure tungsten, the alkali tungstate solution may be used without further purification and converted to tungsten by
methods already discussed. If purification is necessary, this can be done readily and the alkali tungstate solution used as feed for the LIX process. The process uses about 12 kW-hr/kg of tungsten processed. Although the process promises to be quite inexpensive, the fact that it is restricted to tungsten carbide or high-tungsten alloys probably would prevent its wide adoption, since these materials can be recycled more cheaply by routes already mentioned.

Anodic dissolution of tungsten as a method of recovery from scrap has also been investigated in recent years. Balikhin et al. (1972) applied the technique to thoriated tungsten. Ramakrishnan and Nagarkatte (1966) in their work observed that addition of potassium perchlorate to the electrolyte in an amount of 5 mg/liter increased the current efficiency by about 15%. Zueva et al. (1973) investigated anodic dissolution of tungsten–molybdenum alloys in acid media with a view to separating the molybdenum and tungsten. They found unstable behavior with nitric acid using alternating current but obtained stable behavior with metal removal rates of up to 20 mg/cm²-min with direct current at current densities of 2 A/cm² using concentrated hydrochloric acid as the electrolyte. Segregating the anode and cathode compartments helped to prevent cathodic reduction of Mo(VI).

The traditional methods of recycling tungsten scrap are described by Smithells (1953). The tungsten is either burned in a stream of air or reacted with sodium nitrate at high temperature. In the first method, the scrap must be agitated frequently to break up layers of oxide that prevent reaction of the underlying metal, and in the second, care is necessary because the reaction is quite violent. Both methods produce WO₃ and may be operated at efficiencies approximately 75% recovery. Concerning the method of roasting in air, Kalashnik et al. (1973) introduced a modification for molybdenum–tungsten scrap in which the oxidation is conducted at a temperature below 800°C, in which case about 90% of the molybdenum is volatilized away with insignificant tungsten loss. Gokhale and Gupta (1973) reported extensive investigation of the air oxidation technique to the recovery of heavy metal scrap and concluded that the method was inferior to oxidation with sodium nitrate.

Recent practice in the process involving oxidation of scrap with sodium nitrate or nitrite is to mix the oxidizing agent with sodium carbonate and roast at 800°C for about 1 hr. The proportions of oxidizing agent to sodium carbonate vary from 3:1 for a tungsten steel (Topalov et al., 1966; Danev, 1971) to 1:3 for tungsten chips and grinding dusts (Société Electrométallurgique de Saint Etienne, 1953). Tungsten carbide scrap may also be recycled by this method (Karczynski, 1964). The function of the sodium carbonate is to dilute the oxidizing agent and cause the reaction to take place in a more controllable fashion. The oxidizing roast converts the tungsten to WO₃ if air is used as the oxidizing agent and to sodium tungstate if sodium nitrate is used. If sodium tungstate is the product, the cake from the roasting process is ground and leached with hot water and the solution filtered. This removes impurities such as iron, cobalt, and nickel, which form insoluble carbonates. If the product is tungsten oxide, either from an air oxidation or from some form of scrap already in oxide form, such as spent catalyst (Stadler and Jiricek, 1968), it is leached with a solution of sodium hydroxide or sodium hydroxide and sodium carbonate. From this point, the resulting sodium tungstate solution can be treated in any of the conventional ways as mentioned in Sec. 2.4.2.
Reduction of Tungsten Oxides, Halides, and Ores

3.1. GENERAL BACKGROUND

In selecting a reducing agent for a particular ore or oxide, a large negative value of free energy change for the reduction reaction is generally desirable. This can be calculated from the energy of formation of the reactants and products. Other factors that should be considered are high boiling point of the element, low melting point of its oxide, and cost of the material. Comparison of these factors for commonly used reductants is shown in Table 3.1 (Belitskus, 1972). Calcium has the greatest reducing potential at temperatures up to about 2100°C; magnesium has nearly as much potential at low temperatures. Both of them, however, lose effectiveness at high temperatures due to their low boiling points. Aluminum is generally superior to silicon over the entire temperature range and surpasses magnesium at about 1600°C. Carbon is a relatively poor reductant at low temperatures but improves with increasing temperature.

Table 3.1. Factors Affecting Use of Various Elements for Reducing Metal Oxides

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Heat of formation for the oxide at 25°C (kcal/mole O₂)</th>
<th>Boiling point of element (°C)</th>
<th>Melting point of oxide (°C)</th>
<th>Equivalent weight</th>
<th>Cost per kilogram equivalent ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>-304</td>
<td>1482</td>
<td>2580</td>
<td>20</td>
<td>44.00</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-288</td>
<td>1103</td>
<td>2800</td>
<td>12</td>
<td>9.46</td>
</tr>
<tr>
<td>Aluminum</td>
<td>-267</td>
<td>2467</td>
<td>2045</td>
<td>9</td>
<td>5.94</td>
</tr>
<tr>
<td>Silicon</td>
<td>-216</td>
<td>2480</td>
<td>1710</td>
<td>7</td>
<td>2.20¹</td>
</tr>
<tr>
<td>Carbon</td>
<td>-94</td>
<td>4200</td>
<td>-57(CO₂)</td>
<td>6⁵</td>
<td>&lt;0.22⁴</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-116</td>
<td>-253</td>
<td>0</td>
<td>1</td>
<td>&lt;0.22²</td>
</tr>
</tbody>
</table>

Desirable High (—) High Low Low Low

¹ Belitskus, 1972.
⁵ For temperatures above 710°C, where CO is the major oxidation product.
⁶ As 50% ferrosilicon.
⁴ As coke.
For the initiation of the reaction, heat must be supplied. If the heat of reaction is high, sufficient heat is generated and the reaction will be self-sustaining. Reductions with calcium, magnesium, and aluminum are ordinarily sufficiently exothermic that additional heat supply is unnecessary. On the other hand, silicon, carbon, and hydrogen reductions are usually conducted with a continuous external heat supply.

On the basis of the free energy and enthalpy changes, it appears that hydrogen is a poor choice. However, this is not the case, since product purity and product form are of major concern for the reduction of tungsten oxides. This is due to the fact that good fabricability and ductility of tungsten final products rely heavily upon the purity of the metal. The goal is the production of tungsten powder, and a high intensity of heat to melt the metal is not required.

Since high-purity hydrogen is readily available, it is universally used as a reductant for tungsten oxides in the industry today. For tungsten used as an alloy addition to steel or superalloys, the purity requirement is less stringent, and carbon may be used for the reduction process. Tungsten powder thus produced usually contains some silicon, iron, carbon, sulfur, and phosphorus impurities, which will be discussed in more detail in Sec. 3.4. Metals such as calcium, aluminum, and silicon have been used in small scale or for some special purpose to reduce tungsten from its oxides, but after reduction, a refining process such as electrorefining or electron-beam melting is necessary. The final shape thus produced is not fine powder, and this also causes difficulties during consolidation and fabrication.

Recent demands for higher purity, submicron particle size, and special control of particle size distribution have been emphasized in the industry, and an original laboratory-scale process, namely, hydrogen reduction of tungsten halides, has been developed to production scale in recent years.

In this chapter, hydrogen reduction of tungsten oxides will be discussed in detail, followed by a discussion of carbon reduction. Reduction of oxides with metals and electrorefining and reduction of tungsten halides will also be discussed later in this chapter. Electron-beam melting or refining will be deferred to Chapter 4.

3.2. FROM APT TO TUNGSTEN OXIDES

Industrial production of tungsten starts with tungsten ore that is treated and extracted to form ammonium paratungstate (APT), \(5(\text{NH}_4)_2\text{O}\cdot12\text{WO}_3\) as mentioned in the previous chapter. APT may be reduced directly to tungsten or converted to oxides before the final reduction. In the direct reduction process, the product gases include large amounts of ammonia and water vapor, which makes the recovery of hydrogen rather difficult. It is, therefore, a general practice to convert APT to tungsten oxides and then reduce the oxides to metallic powder.

When APT is reduced to tungsten oxides, it displays different colors according to its compositions (Li and Wang, 1955). The major distinctions are as follows: tungsten trioxide, \(\text{WO}_3\), or tungstic oxide, as it is generally called, is yellow; tungsten dioxide, \(\text{WO}_2\), is brown; and the intermediate oxide, \(\text{W}_4\text{O}_{11}\), a mixture of \(\text{W}_{18}\text{O}_{49}\) and \(\text{W}_{20}\text{O}_{55}\), is purple-blue. For details of compositions of the oxides, the reader is referred to Sec. 7.3.3.1. For simplicity, the oxides of tungsten will be referred to as
yellow, brown, or blue hereafter in this chapter. These nomenclatures are generally
adopted by the industry.

Since APT can be converted into yellow oxide by heating in air above 250°C
(482°F) with decomposition products of ammonia and water vapor, this is generally
accomplished by passing of a stream of filtered air through the furnace. When blue
oxide is desired, a slightly reducing atmosphere is employed. This is obtained by
passing a small amount of hydrogen through the furnace or by simply keeping the
furnace roughly sealed off from the outside atmosphere. Since the blue oxide
contains less oxygen than the yellow oxide, a smaller amount of reducing agent is
required in the subsequent step of reduction. The process with blue oxide as the
intermediate product is therefore the general practice in the industry. The furnaces
used for conversion are essentially of two types, which, along with the processes to
produce blue as well as yellow oxides are described below.

3.2.1. **Stationary Furnace**

In this type of furnace (Fig. 3.1), APT is loaded in shallow boats, which are
stoked into a tube of round or rectangular cross section. The tubes and boats are
generally made of Inconel or corrosion-resistant steel casting with ACI (Alloy
Casting Institute) designations of HH, KH, and HW. For round tubes, the inside
diameter ranges from 102 mm (4 in.) to 152 mm (6 in.) with lengths to 9.14 m (30 ft),
about two-thirds of which is located in the heating zone. The tubes are usually
arranged in two rows and number from eleven to nineteen. The furnace is either gas
fired or electrically heated in three or four separate zones outside of the tube.

Before stoking, the boats are placed on a temporary support in alignment with
the tube. Automatic stokes push all boats simultaneously into the tube. Attached to

![Fig. 3.1. Stationary hydrogen reduction furnace. (Courtesy of Teledyne Wah Chang Huntsville, Alabama.)](image-url)
the stoker is a doughnut-shaped rubber seal, which is inflated with pressurized hydrogen during stoking in order to seal off the entrance of the tube. It deflates when the stoker retracts from the furnace tube.

When blue oxide is desired, in the stationary furnace process, a slow-flow of hydrogen opposite to the charge direction is used, and the temperature ranges from 490°C (914°F) at the front zone to 600°C (1112°F) at the rear. The boats are stoked every 15–20 min so that they gradually move from a lower temperature zone to a higher one. The total time for the boat traveling through the furnace is usually 4.5–5 hr.

For a 102-mm (4-in.) diameter tube, the inside dimensions of the boat may be $43 \times 61 \times 470$ mm ($1.7 \times 2.4 \times 18.5$ in.) with a wall thickness of 6.4 mm (0.250 in.). The load per boat is then about 1800 g of APT. When the converted blue oxide is cooled at the rear end of the tube, it is discharged. The oxide is then passed through a vibrating screen of 60 mesh or 50 mesh in order to break the agglomerates and prevent the formation of coarse particles during the subsequent reduction.

At the discharge end, hydrogen is maintained at a positive pressure of 114–152 mm (4.5–6.0 in.) of water and led into the tube. After leaving the stoke end, the gases are generally led to the hydrogen regeneration system (Fig. 3.2). The system consists of a scrubbing tower, where the ammonia is removed; a deoxidizer, which is usually made of a set of tube furnaces stuffed with a scrap metal heated to 600–700°C (1112–1292°F); a cooling tower; a drying tower containing CaCl$_2$, KOH, silica gel, activated alumina, or phosphorus pentoxide; and a compressor to bring hydrogen to the desired pressure level.

An alternate type of stationary furnace is of the four-muffle type (Fig. 3.3) (Mel'nikov et al., 1963). The overall dimensions of this furnace are $2.1 \times 2.65 \times 7.4$ m ($82.7 \times 104 \times 291$ in.); the width of the stainless steel muffle is 300 mm (11.8 in.); the length of the hot zone is 3.65 m (143.7 in.). Layers of boats are loaded into the furnace through a side opening with a water-cooled door and rubber sealing. Pneumatic or hydraulic pushers are used for moving the boats at a speed ranging from 10 to 1000 mm/min. In order to prevent air from infiltrating into the hydrogen regeneration system, an electrical locking device is provided that closes the main hydrogen feed valve in case any of the muffle doors should remain open.

Output of the four-muffle furnace is eight times greater than that of the ordinary eleven-tube furnace, and the power consumption per unit weight of tungsten is only a third of that consumed by the eleven-tube furnace. However, the shortcomings of the four-muffle furnace are the need to load the boats by hand, and the nonuniformity of the product; the intermittent operation of the furnace invariably involves some losses of hydrogen (Mel'nikov et al., 1963).

When yellow oxide instead of blue oxide is desired in the first step of reduction using a stationary furnace of either type mentioned above, no hydrogen is required. In this case, filtered air is passed over the charge in order to carry away ammonia and water vapor, which are released during the decomposition of APT.

### 3.2.2. Rotary Furnace

A general view of a rotary furnace is shown in Fig. 3.4. The furnace chamber is
yellow, brown, or blue hereafter in this chapter. These nomenclatures are generally adopted by the industry.

Since APT can be converted into yellow oxide by heating in air above 250°C (482°F) with decomposition products of ammonia and water vapor, this is generally accomplished by passing of a stream of filtered air through the furnace. When blue oxide is desired, a slightly reducing atmosphere is employed. This is obtained by passing a small amount of hydrogen through the furnace or by simply keeping the furnace roughly sealed off from the outside atmosphere. Since the blue oxide contains less oxygen than the yellow oxide, a smaller amount of reducing agent is required in the subsequent step of reduction. The process with blue oxide as the intermediate product is therefore the general practice in the industry. The furnaces used for conversion are essentially of two types, which, along with the processes to produce blue as well as yellow oxides are described below.

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Before stoking, the boats are placed on a temporary support in alignment with the tube. Automatic stokes push all boats simultaneously into the tube. Attached to
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### 3.2.2. Rotary Furnace

A general view of a rotary furnace is shown in Fig. 3.4. The furnace chamber is
Reduction of Tungsten Oxides, Halides, and Ores

Fig. 3.2. Hydrogen regeneration system.

Fig. 3.3. Four-muffle hydrogen reduction furnace: (1) framework, (2) casing, (3) pneumatic pusher, (4) insulating brickwork, (5) muffle, (6) unloading section (Mel'nikov et al., 1963).
generally divided into three zones by means of disk partitions, and the material being processed travels from zone to zone through central holes in these partitions. The purpose of the partitions is to retain the material being reduced and to stir and blend the powder inside the furnace. Longitudinal vanes are arranged between the partitions and thus help stir the material and prevent the formation of lumps.

The lower part of the loading hopper of the furnace contains a mixer consisting of a roller with multiple pins welded perpendicularly to its surface; these pins continuously stir the powder and prevent it from compacting. The powder is fed by a screw feeder, which also seals the furnace from the outside atmosphere. The loading of the furnace is a continuous process, while the product is unloaded at hourly or other intervals. Two strikers are mounted at the tube ends, and each strikes the tube four times during a revolution. The striker consists of a weight hanging on a lever that rotates on a stationary shaft. The weight carries a roller, which rests on one of the four teeth welded to the rotating tube. As the tube rotates, the roller falls from a tooth and strikes the tube. This prevents the powder from sticking to the tube wall.

A dust chamber with baffle plates is provided under the loading hopper for catching the dust carried away by the gas, which passes through the furnace in a direction opposite to that of the charge. The dust chamber is cleaned intermittently by removing the dust by means of a manually operated screw conveyor.

The rotary furnace is either gas-fired or electrically heated, and the feeding is automatic and continuous. When yellow oxide is desired, a stream of filtered air is introduced inside the furnace. When the furnace is used for producing blue oxide, a low vacuum with the pressure difference between inside and outside of the furnace of 38.1 mm (1.5 in.) of water is generally maintained. Under this roughly sealed condition, APT is decomposed into blue oxide, ammonia, and water vapor at a temperature of 800–900°C (1472–1652°F). Generally, the furnace is divided into three heating zones, the temperature of which may be 850°C, 875°C, and 900°C, respectively. Since the process is continuous, the production rate is high, as compared to stationary furnaces (see Table 3.2). Furthermore, no loading boats are used, which makes the process more economical.
Table 3.2. Production Data for the Hydrogen Reduction Process of Tungsten Oxide to Tungsten

<table>
<thead>
<tr>
<th>Type powder</th>
<th>Fisher subsieve particle size (µm)</th>
<th>Statical furnace</th>
<th>Rotary furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature in three zones (°C)</td>
<td>Production rate per furnace (kg/day)</td>
<td>Boat load (g WO₃)</td>
</tr>
<tr>
<td>C3</td>
<td>0.8</td>
<td>600–700–800</td>
<td>360</td>
</tr>
<tr>
<td>C5</td>
<td>1.25</td>
<td>600–750–850</td>
<td>450</td>
</tr>
<tr>
<td>C6</td>
<td>1.80</td>
<td>650–800–880</td>
<td>590</td>
</tr>
<tr>
<td>C8</td>
<td>3.50</td>
<td>740–840–920</td>
<td>820</td>
</tr>
<tr>
<td>C10</td>
<td>4.50</td>
<td>800–900–920</td>
<td>1140</td>
</tr>
<tr>
<td>C20</td>
<td>6.50</td>
<td>900–950–990</td>
<td>1360</td>
</tr>
<tr>
<td>C40</td>
<td>8.50</td>
<td>900–990–990</td>
<td>1680</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang, Huntsville, Alabama.
* Using Teledyne Wah Chang Corporation powder designation; see Sec. 4.2.1.
* The furnace contains fourteen tubes, each 102 mm diameter x 9140 mm; boat size 43 x 61 x 470 mm (1.7 x 2.4 x 18.5 in.).
* The dimensions of rotary furnace tube: 254 mm diameter x 4880 mm (10 in. diameter x 192 in.).

Another type of rotary furnace consists of two concentric tubes with the annular space in between as the furnace chamber (Fig 3.5) (Melnikov et al., 1963). In this furnace chamber, T-shaped strips are attached to the internal and the external tubes in a staggered arrangement. This helps to stir the material, increase the heating surface of the powder, and facilitates a uniform distribution of the material over the chamber. The furnace is generally divided into three heating zones with an inclination of 0–7° and a rotation speed of 3–17 rpm. Each end of the tube carries a shaking mechanism consisting of a roller secured to the striker, which is connected to a spring. Each striker performs four impacts during a revolution of the tube.

APT is fed into the furnace from a hopper by means of a feeding screw from the loading chamber located at the end of the tubes and aligned with the furnace by spring suspensions. A similar arrangement is made at the unloading end, except that water jackets are used for the hopper and the unloading feed screw. The capacity and efficiency are comparable with that of the rotary furnace of the first type mentioned above.

![Fig. 3.5. Cross sectional view of an annular rotary furnace: (1) nichrome brackets, (2) external heater, (3) internal heater, (4) internal tube, (5) T-baffles, (6) external tube (Melnikov et al., 1963).](image-url)
3.3. HYDROGEN REDUCTION OF TUNGSTEN OXIDES

After APT is converted into yellow or blue oxide, it is then reduced by hydrogen to metallic tungsten. The furnaces used are the same as those described in the previous section. The reactions taking place during the reduction are expressed by the following equations (see Sec. 7.7.1 for details):

\[4\text{WO}_3 + \text{H}_2 = \text{W}_4\text{O}_{11} + \text{H}_2\text{O}\]  \hspace{1cm} (3.1)

\[\frac{1}{3}\text{W}_4\text{O}_{11} + \text{H}_2 = \frac{4}{3}\text{WO}_2 + \text{H}_2\text{O}\]  \hspace{1cm} (3.2)

\[\frac{1}{2}\text{WO}_2 + \text{H}_2 = \frac{1}{2}\text{W} + \text{H}_2\text{O}\]  \hspace{1cm} (3.3)

A plot of equilibrium constants \(K_p\) for these equations versus temperature is shown in Fig. 3.6 (Chaudron, 1920), where \(K_p = P_{\text{H}_2}\text{O}/P_{\text{H}_2}\). The equilibrium constants for these reactions are (van Liempt, 1922; Smithells, 1953)

\[\log K_{p_1} = -\frac{2468}{T} + 3.15\]  \hspace{1cm} (3.4)

\[\log K_{p_2} = -\frac{817}{T} + 0.88\]  \hspace{1cm} (3.5)

\[\log K_{p_3} = -\frac{1111}{T} + 0.845\]  \hspace{1cm} (3.6)

where \(T\) is the Kelvin temperature. It is apparent from Fig. 3.6 that an increase in temperature shifts the reactions in the direction of reduction. For the last stage of reduction, from \(\text{WO}_2\) to tungsten at 850°C, the value of \(K_{p_3}\) is about 45%, which means the reduction of the metal can occur with a significant concentration of \(\text{H}_2\text{O}\) vapor in the gas phase. However, in industrial practice, hydrogen with minimum moisture content is used because of a catalytic problem. According to Leavitt (1957), the reduction of \(\text{WO}_2\) by hydrogen is catalyzed by tungsten metal. The catalytic effect is due to the dissociation of hydrogen molecules absorbed at the surface of the metal. This catalytic effect of tungsten is strongly inhibited by the presence of water vapor, with a consequent deleterious effect on the kinetics of the reduction. Presumably the effect is due to adsorption of oxygen on the tungsten surface as a diffusion barrier.

In a stationary furnace, the major parameters that effect the reduction rate are the furnace temperature, the amount of oxide loaded in the boat, the rate of boat movement, the rate of hydrogen circulation, and the moisture content of the hydrogen. The higher temperature favoring reduction of the oxide has been explained previously.

The load of oxide in the boat effects the reduction rate essentially because of its
depth. It has been observed (Parsons, 1965) that the reduction of tungstic oxide above 625°C (1157°F) in a static powder bed is controlled by the diffusion rate of water vapor out of the bed. That the diffusion rate is inversely proportional to the depth of the bed is apparent from the following discussion.

For water vapor diffusion through the powder bed, the classic rate of diffusion equation can be applied (Parsons, 1965):

\[ U_a = \frac{DP}{RT\chi} \frac{P_{a1} - P_{a2}}{P_{bm}} \]  

(3.7)

where \( U_a \) is the diffusion rate of water vapor (moles/sec cm\(^2\)); \( D \) is the diffusivity (cm\(^2\)/sec); \( P \) is the pressure (atm); \( R \) is the gas constant (cm\(^3\) atm/deg moles); \( T \) is the absolute temperature (°K); \( \chi \) is the diffusion path length (cm); \( P_{a1} \) is the water vapor partial pressure at equilibrium for the reaction temperature and oxide system (atm); \( P_{a2} \) is the partial pressure of water vapor in the supplied hydrogen, obtained from dew point measurement (atm); \( P_{bm} \) is the log mean partial pressure of hydrogen (atm).

The following empirical equation is also used (Parsons 1965):

\[ t = (6.66 \times 10^{20} \rho T^{-5.7}(fh)^{1.6} \]  

(3.8)

where \( \rho \) is the bulk density of oxide (g/cm\(^3\)), \( f \) is the fraction of oxide reduced, \( t \) is the reduction time (sec), and \( h \) is the bed depth (cm). Figure 3.7 shows some of the reduction curves obtained at different temperatures.
Fig. 3.7. Oxygen loss during reduction at constant bed depth and specified temperature (Parsons, 1965).

The rate of boat movement is inversely proportional to the length of time for reduction; a high rate of boat movement, therefore, results in a low rate of reduction. The high rate of hydrogen circulation tends to shift the reactions of Eqs. (3.1)–(3.3) to the right and hence favors reduction. On the other hand, the high moisture content of hydrogen tends to shift these reactions in the opposite direction and thus impedes reduction.

Petrdlik (1949) investigated the effects on amount of reduction with a two-zone furnace, and the results are shown in Fig. 3.8. With a constant temperature of 480°C at zone 1 and 620°C at zone 2, a speed of boat movement of 30 mm/min, a boat length of 300 mm, and the flow rate of hydrogen held at 600 liters/hr, the correlation of reduction and the moisture content in hydrogen is shown in Fig. 3.9.

Theoretically, the volume of the powder decreases during reduction due to an increase of density from 7.2 g/cm³ for WO₃ and 12.1 g/cm³ for WO₂ to 19.3 g/cm³ for tungsten. The equilibrium between tungsten and water vapor at high temperatures is represented by

\[ W + 2H_2O = WO_2 + 2H_2 \]  (3.9)

The reaction tends to the right as the moisture content in the gas is increased or when the temperature is raised. The sublimation of the oxide begins when the partial pressure of the material in the gas phase equals the vapor pressure of the pure substance at that temperature. It is a function of total pressure, the rate of hydrogen flow, and the particle size of the powder. The vapor pressure of small particles is greater than that of large particles, and thus, at temperature of reduction, the vapor of the fine particles will deposit back on the surface of coarse particles. The result is the coarsening of the metal particles.
Fig. 3.8. Relation of the amount of reduction to (1) temperature, (2) load of oxide in boat, (3) rate of hydrogen circulation, and (4) speed of boat movement (Petrilik, 1949).

Fig. 3.9. The amount of reduction vs. moisture content in hydrogen for reduction of tungsten (Petrilik, 1949).
The temperature affects the moisture content in the reaction gas, which, in turn, affects the particle size of the reduced powder. When fine powder is desired, a high rate of hydrogen flow should be used to carry away water vapor generated during reduction. The moisture content of the fresh hydrogen should be as low as possible. The concentration of water vapor in the furnace also depends upon the depth of oxide loaded in the boat and the rate of the boat movement. To avoid coarsening of the metal powder, another practice in the industry is to adjust the temperature in different zones separately, so that the reduction takes place gradually from lower to higher temperatures.

An empirical equation for the relationship between the particle size of the reduced powder, the time and the temperature of reduction, the depth of the bed, and the original oxide particle size is (Parsons, 1965)

\[
\log F = 0.33 \log t - 0.25 \log h + 0.002 T + 0.028 D - 3.40
\]  \hspace{1cm} (3.10)

Substituting for \( t \) in Eq. (3.5), the following is obtained:

\[
\log F = 3.54 + 0.33 \log \rho - 1.9 \log T + 0.28 \log h + 0.002 T + 0.028 D
\]  \hspace{1cm} (3.11)

where \( F \) is the particle size of metal powder (FSSS) (\( \mu m \)); \( \rho \) is the bulk density of oxide (g/cm\(^3\)); \( t \) is the reduction time (sec); \( T \) is the reduction temperature (\(^\circ\)K); \( h \) is the bed depth (cm), and \( D \) is the particle size of the original oxide, varying from 1 to 12 \( \mu m \).

Starting with the same blue oxide, the detailed production data for different particle sizes of tungsten in stationary and rotary furnaces are shown in Table 3.2.

Hydrogen used for reduction should be at least of 99.5\% purity and is usually electrolytically produced from distilled water, with addition of NaOH or KOH as the electrolyte. The fresh gas is either introduced through the regenerating system or is purified and dried separately before being led to the furnace. For measuring the moisture content of the gas, a dew point instrument is used. The preferable dew point range is from \(-40\) to \(43.3^\circ\)C (\(-40\) to \(110^\circ\)F). Safety devices are employed to avoid air leaks in the system and prevent possible explosions. The hydrogen is usually held in a storage tank with an overpressure of \(114\) to \(140\) Torr, after contact with the deoxidizer of the regenerating system and before entering the reduction furnace.

When the rotary type of furnace is used, the raw material, as mentioned in the previous section, is fed from a hopper by means of a screw feed, through which the oxide acts as a rough seal. The material feeds through the reduction tube by gravity; the tube is inclined toward the discharge end and is slowly rotated. The metal powder produced falls into a sealed container.

A drawback to the rotary furnace process is that the powder product is less uniform in particle size than that of a stationary furnace. Another difficulty encountered is caking and sticking of the powder to the inner wall of the tube; this problem may be overcome to some extent by fitting a hammer device striking the outside wall of the tube, as mentioned in the previous section.

In some practices, \(\text{WO}_3\) is used as starting material and reduced in two stages: first to \(\text{WO}_2\) and then to metallic tungsten. In both stages, the same types of furnaces, either stationary or rotary, may be used. It is claimed that, due to the large difference between the bulk volume of \(\text{WO}_3\) and that of \(\text{WO}_2\), better utilization of the available volume in the furnace is achieved by a two-stage reduction process (Meerson, 1970).
The temperature ranges from 500 to 700°C for the first stage and from 700 to 850°C for the second stage.

3.4. CARBON REDUCTION OF TUNGSTEN OXIDES

Before hydrogen reduction was developed, tungsten powder was made by reducing the oxide with carbon. Its use nowadays is confined to purposes where high purity and particle size control are not essential. Tungsten reacts with carbon above 850°C, and the completely saturated compound is produced rapidly at 1400–1410°C (Brownlee et al., 1947). Two well-defined carbides exist — W₂C and WC — both of which are stable up to 2400°C. Tungsten powder produced by carbon reduction is therefore invariably contaminated with carbide. In addition, the carbon used for reduction generally contains some mineral matter, and some other impurities are incorporated in the resulting powder. The purity of carbon-reduced powder ranges from 98 to 99.6%, with common impurities of silicon, iron, carbon, sulfur, and phosphorus.

It has been reported that when tungstic oxide and carbon are mixed and reacted at 650–850°C, the product is a blue oxide (Davis, 1919). In the range 900–1050°C, the brown oxide is formed. For complete reduction to metal, a temperature higher than 1050°C is necessary.

Tungsten oxide used for carbon reduction is heated to 500°C in air to free any moisture content; otherwise the water vapor generated disrupts the charge. The theoretical amount of carbon is 15.5% of the weight of WO₃ if the carbon is oxidized to CO, and 7.7% if CO₂ is formed. In practice, it is found that 12–14% is sufficient for complete reduction without unduly raising the carbon content of the metal. The common form of carbon used for this purpose is lampblack, which is intimately mixed with tungstic oxide by ball milling. Owing to large differences in density, there is a tendency for the ingredients to segregate, but this may be overcome by adding up to 10–30% of the carbon required in the form of colophony. The mixture may be pressed into briquettes or rammed into the crucibles made of graphite or fireclay. The covers should be firmly luted on with clay to prevent air leaking from the outside. Alternatively, the charge may be covered with a mixture of pitch and lampblack, which forms a protective crust upon heating. The crucibles are heated in any form of furnace, but if fine powder is required, the temperature must be carefully controlled. It is usually heated to 1300–1400°C in 8 hr, held there for another 8 hr, and then slowly cooled for another 8 hr.

It was reported that an automatic graphite-tube furnace was built for carbon reduction in the Soviet Union (Mel’nikov et al., 1963). The furnace, with a graphite tube protected by a graphite screen, has at its ends graphite blocks that hold the tube in position. The blocks act as electric terminals and are pressed against flanges. Coolers are arranged at the furnace inlet and outlet. Provisions are made for the examination and replacement of damaged boats on the trough. The maximum temperature for the furnace is 1700°C; power consumption is 24 kW; the graphite tube is 170 mm O.D. × 140 mm I.D. × 1500 mm long; overall dimensions are 1.7 × 3 × 7.1 m; production output is 350–380 kg in 24 hr.

The product from the carbon reduction process is usually a friable grayish-
black material containing 92–98% tungsten, which may be further purified by crushing and tabling. The high density of tungsten makes this method effective for the removal of residual carbon and tungstic oxide.

During the process of manufacturing tungstic acid, calcium or sodium tungstate is produced as an intermediate product, which may be directly reduced by carbon. This is usually economically advantageous, but the purity of the product is sacrificed, because these salts are less pure than prepared oxides (Smithells, 1953). A general process is to mix 66% Na₂WO₄, 25% NH₄Cl, and 9% charcoal, and heating to 1000–1150°C for 15 hr in fireclay crucibles. The reaction takes place as follows:

\[ 2\text{NH}_4\text{Cl} + \text{Na}_2\text{WO}_4 + 3\text{C} = 2\ \text{NH}_3 + 2\text{NaCl} + \text{H}_2\text{O} + 3\text{CO} + \text{W} \]  

(3.12)

The sodium chloride forms a fused layer on the surface of the charge and prevents oxidation during cooling. The product mixture is then crushed and treated with hot water to remove the salt.

Calcium tungstate may be mixed with 12–13% charcoal, moistened with water and briquetted, and then fired at 1100–1200°C in crucibles and cooled in a reducing atmosphere. After tabling, the residue is treated with dilute hydrochloric acid to remove any undissolved lime (Head, 1917).

### 3.5. REDUCTION OF OXIDES WITH METALS

Among metals that are generally used for ore or oxide reduction, aluminum is most widely employed because of its high boiling point and relatively low cost (Table 3.1). Calcium comes into second place due to the high negative value of heat of formation of its oxide and therefore the ease with which the reaction tends to its completion. To a lesser extent, other elements, such as silicon and zinc, may also be used as reducing agents. These processes will be discussed in the following subsections.

#### 3.5.1. Aluminothermic Reduction

Aluminothermic reduction has been widely used for refractory metals, such as vanadium, niobium and tantalum (Belitskus, 1972). The charge generally consists of a finely divided oxide or ore, aluminum powder, and a flux (e.g., lime or fluorspar), and a thermal booster, such as sodium chlorate or potassium nitrate. The function of a flux is to lower the melting point of the slag, and, hence, to help the separation of the slag and the reduced metal. The thermal booster is to increase the energy output due to the exothermic reaction between the booster and aluminum.

The charge of reactants is intimately mixed, placed in a closed container lined with refractory materials, and fired. The reaction may be initiated by igniting a small amount of aluminum or magnesium and barium or sodium peroxide powders atop the charge. The slag protects the underlying metal from oxidation during cooling and is removed afterward by mechanical means.

For tungsten reduction, a recent work (Gupta and Jena, 1967) used yellow tungstic oxide as raw material and sulfur as flux in order to produce a low melting
point slag of $\text{Al}_2\text{O}_3 - 16.7\%$ $\text{Al}_2\text{S}_3$ with calcium and sulfur as the trigger mixture. By varying the amount of aluminum in the charge from 90 to 110% of the stoichiometric value, the metal yield increased from 61 to 82%. The reduced tungsten with high contents of aluminum, sulfur, and oxygen was purified by arc melting under argon atmosphere, and the purity reached a level higher than 99.8%.

A process was developed for producing tungsten from its ore (Svanstrom and Ramqvist, 1971) using aluminum and/or silicon as reductant. The operation is preferably carried out in an electric arc furnace with a graphite electrode and crucible at 1800–2200°C. Charging may be made continuously with intermittent tapping of slags. The amount of silicon is so selected that the reduced melt will have a composition between $\text{W}_5\text{Si}_3$ and $\text{WSi}_2$. The tungsten alloy obtained may be crushed and treated with hydrogen chloride gas at elevated temperatures (see Sec. 2.6). Porous pure tungsten with large specific surface thus obtained is particularly suitable as starting material for the preparation of tungsten carbonyl.

### 3.5.2. Reduction with Calcium

Calcium reduction of refractory metals is generally used only on a laboratory scale because of the high energy generated in the reduction and the high cost of calcium. The reduction is usually carried out in a closed steel container lined with refractory materials, with a mixture of tungstic oxide and calcium as the charge. It was reported that maximum yield was obtained with an excess of 35–50% of calcium in the charge; an addition of sulfur to the charge in the amount of 1–1½ moles per mole of tungstic oxide resulted in better metal consolidation and slag separation (Good et al., 1961). This method can also be used to produce tungsten alloys using mixed metal oxides in the charge. Tungsten or its alloys thus produced can be consolidated or purified by arc melting, which will be discussed in Chapter 4.

### 3.5.3. Reduction with Other Metals

A process using zinc as reductant for $\text{WO}_3$ is carried out at 750–850°C in hydrogen, nitrogen, coal gas, or other nonoxidizing atmosphere (Okage, 1959). It is claimed that the reaction is complete within a few minutes and the resulting mixture of tungsten and $\text{ZnO}$ is treated with hydrochloric or sulfuric acid to separate zinc from tungsten, and zinc can then be recovered as $\text{ZnCl}_2$ or $\text{ZnSO}_4$. Alternatively, the reduced tungsten and zinc oxide are heated to 910°C in a stream of hydrogen; the zinc thus reduced is recovered by evaporation, while the tungsten remains solid. This process claims fast operation, high yield with high purity, and fine particle size of tungsten powder obtained.

### 3.6. HYDROGEN REDUCTION OF TUNGSTEN HALIDES

Although tungsten production by hydrogen reduction of APT is an established process, it does have some limitations. For one thing, automation of the complete process is difficult due to many different steps involved from ore to metal. For another, the increasing demand for high purity, ultrafine particle sizes, and narrow
particle size distribution by some special applications can hardly be met.

To answer these requirements, chlorination of tungsten followed by hydrogen reduction processes have been developed. However, as mentioned in Sec. 2.5.3, the original process concept of converting tungsten ore to tungsten–silicon alloy and using the alloy as raw material has difficulties. Furthermore, fractional distillation to eliminate impurities such as molybdenum is also limited. Except for a commercial scale plant that has been established using scrap metal as starting material, the chlorination process as a major production practice is still pending further development.

The reduction apparatus used in this process is shown schematically in Fig. 3.10 (Tress et al., 1966). The equipment consists of three concentric tubes—the inner tube serves as an inlet for chloride carried in a stream of argon; the sheath gas, chlorine or argon, is introduced through the intermediate tube; and hydrogen is supplied through the outer tube.

The key to this process is reduction in the vapor phase in free space, whereby, through control of dilution, only a minimum number of atoms and molecules of the reacting species can form agglomerates and ultrafine, submicron particle size and narrow particle size distribution can be obtained. The sheath gas is introduced because it serves to position the chloride–hydrogen flame at some distance from the orifice. Thus, the formation of metal at the tip of the orifice and the plugging of the apparatus is prevented. The hydrogen used should be purified to remove traces of moisture, nitrogen, and hydrocarbons.
Table 3.3: Process Data for Reduction of Tungsten Hexachloride

<table>
<thead>
<tr>
<th>Run</th>
<th>WCl₆ feed rate (g/hr)</th>
<th>H₂ flow rate (liters/hr)</th>
<th>Reduction temperature (°C)</th>
<th>Preheat temperature (°C)</th>
<th>Tungsten particle diameter (µm)</th>
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</table>

* Tress et al., 1966.

By adjusting the flow rate of the argon carrier gas, the rate of tungsten hexachloride input can be controlled. The hydrogen flow is adjusted to produce a desired hydrogen-to-chloride ratio. The furnace usually is divided into two zones; the first is used to preheat the reactants and the second provides the proper reduction temperature. By varying the feed rate of WCl₆, the flow rate of hydrogen, and the temperature of two different zones, different particle sizes can be obtained. Table 3.3 shows some process data and the particle sizes of the reduced powder (Tress et al., 1966).

The metal powder may be collected by gravity settling with or without the use of an electrostatic precipitator; or the reaction gases may be filtered through a large column of steel wool and trapped powder shaken free of wool and separated from small steel fragments by magnetic means. Because of the extremely fine size of the powder particle, it is difficult to devise a collection system with high efficiency. However, it is reported that a mechanical trap in series with an electrostatic precipitator gives an efficiency greater than 97%.

For chemical analysis and properties of the ultrafine tungsten powder, the reader is referred to Table 4.3. Although its oxygen content is comparatively higher...
Fig. 3.11. Tungsten powder obtained by hydrogen reduction of \( \text{WCl}_6 \) in gas phase, scanning electron microscope (Ramqvist, 1971). (a) Type A, (b) type B.
than conventional APT powder, all substitutional impurities are rather low. The ultrafine tungsten powder is not pyrophoric even when the particle size is less than 0.05 \( \mu m \). This is probably attributable to the smooth shape and surface and the lack of fine tailings in the powder. Scanning electron microscope photographs of several types of ultrafine tungsten powder are shown in Fig. 3.11. Comparing these with Fig. 4.2, it is apparent that the conventional APT powder is rather angular in shape and wide in particle size distribution.

Spherical powder with large particle sizes (40–650 \( \mu m \)) obtained from WF\(_6\) by a vapor deposition process was developed by Allied Chemical Co. (1963). Although a special method, such as isostatic pressing, is required for compacting (see Sec. 4.4.2), the shrinkage of the powder is very uniform, and thus, good dimensional control can be obtained during sintering. Furthermore, the sheet material produced by this process has a higher recrystallization temperature, higher hardness, and lower bend transition temperature than commercial tungsten. A rocket nozzle insert made from this process demonstrated excellent resistance to cracking under thermal stress and to erosion (Hodge, 1964). Tungsten halides may also be reduced by metals, such as magnesium or sodium (Good and Block, 1961).

The vapor deposition process, which combines the reduction of tungsten hexachloride and deposition of the metal onto a solid substrate, will be discussed in Sec. 4.4.6.

### 3.7. MANUFACTURE OF FERROTUNGSTEN

Ferrotungsten manufacturing for the steel industry used to dominate the market for tungsten (Li and Wang, 1955); it was still the largest item, amounting to 1.42 million kg (3.13 million lb), among all different uses in 1972 (see Chapter 10). Ferrotungsten can be made by the aluminothermic, silicothermic, or crucible method, but the direct reduction of the tungsten ore in the electric furnace with carbon, followed by refining and decarburization is a common process now adopted in the industry. For high quality steel making, sintering of blends of tungsten and iron powders is used. This is a production method prevailing in United States.

#### 3.7.1. Reduction with Carbon in Crucibles

This was the method generally used in the 1900s. The tungsten concentrate is placed in a clay-lined crucible with a mixture of coke or charcoal, flux, and tool-steel scrap and heated in a gas-fired furnace. The reduction mechanism is similar to that to be described in Sec. 3.7.5. The drawback of this process is that the crucible life is comparatively short. For a 30\% tungsten alloy, a crucible will last about three heats, and for a 65–75\% product, it will last only one heat (Li and Wang, 1955).

#### 3.7.2. Aluminothermic Method

Since the reaction between aluminum and the tungsten charge is exothermic, the process is self-sustaining. Tungsten oxide or tungsten concentrate is reduced
with aluminum powder in a magnesia or other refractory crucible with a mixture of sodium or barium peroxide and aluminum powder for ignition. The gangue of the ore can be slagged off by using fluxes such as lime, soda ash, fluor spar, or borax, in conjunction with the alumina resulting from the reaction. To promote the reaction speed, the charges are preferably in powder or small granular form. The product formed is generally free from carbon but may contain aluminum and other metallic elements such as copper or manganese that may be present in the ore.

### 3.7.3. Silicothermic Method

In this process, scheelite is generally used, which is placed upon a molten bath of ferrosilicon, and the reactions take place as follows (Li and Wang, 1955):

- with $20\%$ ferrosilicon:
  \[ 3\text{CaWO}_4 + 4\text{Fe}_2\text{Si} = 2\text{Fe}_2\text{W} + \text{Fe}_3\text{W} + 3\text{CaSiO}_3 + \text{FeSiO}_3 \quad (3.13) \]

- with $33\%$ ferrosilicon:
  \[ 3\text{CaWO}_4 + 4\text{FeSi} = 3\text{FeW} + 3\text{CaSiO}_3 + \text{FeSiO}_3 \quad (3.14) \]

- with $50\%$ ferrosilicon:
  \[ 3\text{CaWO}_4 + 2\text{FeSi}_2 = \text{Fe}_3\text{W}_3 + 3\text{CaSiO}_3 + \text{FeSiO}_3 \quad (3.15) \]

### 3.7.4. Metallothermic Method

As developed by Yelyutin (1938), the process is in fact a combination of the alumi nothermic and silicothermic methods mentioned above. This may be a practical process to produce ferrotungsten without an outside heat supply. The charge usually consists of tungsten concentrate, ferrosilicon, aluminum, steel scrap, and some fluxes. All these materials should be in powder or granular form, weighed in proper proportion, and blended thoroughly to insure complete reaction. A mixture of barium peroxide and ferrosilicon may be used to start the ignition. As a rule, the entire process of reduction is completed within a few minutes. After the reduction and the solidification of the slag, the hearth is broken up for removal of the block of ferrotungsten.

The process as practiced at the I.G. Farben Works, Germany, is as follows (Li and Wang, 1955): The usual charge consists of 600 kg ground tin-free wolframite, 52.5 kg ferrosilicon (75\% Si), 45 kg aluminum powder, 22.5 kg ground aluminum scrap, 24 kg ground magnesium scrap, 30 kg iron chips, and 50 kg ground magnetite. A typical product is 395 kg ferrotungsten with 75\% tungsten, less than 0.1\% carbon, 0.23\% manganese, 0.9\% silicon, and 0.08\% aluminum. The slag usually contains 5\% tungsten, which can be reclaimed by treating in an electric furnace as mentioned in the following section.
3.7.5. Reduction in Electric Furnace

In this method, tungsten concentrate, especially ferberite, is generally used as the raw material, which is reduced with carbon in a knock-down electric furnace. Reduction with carbon takes place according to the reaction

\[ \text{FeWO}_4 + 4\text{C} = \text{FeW} + 4\text{CO} \]  

(3.16)

Theoretically, the reduction of 100 parts of alloy from 126 parts of ferberite requires 20 parts of carbon, but practically, about 25% excess of carbon is charged. Small amounts of lime and fluor spar are used to flux the silica. A typical operation consists of batches of charges added at intervals of half an hour. After three or four batches of charges, the furnace is tilted for pouring of slag. This cycle is repeated until a proper-sized, say, 685 kg (1500 lb), button has been formed. After cooling, the furnace is torn down for removal of the button. A typical composition of the button is 70% tungsten, 3% carbon, 0.05% phosphorous, and 0.01% sulfur. The slag produced usually contains 0.7–10% tungsten, although there is considerable mechanical loss, due principally to dusting, up to some 5%.

If the ferrotungsten button is not fit for use, it can be refined by the same process with a charge of 2 parts of the button material in chunk form and 1 part of the ore concentrate, with some fluor spar (less than one-tenth of the charged weight of ferrotungsten). The refining reduces the carbon content from 3 to 0.8% and the phosphorous content from 0.5 to 0.01%, without much reduction for sulfur, and increases the tungsten from 70 to 75%. The refining slag contains 5–20% tungsten and is remelted in a special run for reclamation.

According to the type of the slag, the process can be made basic or acidic. In general, the advantages of making acid electric furnace ferrotungsten are higher recoveries because of the lessened tendency of tungsten to go into a slag of high silica content as compared with its tendency to enter into a slag high in lime, and production of a ferrotungsten practically free of lime. The principal disadvantage is that the ore must be more nearly dead roasted to free sulfur and arsenic. Under basic conditions, the lime can be depended upon to slag off greater amounts of these elements than would thus be removed by siliceous slags.

The furnace used in the industry is approximately 1.52 m (60 in.) high and 1.37 m (54 in.) wide with a hearth area about 1.5 m² (16 ft²). Charges of 680 kg (1500 lb) are average, with the produced ferrotungsten button weighing about 6360 kg (14,000 lb). Yields are usually above 90%.

The smelting time for a charge of 680 kg ranges from 6 to 7 hr. Tungsten recovery in the ferroalloy is about 92%, with fume loss of 4%, slag loss 0.5%, and handling loss 4.5%. Power consumption is about 11,000 kW-hr mt⁻¹ and electrodes are about 300 kg mt⁻¹.

3.7.6. Powder Metallurgy Process

Almost all of the domestic ferrotungsten in the United States is currently produced by a powder metallurgy process. This process (Forbes et al., 1968) uses a mixture of 15–35% by weight of tungsten powder (10–100 μm), and 65–85% of iron.
Table 3.4. Comparison of Solution Time of Ferrotungsten, Temperature Drop of Steel Bath, and Tungsten Recovery for Various Addition Agents

<table>
<thead>
<tr>
<th>Addition agent</th>
<th>Solution time (sec)</th>
<th>Temperature drop (°C)</th>
<th>Recovery (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (79.18% W) ferrotungsten</td>
<td>38</td>
<td>14</td>
<td>94</td>
</tr>
<tr>
<td>30% Ferrotungsten</td>
<td>60</td>
<td>29</td>
<td>93</td>
</tr>
<tr>
<td>P.M. 80% W–20% Fe (^\text{a})</td>
<td>21</td>
<td>7</td>
<td>87</td>
</tr>
<tr>
<td>P.M. 50% W–50% Fe (^\text{a})</td>
<td>30</td>
<td>14</td>
<td>82</td>
</tr>
</tbody>
</table>

\(^{a}\) Forbes et al., 1968.
\(^{b}\) Ferrotungsten produced by powder metallurgy method.

powder (48–200 mesh). The indicated sizing and proportions of ingredient powders are important in order to provide a product having a suitable handling strength and density and the desired structure. After proper blending, the mixture can be pressed into pellets 9.5 mm (\(\frac{3}{8}\) in.) in diameter, using conventional steel dies with a pressure of 2.8 kg/mm\(^2\) (4 ksi). The pressed articles are further sintered during or after pressing at a temperature of 1400°C (2552°F) for 15 min to provide increased handling strength and satisfactory density, between 50 and 75% of the maximum theoretical density of the mixture.

Instead of mechanical pressing, the blended mixture may be compacted by passing through rolls to provide sheet products about 3.2 mm (\(\frac{1}{8}\) in.) thick and then sintered at 1350°C (2462°F) for about 4 hr. The sheet can be crushed to 6.4 mm \(\times\) down (\(\frac{1}{4}\) in. \(\times\) down) size and used as addition agents in steel bath.

The structure of the pressed and sintered article is porous and comprises a matrix of iron in which the tungsten particles, in substantially their original size and shape, are embedded. The advantages of this product are (1) upon addition to molten steel, the fine tungsten particles are released and dissolved rapidly, while the losses ordinarily encountered with tungsten powder additions are avoided; (2) the density of the pellets is such that they do not sink rapidly but descend through a molten steel bath at a convenient and effective rate. The solution time of the pressed and sintered articles compared with ferrotungsten otherwise produced, together with the temperature drop of the steel bath and percent recovery of tungsten, are shown in Table 3.4 (Forbes et al., 1968). It is apparent that the powder metallurgy articles give substantially improved solution times and lower temperature drop in the steel bath.

In order to improve tungsten recovery, tungsten powder containing 0.15–0.25% oxygen is blended with iron powder and carbon in the stoichiometric amount to form CO with the oxygen in the tungsten.
Consolidation of Tungsten

4.1. BACKGROUND

Since the melting point of tungsten, 3410°C (6170°F), is the highest among all metals, the general approach for consolidation of common metals, such as by melting, was beyond the capacity of the facilities used in the early years of the industry. Just and Hannaman (1904) developed a paste method in which a mixture of incompletely reduced tungsten powder was extruded with an organic binder. The extruded filament was then heated in a reducing atmosphere (hydrogen or hydrogen plus nitrogen) to drive out moisture and organic binders. The colloidal method, developed by Kuzel (1906), was similar to the above method, except the paste, without a binder, consisted of colloidal low-oxide of tungsten. When the extruded filament was heated in hydrogen, the colloidal substance was reduced to metal.

Another method of making tungsten filaments was amalgamation, a process in which fine tungsten powder mixed with cadmium or cadmium–bismuth amalgam was extruded into wire. During heating, the low-melting point metals sublimed and tungsten remained as a solid (Agte and Vacek, 1954). Coolidge (1910) laid the foundation for the modern powder metallurgy of tungsten. In his process, tungsten acid was reduced by hydrogen at 800°–950°C (1472°–1742°C) then pressed without a binder. The compacts in rod form were presintered at 1000°C (1832°F) and then sintered by a direct electrical heating at higher temperatures.

For the last two decades, the vacuum-arc melting process has been widely applied commercially to reactivate metals, e.g., titanium and zirconium; this technique has been applied to the consolidation of tungsten in some developmental projects. However, the arc-cast tungsten has large grains and is exceptionally brittle along grain boundaries. The commercial production of tungsten today is consequently still within the boundary of the powder metallurgy techniques.

4.2. POWDER METALLURGY

The quality of sintered products depends upon the properties of the raw material, tungsten powder. Characteristics of a powder include (1) purity, (2) particle
size, (3) particle shape, (4) porosity or density of an individual particle, (5) microstructure, (6) lattice defects, (7) specific surface, (8) particle size distribution, (9) apparent density of bulk powder, (10) tap density, (11) flowability, and (12) compressibility.

Since tungsten powder is essentially in the range of subsieve size, less than 37 μm, or even submicron size, far smaller than other metallic powders commercially used, porosity of an individual particle, microstructure, and lattice defects are generally neglected. Furthermore, since tungsten powder used in powder metallurgy is essentially all produced by the same process, namely, hydrogen reduction of tungsten oxide, the differences in above-mentioned factors 4, 5, and 6 are rather limited.

### 4.2.1. Selection of Powder

Although interstitial and some substitutional impurities at moderate levels can be reduced during sintering, nonvolatile substitutional impurities cannot be so reduced. Impurities remaining in the sintered products will greatly affect the ductility and fabricability due to grain-boundary brittleness or premature recrystallization. As the required configuration of tungsten mill products for space or nuclear industries in recent years are rather intricate, the fabrication of a more ductile material is desired. This means that the trend is to search for higher purity of

<table>
<thead>
<tr>
<th>Table 4.1. Typical Chemical Analysis of Hydrogen-Reduced Tungsten Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Nonvolatile matter</td>
</tr>
</tbody>
</table>

\(^a\) Grade I refers to a relatively low grade powder.

\(^b\) Grade II refers to a high commercial grade powder, such as C-5, C-6, C-8, C-10, or C-20.

\(^c\) Grade III refers to a very high purity grade.

\(^d\) The oxygen content varies with the average particle size.
tungsten powder. Table 4.1 shows the chemical analysis of three grades of tungsten powder that are produced by hydrogen reduction of oxides.

Various methods of particle size determination in the industry are (1) screen analysis, (2) microscopic analysis, (3) sedimentation methods using liquid as a medium (turbidimeter, Cenco Photometer, etc.), (4) elutriation methods using air as a medium, (5) permeability methods such as the Fisher subsieve sizer, and (6) electrolytic resistivity or electron modulation methods such as by Coulter counter.

Tungsten powder is available in a wide range of average particle sizes from 0.015 to 500 \( \mu m \), but the readily available commercial hydrogen-reduced powder is in the range from 1 to 10 \( \mu m \). The average particle sizes of these powders are shown in Table 4.2; the particle size distribution curves are shown in Fig. 4.1; and the scanning electron microscopic views of the powders are shown in Fig. 4.2.

Generally speaking, tungsten powder with an average particle size from 0.5 to 40 \( \mu m \) is used for producing tungsten carbide; a fine powder such as C-5 type is used

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Average particle size (FSSS) (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-3</td>
<td>0.70–0.8</td>
</tr>
<tr>
<td>C-5</td>
<td>1.05–1.20</td>
</tr>
<tr>
<td>C-6</td>
<td>1.80</td>
</tr>
<tr>
<td>C-8</td>
<td>2.60–3.50</td>
</tr>
<tr>
<td>C-10</td>
<td>4.50–5.50</td>
</tr>
<tr>
<td>C-20</td>
<td>6.50–7.02</td>
</tr>
<tr>
<td>C-40</td>
<td>8.00–8.50</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Huntsville, Alabama.

![Fig. 4.1. Typical particle distribution curves for various types of tungsten powder. (Courtesy of Teledyne Wah Chang Huntsville, Alabama.)](image)
Fig. 4.2. Scanning electron microscope view of hydrogen-reduced tungsten powder: (a) C-5 type powder,
(b) C-8 type powder, (c) C-10 type powder, (d) C-20 type powder.
for cutting tools, while coarser powder is used for mining drills. C-8 and C-10 type powder, with average particle sizes ranging from 3 to 5 μm are used for fabricating light-weight mill products, such as rod or wire. Within this range, the finer powder is used for indirect sintering, while the coarser powder is used for direct sintering. This is because higher temperatures can be achieved in direct sintering than in indirect sintering. Furthermore, the relatively higher porosity of the coarser powder is required to build up the electrical resistance for direct sintering. C-20 and coarser powders are used for fabricating heavy mill products, or for a metal-infiltrated tungsten matrix (see Sec. 8.5.2).

The relationship between the average particle size as determined by the Fisher subsieve sizer and the green density is shown in Fig. 4.3. The green density of powder compacts is low when the particle size is fine, and it increases with increasing average particle size of the powder. This is due to the fact that during compaction a greater friction between particles is encountered owing to greater surface area for fine than for coarse powders. The slope of increasing density is large in the neighborhood of 2–3 μm and tends to level out when the particle size approaches 8 μm. This can be explained by different size distributions for different particle-size powders. Generally, the particle size distribution for powder of coarse particle size (approaching 8 μm) is narrower than that for finer particle size (Poster, 1962). The decreased interparticle friction of the coarser powder is offset by the poorer particle packing brought about by a narrower particle size distribution.

Using grades C-5, C-8, C-10, C-20, and C-40 tungsten powder for blending, the effect of the resultant average particle size on the compressive green strength is shown in Fig. 4.4. The maximum strength reached at a grain size between 4 and 5 μm is probably attributed to the wide particle size distribution of C-10, the average particle size of which is 4–5.4 μm.

![Graph showing relationship between particle size and green density.](image)

Fig. 4.3. Relationship between particle size and green density. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
Fig. 4.4. Effect of particle size on the compressive strength of green compacts. (Courtesy of Teledyne Wah Chang Albany, Oregon.)

Good particle packing is usually achieved by blending powders with two entirely different average particle sizes, such as 1.5 and 25 µm, as shown in Fig. 4.5 (Poster, 1962). The maximum density obtained in this case is usually for a fine-to-coarse ratio of 1 : 3. The drawback of this blending is that, due to different rates of grain growth during sintering for different particle sizes of powder (see Sec. 4.2.3.1), a nonuniformity of grain structure will result. However, this effect can be greatly reduced by blending powders with two different average particle sizes not far apart, such as C-5 (average particle size 1–1.4 µm) and C-8 (average particle size 3–4 µm).

Fig. 4.5. Green density for various mixtures of 25- and 1.5-µm powders (Poster, 1962).
Although no maximum appears in the fraction-versus-green density curve in this blending technique (Fig. 4.6), a fairly high green density for handling and a high sintered density of the final product can be obtained. For example, by blending of 25% C-5 with 75% C-8, a green density of 63% and a sintered density of more than 94% of the theoretical can be attained.

Ultrafine powder (Table 4.3) has been developed (Ripley and Lamprey, 1963), and the compacts of this powder can be sintered to 94% theoretical density at 1550°C for 30 min. It has also been demonstrated that additions of up to 25% of ultrafine tungsten to a powder size ranging from 1 to 10 μm increase as-sintered density by as much as 9% (Barth and McIntire, 1965).

During compaction of powder, strength between particles depends to a large extent upon the atomic bonding and welding of contact surfaces. Ductile metal particles form these bonds under pressure, while for hard particles such as tungsten, the strengthening is limited to areas of contact formed by abrasion between particles. In this case, angular- or irregular-shaped particles, which cause interlocking, are preferred. Although commercial hydrogen-reduced powders are not angular in shape, some powders do show more irregularity than others. Figure
Table 4.3. Chemical Analysis and Properties of Ultrafine Tungsten Powder

<table>
<thead>
<tr>
<th>Impurity or property</th>
<th>Analysis</th>
<th>Impurity or property</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1 ppm</td>
<td>Si</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5 ppm</td>
<td>Sn</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>1 ppm</td>
<td>C</td>
<td>0.002–1.0%</td>
</tr>
<tr>
<td>Cu</td>
<td>1 ppm</td>
<td>Cl</td>
<td>0.01–0.3%</td>
</tr>
<tr>
<td>Fe</td>
<td>5 ppm</td>
<td>H</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Mg</td>
<td>1 ppm</td>
<td>N</td>
<td>10–440 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>1 ppm</td>
<td>O</td>
<td>0.07–4.3%</td>
</tr>
<tr>
<td>Mo</td>
<td>10 ppm</td>
<td>Apparent density</td>
<td>1.21 g/cm³</td>
</tr>
<tr>
<td>Na</td>
<td>1 ppm</td>
<td>Tap density</td>
<td>4.0 g/cm³</td>
</tr>
<tr>
<td>Ni</td>
<td>3 ppm</td>
<td>Surface area</td>
<td>10–20 m²/g</td>
</tr>
</tbody>
</table>

* Data from Rummel, 1971; Ripley and Lamprey, 1963; Tress *et al.*, 1966.

4.7 (Poster, 1962) shows the effect of particle shape on the green density and green strength at different compacting pressures. The gain of green strength with irregularly shaped particles is at the sacrifice of green density. This can easily be explained by the fact that the irregularly shaped particles having a greater surface area develop more friction during compaction.

Poster (1962) also used two lots of tungsten powder with similar average particle size and particle size distribution. One lot was made by hydrogen reduction, and the other was made by electrolysis of fused salts resulting in dendritic powder particles. When they were compacted under the same pressure, the same

Fig. 4.7. Green crushing strength and density as a function of compacting pressure for regular- (broken lines) and irregular-shaped (solid lines) powder particles (Poster, 1962).
green density, 11.5 g/cm$^3$, was obtained. However, the green strength for the hydrogen-reduced powder was 35 kg/cm$^2$ (500 psi), while that for the electrolytic powder was 176 kg/cm$^2$ (2500 psi).

The apparent density of a powder is defined as weight per unit volume measured according to a specified method of loading a receptacle. The industrial practice, using the Scott apparatus for measurement, is expressed in g/in.$^3$ (Scott density). This density increases generally with increasing Fisher subsieve average grain size, although it is also a function of the particle shape and size distribution.

The tap density is defined as the maximum density of a powder after continued tapping of the receptacle. It may be expressed in g/liter$^3$ (Haertlein and Sachse, 1966). The reciprocal, the tap volume, is generally determined by pouring 10 g of powder into a graduated cylinder and tapping the cylinder, either by hand or by automatic means, until a constant volume has been reached (Skaupy, 1943). This is usually expressed in milliliters per 10 g of powder. For example, the tap volume for Wah Chang C-5 powder is approximately 2.3 and that for C-8, C-10, and C-20 powders is approximately 1.7 ml/10 g.

Rate of flow is measured by a flowmeter, which is a cone-shaped container with a small orifice at the bottom (Haertlein and Sachse, 1966). The rate of flow determines the time required for filling the die and thus determines the production rate and economy of the process.

Compressibility is usually defined as the ratio of the green density to the apparent density of the powder. Compressibility is a function of the pressure and will increase with increasing pressure until a final value is reached. A knowledge of the compressibility of a powder is required for press and die designing.

Metal powders are generally shipped and stored under inert or reducing gas environment in sealed containers. After the seal is broken, storage under atmosphere for any length of time should be avoided, because this will result in pickup of oxygen and moisture from the air.

4.2.2. Compacting

There are essentially two types of presses commercially used for powder compacting: (1) mechanical presses with the ram being driven mechanically or hydraulically and (2) isostatic presses, which use a liquid compacting medium that is contained in a pressure vessel.

For a mechanical press, dies are usually made of high-speed tool steel. They should be properly heat treated so that the die material is harder than the plunger material. The inner die surface is generally polished by lapping in the direction of the stroke. The size of the compacts depends on the purpose for which the product is to be used, whether for making wire, sheet, or machine pieces. The general dimensions for mechanical press compacts are from 6.4 mm (¼ in.) square to 38.1 mm (1.50 in.) square in cross section and 203–610 mm (8–24 in.) in length. Tungsten powder is usually pressed without a lubricant, but either an ether solution of camphor or a benzene solution of paraffin has been used as a lubricant.

Hydrostatic or isostatic pressing is a compacting operation in which pressure is applied equally in all directions through a transmitting medium. The medium may
be water, oil, rubber, gas, gel, or powder. In general practice, a rubber or plastic container is filled with metal powder, and placed inside a perforated can, which is immersed in a fluid in a high-pressure vessel. The pressure is applied on the fluid by pumping until the final pressure is reached. The hydrostatic press is usually used for large compacts up to a size of 76 mm × 254 mm × 635 mm (3 in. × 10 in. × 25 in.).

Compact density (green density) depends upon the applied pressure, particle size, size distribution of the powder, and size of the compact. The green density of compact bars less than 38 mm (1.5 in.) in diameter obtained from powder particle sizes ranging from 1 to 10 μm are usually 65% to 75% of the theoretical. For large compacts such as rods with diameters greater than 38 mm (1.5 in.), even under hydrostatic pressure, the green density at the center of the rod is not as high as that at the periphery. This results in a lower overall density than for small compacts. For commercially produced large compacts using coarse powder—C-20 (average grain size 5.4–9.0 μm)—as starting material, the green density is essentially below 65% of the theoretical. The applied pressure versus green density curves for various types of powder are shown in Fig. 4.8.

As a rough guide, the relation between as-pressed density and applied pressure is expressed by the equation (Heckel, 1962)

\[
P = \frac{\ln[1/(1-D)] - A}{K}
\]

(4.1)

where \(D\) is the percentage of theoretical density, \(P\) is the applied pressure (kg/mm² or psi), \(K\) is a proportionality constant related to yield strength of the metal (1.08
\( \times 10^{-2} \text{ mm}^2/\text{kg} \) or \( 7.6 \times 10^6 \text{ psi}^{-1} \) for tungsten), and \( A \) is a constant (0.62 for tungsten). The Heckel equation curve is also shown in Fig. 4.8.

The advantages of a mechanical over a hydrostatic press are ease of operation and better dimensional control, but it usually causes the product to be less uniform in density due to friction between die walls, especially in the case of large compacts. Recent development in hydrostatic pressing involves the use of a heat curing type of gel as the pressure transmitting medium. The gel behaves as a liquid under high pressure but has sufficient strength as a solid at normal pressures to hold its shape. Intricate tungsten shapes such as nozzle inserts can be thus produced with only final finish machining (Highriter et al., 1961).

A triaxial compacting technique has been developed by Koerner (1971), who claimed that this technique resulted in significantly higher green densities than either mechanical (uniaxial) or isostatic compaction at all pressure levels. Figure 4.9 presents the schematic of the triaxial compaction unit, which is similar to a dry bag isostatic chamber, except that a piston is required for load application to the top of the specimen. The process begins with isostatic compaction of the loose powder,
followed by the application of shear via a load piston. The major principal stress \( \sigma_1 \) is vertical, and the remaining principal stresses \( \sigma_2, \sigma_3 \) are equal to each other and horizontal. The particles being compacted are reoriented continually due to controlled amounts of shear stress applied. The compacted cavity measures 25.4 mm in diameter × 38.1 mm in height (1-in. diameter × 1\( \frac{1}{2} \)-in. height).

4.2.3. Sintering

After the powder has been compacted, it is sintered at high temperature in order to increase the density to a minimum of 85% of the theoretical in the final product or to be further fabricated into desired shape. It is generally agreed that the sintering mechanism is that of diffusion (Kothari, 1963). In the first stage of the sintering process, bonding between particles takes place, and the strength and hardness increase appreciably. The newly formed bonding areas are termed "necks." In the second stage, these necks grow in size, which requires the transport of material within the sintered mass but does not imply any significant decrease in the amount of porosity, that is, no appreciable shrinkage of material. During the third stage, the necks continue to grow and close off interconnected pore channels, which leads to isolated porosity. When material is transported to the neck regions from the pore surface, the pores themselves become more rounded. The next stage is pore shrinkage by diffusion of vacancies outward, which occurs only with sufficient time at high temperatures. In the last stage of sintering, the small isolated pores shrink and eliminate themselves and, thus, contribute to the growth of large ones (Hirschborn, 1969).

4.2.3.1. Theory of Sintering

At elevated temperatures, a green compact is basically an unstable material in which the large surface area constitutes a driving force for densification during sintering. The reduction in free energy is associated with the decrease in internal surface area in the sintered mass. Neck growth and pore rounding reduce the surface area while maintaining the amount of porosity at a constant level. During pore shrinkage, the surface area of the spherical pores is further reduced. By increasing the average size of dispersed pores while maintaining the total volume constant, the ratio of surface area to volume is also decreased. Pore coarsening during the last stage of sintering is the consequence of the last-mentioned effect.

The pressure applied during compacting deforms the metal plastically to some extent. As a consequence, the metal compacts also experience recovery, recrystallization, and grain growth during sintering. Minor subgrain structures are changed during recovery, and internal strain is relieved. Recrystallization refers to the evolution of new strain-free grains that are low in dislocation density. The driving force for both recovery and recrystallization is associated with free energy reduction essentially resulting from dislocation rearrangement and removal. Grain boundaries represent a positive contribution to the free energy of the material. Removal of grain boundaries or reducing the area of grain boundaries results in a lower energy state and causes grain growth. The motion of grain boundaries
necessary for grain growth may be impeded by the presence of second phases and pores within the solid. The grain boundary moving away from the second phase or pores signifies an increase in the length of the boundary and, hence, an increase in free energy. Once grain boundaries become associated with the second phase or pores, further motion is thereby restricted. The effect of second phases or pores on grain growth is given by the Zener relationship, assuming spherical phases or pores (Hirschborn, 1969):

\[ R = \frac{4r}{3f} \]  

where \( R \) is the radius of curvature of the average grain of the matrix metal, \( r \) is the radius of the second phase, and \( f \) is the volume fraction of the second phase.

In the industry, the oxides of thorium, calcium, iron, etc., are used as additives to tungsten for the purpose of restraining grain growth and increasing the strength of tungsten at elevated temperatures. These oxides are not appreciably volatilized, nor are they soluble in tungsten during sintering. Thoria may be introduced in a finely divided state by adding a solution of thorium nitrate or hydroxide to the tungsten oxide before it is reduced to metal. A rod containing 0.75% of thorium has a grain size of 5000 to 10,000 grains per square millimeter, as compared with 1000 to 1500 grains per square millimeter for a similar rod of pure tungsten. For some applications, thorium is added also for thermionic reasons. This will be discussed later in Sec. 5.6.

The densification rate in sintering tungsten powder can be significantly increased by small additions (1–4%), of group VIII transition elements as activators (Hayden and Brophy, 1963). Among them, palladium and nickel appear to have the greatest effect. With 0.25% palladium, densities of 93.5 and 99.5% of the theoretical are obtained after sintering 30 min and 16 hr, respectively, at 1100°C (2012°F) in hydrogen. Tungsten powder at this temperature and without such added elements can only be presintered. Metallic activation, however, results in a brittle product, although some improvement is possible by a postsintering treatment (Toth, 1965).

The mechanism for this increased densification rate has been proposed (Brophy et al., 1961). The activating element appears on the tungsten particle surface forming a “carrier phase” layer. Tungsten dissolves preferentially into the layer at points of particle contacts and diffuses outward in the interface between the carrier phase layer and the particle itself. The result is a decrease in distance between adjacent particle centers and overall shrinkage of the powder compact. This activation process may prove to be associated with the fact that group VIII transition elements dissolve 10–20% tungsten but are soluble in tungsten only to a very limited extent at the sintering temperature employed.

In practice, tungsten is generally sintered under a reducing gaseous atmosphere, such as hydrogen, because this will eliminate oxygen content of the powder to a large extent. Otherwise, the oxide film coated at the surface of tungsten powder particles impedes the sintering and bonding process and the desired density of the products will never be achieved. The sintering methods, according to the furnace construction, are classified into direct sintering and indirect sintering. These will be discussed in the following sections.
4.2.3.2. Direct Sintering

Small bars less than 38 mm (1.5 in.) square in cross section and 610 mm (24 in.) long are generally sintered by this process. In order to obtain any appreciable strength to withstand handling and clipping during sintering, the compact must first be presintered at 1000–1150°C (1832–2102°F) for $\frac{1}{2}$ hr or so. This is usually carried out by placing the green compacts in molybdenum trays and sintering under hydrogen atmosphere. During presintering, the oxide film surrounding the particles is reduced to metal and a better cohesive strength between particles results.

The final sintering is ordinarily carried out in water-cooled bell jars (Fig. 4.10). Tungsten billets are held between molybdenum or tungsten clips by way of which an electric current is passed through the billet. Since the billets shrink appreciably during sintering, a spring attachment to the clips is necessary so that at least one end is free to move. Mercury contacts are no longer in use owing to the environmental hazards. A window is placed in the furnace wall through which an optical pyrometer can be aimed at the surface of the sintered bar for measurement of temperature. In practice, however, the temperature is also controlled by the current input at a constant voltage. This is generally expressed as a percentage of the amperage at which the sintered bars start to melt. The power required depends on the length and cross section of the sintered bar.

It is important to regulate the current carefully and to avoid a steep rise in temperature. The current must not be too high at the beginning of the run, because there is a danger of melting at grain boundaries or at loosely compacted locations where resistance is higher due to high impurities or point contacts between particles. The current may be raised gradually until a final temperature of 2700–3100°C (4892–5612°F) is reached. The duration at the maximum temperature ranges from 30 to 60 min. Density after the final sintering reaches 88.5 to 96.0% of the theoretical.

Fig. 4.10. Direct sintering furnace. (Courtesy of Teledyne Wah Chang Huntsville, Alabama.)
For example, for small sizes of rod or wire, the powder used is generally of the C-8 or C-10 type, which is mechanically compacted into a bar of the dimensions \(19 \times 19 \times 838\) mm (0.75 \(\times\) 0.75 \(\times\) 33 in.). After loading into the sintering furnace, the temperature is gradually raised by controlling the input current to a maximum temperature of 2800\(^\circ\)C (5072\(^\circ\)F) within 20 to 40 min. The holding time at this temperature is typically 45 min. A typical microstructure of sintered bar of the mentioned size is shown in Fig. 4.11.

### 4.2.3.3. Indirect Sintering

For large billets of tungsten beyond the capacity of the furnace for direct sintering or those used essentially for further fabrication, the indirect sintering process is employed. For this purpose, an indirect resistance or an induction furnace is used.

#### A. Indirect Resistance Furnace

A schematic view of the indirect resistance furnace is shown in Fig. 4.12. The bell-shaped furnace top and the bottom plate are made of water-jacketed copper. An opening on the bottom plate is connected to the vacuum system, which usually consist of a diffusion pump and a mechanical pump. Above the plate is a tungsten or molybdenum pedestal on which tungsten compacts are placed. The heating elements are built of molybdenum strips and supported by molybdenum or tungsten frames. These are surrounded by molybdenum heat shields.

The furnace is first evacuated to a vacuum of \(10^{-5}\) Torr and then backfilled with hydrogen. During the process, a steady flow of hydrogen is sustained so that a flame at the hydrogen outlet pipe can be maintained. The power supply is generally an ac source with a capacity of 40 V and 10,000 A.
Tungsten billets used for indirect sintering are generally compacted by hydrostatic pressing rather than by mechanical means to the dimensions of 19–50.8 mm (0.75–2.0 in.) thick × 203–305 mm (8–12 in.) wide × 254–508 mm (10–20 in.) long. When smooth surfaces or precision dimensions are required for the as-sintered products, they can be machined after compacting or presintering.

If tungsten compacts are placed directly on the pedestal, uneven shrinkage may occur between the compact and the pedestal during sintering that may result in severe cracking or local low-density areas at the bottom of the billet. To overcome this effect, either a granular refractory oxide layer, such as $\text{Al}_2\text{O}_3$, or green tungsten shims about 12.7 mm (0.5 in.) thick are placed beneath the compact. The oxides have comparatively low softening or melting points, and this limits their use to low temperatures for presintering operations only. For higher-temperature sintering, green tungsten shims should be employed.

During indirect sintering, the billet tends to densify more rapidly at the surface than in the interior. Early densification of the billet due to a rapid rate of heating from room temperature to about 800°C (1472°F) decreases the permeability of the surface and thus prevents the escape of oxygen, water vapor and other gaseous materials. A slow rate of heating in the early stage of sintering is therefore essential to the deoxidation of the material. At higher temperatures, say, from 800°C (1472°F) up to the final sintering temperature, the heating rate also should be controlled. If the

---

Fig. 4.12. Schematic view of an indirect resistance sintering furnace: (1) furnace assembly with dome, (2) bottom heat shield, (3) top heat shield, (4) heat shields, (5) heating elements, (6) element support posts, (7) element clamping posts, (8) heat shields, (9) pyrometer window, (10) cooling inlet, (11) cooling outlet. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
Table 4.4. Sintering Schedules for Indirect Resistance Sintering

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–800°C–3</td>
<td>4–800°C–6</td>
<td>4–800°C–6</td>
<td>1$\frac{1}{2}$–450°C–3$\frac{1}{2}$</td>
</tr>
<tr>
<td>1–1500°C–1</td>
<td>$\frac{1}{2}$–900°C–1</td>
<td>$\frac{1}{2}$–900°C–1</td>
<td>1$\frac{1}{4}$–600°C–2</td>
</tr>
<tr>
<td>1–2400°C–10</td>
<td>1–1500°C–1</td>
<td>$\frac{1}{2}$–1200°C–1</td>
<td>1–700°C–3</td>
</tr>
<tr>
<td></td>
<td>2$\frac{1}{2}$–2300°C–12</td>
<td>$\frac{1}{2}$–1500°C–$\frac{1}{2}$</td>
<td>1–800°C–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{1}{2}$–1800°C–$\frac{1}{2}$</td>
<td>1–1100°C–2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1$\frac{1}{2}$–2300°C–10</td>
<td>1$\frac{1}{2}$–1500°C–1</td>
</tr>
</tbody>
</table>

II. Presintering schedule — billet size: diameter greater than 127 mm (5 in)$^a$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4–800°C–6</td>
<td>2–1250°C–$\frac{1}{2}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Courtesy of Teledyne Wah Chang Albany, Oregon.

$^b$ At the end of every schedule, the power is turned off and the furnace is cooled to room temperature under hydrogen atmosphere. The figure at the left side of the temperature indicates time in hours for heating from temperature of the previous step or room temperature to the indicated temperature. The figure at the right side of the temperature indicates time in hours for holding at the temperature.

$^c$ Presintering is not required for billets less than 127 mm in diameter.

heating rate in the later stage is too fast, the temperature gradient built up within the billet will cause thermal stresses and will result in cracking of the material. Furthermore, holding at intermediate temperatures will allow some common metallic impurities to evaporate for purification. Finally, a long period of sintering at the final temperature is required for densification of the billet.

In practice, the heating rate depends upon the size of the particular billet to be sintered. For better control, a stepwise sintering schedule is generally applied, but it can be further adjusted for specific requirements. For example, a slower rate of heating combined with lower final sintering temperature will serve the same purpose as a schedule of a relatively higher rate of heating combined with higher final sintering temperature. Schedules for a billet size of 127 mm (5 in.) in diameter and 203 mm (8 in.) in length aiming at a sintered density of about 93.5% of the theoretical are shown in Table 4.4. For billets larger than 127 mm (5 in.) in diameter, a presintering step is required in addition to lowering the heating rate during sintering. A presintering schedule is also shown in Table 4.4.

The double sintering process is time-consuming and expensive, but during presintering, the billet may shrink by about 8%, and its strength is increased remarkably. With this technique, the handling and machining characteristics of the billet before sintering are improved, and the cracking tendency of the material during sintering is decreased.

The final temperature for indirect sintering, depending upon the particle size of the powder and the compacting pressure, is generally lower than that for direct
sintering. This is because the sintered billet is usually larger and the efficiency of heating is lower in the case of indirect sintering. The billets must be densified to a minimum of 85% of theoretical density if further fabrication by forging or rolling is required (Schwertz et al., 1967).

For tungsten powder with fine average particle sizes, there is more surface area of contact and less porosity between particles than for the powder with coarse particle sizes. This promotes bonding between particles during the early stages of sintering and grain growth in the later stages, and the result is a denser product with larger final grains. The effect of average particle size on the sintered density at different sintering temperatures is shown in Fig. 4.13. The effect of temperature on the sintered density for powders of different average particle sizes is shown in Fig. 4.14, and the average powder particle size versus the sintered grain size is plotted in Fig. 4.15. It should be pointed out that the denser the sintered product, the larger the grain size. Table 4.2 and the above figures indicate that the sintered densities and grain sizes can be predicted from given types of tungsten powder to be used.

An interesting relationship between sintered density and hardness is shown in Fig. 4.16. For powder of medium average particle sizes, ranging from 3 to 5 μm, hardness increases with increasing density up to approximately 93% of the theoretical. This is the maximum density that can be obtained with the powder using the sintering schedules mentioned above (Table 4.4). By using fine powder of average particle size ranging from 1 to 1.2 μm, tungsten can be sintered to 91.8% of theoretical density at 1600°C (2912°F) for 10 hr. When the sintering temperature continues to increase, the density also increases, and so does the hardness. However, when the sintering temperature is increased beyond 1700°C (3092°F) the sintered density increases but the hardness starts to decrease. The reason is that when sintered at 1600°C, the grain size is 40,000 grains/mm² (ASTM No. 12½); but when

![Diagram showing the effect of average particle size and sintering temperature on sintered density.](image)

Fig. 4.13. Effect of average particle size and sintering temperature on sintered density. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
Fig. 4.14. Effect of temperature on sintered density of various types of tungsten powder; values on curves indicate average particle size (FSSS); sintering time 10 hr. (Courtesy of Teledyne Wah Chang Albany, Oregon.)

Fig. 4.15. Effect of average particle size on sintered grain size. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
sintered at 1700°C, the grain size is about 20,000 grains/mm² (ASTM No. 11½). Although the hardness should be affected by the difference of grain size, it is essentially governed by the density of the material in this case. When this powder compact is sintered at 1800°C, the grain size becomes 4000 grains/mm² (ASTM No. 9); at 2200°C, 2000 grains/mm² (ASTM No. 8). These grains are very large as compared to previous ones. The hardness value now is more strongly affected by the grain size than by the density of the material and therefore decreases with increasing value of density.

The relationship of the desired billet size to the green and sintered density is shown in Fig. 4.17. Here, a finer powder, C-5, is blended with a coarser powder, C-8. When the desired diameter of the rod is less than 32 mm (1.25 in.), the green density decreases and the sintered density increases with decreasing particle size of the powder. However, when the rod diameter is greater than 64 mm (2.5 in.), both green and sintered density drops for mixtures containing more than 75% of the fine C-5 powder. This is because that, even under a pressure of 24.6 kg/mm² (35 ksi) in a hydrostatic press, the center of the rod will not reach the desired density due to high surface friction between the powder particles during pressing. Therefore, the overall green and sintered density of large-diameter rods is lower than that of small-diameter ones.

B. Induction Furnace

Alternatively, large tungsten compacts can be sintered in an induction furnace. This type of furnace consists of a graphite susceptor, an insulating brick wall, and an induction coil. Helium is flushed through during sintering, and a positive pressure is
Fig. 4.17. Green (bottom) and sintered (top) densities of tungsten rods with different diameters made from mixtures of C-5 and C-8 powders; $\phi =$ diameter, S.C. = single compacting, D.C. = double compacting. (Courtesy of Teledyne Wah Chang Albany, Oregon.)

maintained by passing the exit gas through a bubbler with a few centimeters of water as a hydraulic head. The tungsten compact is placed inside a graphite crucible, which, in turn, is placed inside the susceptor. Between the tungsten compact and the crucible, loose tungsten powder is packed and used as a getter to protect the compact from carbon contamination. The sketch of the furnace and the protective packing is shown in Fig. 4.18 (Wilkinson, 1970).

To further protect the compacts from carbon contamination, some new designs eliminate the carbon susceptor. The induced current is built up and heat is generated on the tungsten compact itself. The water-cooled induction coil is built into castable ceramic, which is encased by insulating bricks. A hydraulic elevator is located below the opening at the bottom of the furnace and is used to load and hold the compacts in position. This is shown schematically in Fig. 4.19. Typically, the compact is rectangular in shape, about 35 x 250 x 700 mm (1.38 x 9.8 x 27.6 in.). Hydrogen atmosphere is generally used for this type of furnace during sintering.

The final sintering temperature ranges from 2100 to 2700°C (3812 to 4892°F), depending upon the particle size of the powder and the pressure used for

Fig. 4.19. Induction furnace without susceptor.
compacting. During heating, the temperature is raised gradually at a rate of about 400°C (720°F) per hour and is held at the maximum temperature for 6–10 hr.

4.3. ARC MELTING

Since arc melting is generally performed under vacuum or in an inert atmosphere at higher temperatures than for sintering, it is expected that further purification can be achieved and better properties will result. Although arc melting is not commercially employed for tungsten consolidation, it has been adopted in a few scaled-up development projects and is in production for special applications.

4.3.1. Conventional Arc Melting

Figure 4.20 shows a schematic view of an arc melting furnace. It consists of the following major parts:

1. The crucible: The crucible with an inside diameter of 51–305 mm (2–12 in.) is generally made of unalloyed copper or Empcoloy 97 (Cu–1% Cr), the latter is of higher strength than the former. The top flange is clamped to the furnace body and sealed by an O-ring. The crucible is surrounded by a water jacket. In most designs, water enters at the bottom of the crucible, sweeps up the side walls and out at the top. A low-amperage induction coil is often wound around the water jacket. The magnetic field from this coil interacts with the radial component of the melting current to cause the molten pool to rotate in the horizontal plane. This stirring action suppresses the formation of coarse, columnar grains in ingots, particularly if the coil current direction is periodically reversed.

2. The furnace body: The body is rigidly clamped to the flange of the crucible during melting. A seal is built into the body surrounding the electrode ram to allow the free sliding of the ram. Usually an O-ring seal is used and the surfaces of the ram outside the furnace chamber may be coated with vacuum grease. Sight ports are built into the body with optical devices so that the operator can view the arc and pool on a projected screen during melting.

3. The electrode and electrode ram: The electrode is made of sintered tungsten bars assembled by TIG welding for diameters smaller than 63 mm (2.5 in.) or by threading for larger diameters (Schwartz et al., 1967). Machining of tungsten threads should be performed at 430°C (806°F) to avoid brittle fracture problems. The electrode is threaded to the bottom end of the electrode ram, which is made of copper and chromium plated to give it a smooth and scratch-resistant surface. Because the electrode ram operates at a high current density, and because its lower end is exposed to heat from melting, a water cooling system is required. Water is led from the top into a metal tube at the center of the hollow ram; the tube extends to the bottom so that the water impinges on the lower end of the ram interior and circulates upward through the annular space outside the tube. The distance between the molten pool and the electrode tip is automatically controlled by electronic or electromechanical devices during melting. These control systems are based on the fact that the voltage varies slightly with the length of the arc, so that the voltage...
Fig. 4.20. Arc-melting furnace with optimum coaxial arrangement (Schlatter, 1974).

signal provides a means of adjusting the spacing between the electrode and the molten pool. In addition, an optical system is installed for visual indications in order to prevent crucible burn-throughs. If the arc strikes the crucible wall as the result of misalignment or for other reasons, a green emission will be noticed in the arc through the optical system.

4. The vacuum system: This system usually consists of a multiple-stage pumping system with Roots blowers backed up by rotary oil-sealed mechanical
pumps. The operating vacuum is generally of the order of a few millitorr. If a better vacuum is required, a diffusion pump may be added in parallel. To achieve a high-throughput pumping system, all conduits should be as short as possible with a minimum number of elbows, and the pipe diameters should be made to generous specifications.

5. Power supply: The power source is generally d.c. with a voltage of 25–40 V and a current capacity of up to 40,000 A. In the case of d.c. straight polarity, i.e., electrode negative and ingot positive, 90–95% of the power is dissipated at the molten pool. In the case of reverse polarity, the power will be essentially consumed at the electrode and little purifying will be achieved during melting. In a rare case, when an a.c. source is applied, the power is split equally between the electrode tip and the molten pool.

Before loading, a few kilograms of tungsten scrap (chips) are placed at the bottom of the crucible so that when the melting starts with low power input, the initial molten pool will be formed from the scrap. After the startup period, power is increased rapidly in order to maintain a full pool. If a solid collar is observed surrounding the pool, the power applied is too low, and a spongy sidewall will be obtained. During the last few minutes of melting, it is desirable to lower the power slowly, allowing the size of the pool to decrease until it freezes off. This minimizes the size of the shrink pipe formed during solidification at the top of the ingot.

The ratio of the diameters of electrode to crucible ranges from 40 to 60% (Schwertz et al., 1967), or the annular clearance between the electrode and the crucible wall is at least 25 mm (1 in.) (Riesen et al., 1964).

The melting rate \( R \) in grams per second, for tungsten and tungsten-base alloys (in composition from 92% and up) is expressed in the following empirical equation (Ratliff and Ogden, 1963):

\[
R = \frac{4.88(P - 100)}{d(0.8D_e^2 + 0.2D_i^2)}
\]  

(4.3)

where \( P \) is power (kW), \( d \) is the electrode density (fraction of theoretical), \( D_e \) is the diameter of electrode (cm), and \( D_i \) the diameter of ingot (cm). The formula can alternatively be used to calculate the power required to cast a tungsten ingot of a given diameter for a given electrode. A proper melting rate is not only of economic importance, but it helps control the degree of purification.

Arc-melted tungsten ingots are characterized by a coarse, columnar grain structure, the grains appear to grow in the direction normal to the liquid–solid interface during solidification. A typical cross section of a small-diameter ingot is shown in Fig. 4.21.

Crack formation is occasionally encountered during the arc melting of tungsten ingots whose diameters are larger than 127 mm (5 in.). Because the different parts of the ingot solidify at different times and cool at different rates, thermal shrinkage produces a pattern of residual stress that induces cracking. Most cracks appear to originate near the top center of the ingot; they are usually intergranular in nature and may propagate throughout the ingot. Embrittlement due to impurities at grain
boundaries seems to be the main cause of cracking. The tendency for impurities to concentrate at the top center of the ingot is due to the fact that this part of the ingot is the last to solidify and, therefore, by differential solidification, contains a higher concentration of impurities. The measures to prevent cracking are:

1. Remove the ingot from the crucible while hot and transfer it to a furnace heated under hydrogen atmosphere for stress relieving.
2. Stop the water flow in the crucible water jacket when power is cut off in order to allow the ingot to cool slowly and thus reduce the thermal stress.
3. Melt the ingot on a deep pad of tungsten machine turnings. Unlike the normally employed base material, this pad does not completely melt and allows the ingot to cool slowly.
4. “Cap” the ingot with another metal more ductile than tungsten, e.g., molybdenum. This is done by making the top end of the electrode of molybdenum and continuing to melt after the tungsten is gone. The upper portion of the ingot is usually contaminated with the capping material and must be removed by machining.
5. Add other elements as scavengers to reduce interstitial impurities or as grain refiners to control grain size. As a scavenger, a small amount of titanium or carbon is added in order to combine with oxygen and then disperse in the matrix. As a grain refiner, boron has been used. Thoria, used as a grain refiner in powder metallurgy, cannot be utilized in arc melting, because the alloying ingredients tend to agglomerate instead of dispersing.

The impurities in arc-melted material are generally lower than in powder metallurgy material. This is especially true for elements such as carbon, oxygen, hydrogen, and some common metallic impurities (see Table 4.5). For the mechanical properties of arc-cast tungsten compared with that of powder metallurgy and other materials, the reader is referred to Sec. 6.3.
Table 4.5. Chemical Analysis of Electron-Beam- and Arc-Melted Tungsten^\textsuperscript{a}

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Arc-melted tungsten (average of five ingots)</th>
<th>Electron-beam-melted tungsten (after two remelts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>$5 \pm 2$</td>
<td>$3 \pm 1$</td>
</tr>
<tr>
<td>N</td>
<td>$10 \pm 2$</td>
<td>$6 \pm 1$</td>
</tr>
<tr>
<td>C</td>
<td>$6 \pm 1$</td>
<td>$6 \pm 3$</td>
</tr>
<tr>
<td>H</td>
<td>$&lt;1$</td>
<td>$&lt;1$</td>
</tr>
<tr>
<td>Al</td>
<td>$9 \pm 5$</td>
<td>$&lt;2$</td>
</tr>
<tr>
<td>Fe</td>
<td>$25 \pm 15$</td>
<td>2</td>
</tr>
<tr>
<td>Mo</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>$4 \pm 3$</td>
<td>$&lt;2$</td>
</tr>
<tr>
<td>Si</td>
<td>$10 \pm 2$</td>
<td>$&lt;3$</td>
</tr>
<tr>
<td>Ta</td>
<td>n.d.\textsuperscript{b}</td>
<td>20\textsuperscript{c}</td>
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</tbody>
</table>

\textsuperscript{a} Klopp et al., 1965.
\textsuperscript{b} Not determined.
\textsuperscript{c} Minor tantalum contamination noted as a result of melting onto a retractable Ta–10%W pad.

4.3.2. Centrifugal Arc Casting

This is a modified arc-melting process in which metal is arc melted and then poured into a spinning mold. It is also called "skull casting," since a skull-shaped metal layer is left in the crucible after a pour is made. A centrifugal casting furnace is shown schematically in Fig. 4.22 (Calvert and Beall, 1966). The electrode assembly consists of a water-cooled copper shaft to which the consumable electrode is attached and a pneumatic cylinder. The pneumatic cylinder rapidly withdraws the electrode from the ladle when the arc is terminated. Delays are thus avoided in pouring the molten metal from the ladle to the mold. The water-cooled crucible made of high-purity copper is shaped like a cup, with its depth being equal to its diameter. Tungsten has been melted commercially in crucibles up to 510 mm (20 in) in diameter.

The spin-casting mechanism can be rotated horizontally or vertically. In Fig. 4.22, the vertical-axis spinning mechanism is shown. The rotary drum, which houses the mold, can be driven from 500 up to 2000 rpm; a force of 140–390 g (gravity) can be imparted to the casting. The power supply and the vacuum system are essentially the same as that of an arc-melting furnace.

At the beginning of the operation, the crucible is charged with scrap tungsten metal, such as the machine chips or fragments for the starter pad. Alternatively, a preformed protective skull may be placed inside the crucible. Generally, the metal loaded into the crucible comprises approximately 40% of the total weight of the heat, which is about 320 kg (700 lb) for a crucible of 510-mm diameter. The vacuum achieved is generally in the range of $1 \times 10^{-3}$ Torr and a leak rate of less than 10 μm liters per second is considered acceptable.

Because of the high melting point of tungsten, mold material has been limited almost entirely to graphite with the lowest ash content and highest density. To
prevent carbon pickup, gates and mold surfaces may be coated with tungsten by the plasma flame spray process, and the runners may be lined with tungsten sheet.

Vertical-axis spin-casting furnaces can produce plates, rods, bars, and cylindrical billets as well as complex shapes, while only hollow cylinders with straight inside walls have been formed by horizontal-axis furnaces. A much higher spinning speed is employed for horizontal-axis casting because of the possibility of liquid metal slumping down from the top dead center.

The grains of centrifugally cast billets are much smaller than those in conventional arc-melted ingots (Fig. 4.23) (Calvert and Beall, 1966). Furthermore, the former are equiaxed and the latter are generally columnar. Thus, the centrifugally cast material is much more desirable for subsequent fabrication.

![Diagram of centrifugal arc-casting furnace](image)

Fig. 4.22. The centrifugal arc-casting furnace (Calvert and Beall, 1966).
4.4. OTHER CONSOLIDATION METHODS

Because of special applications or particular requirements for some products, other consolidation processes have been developed for tungsten. These are outlined below.

4.4.1. Hot Pressing

Both the pressure and the temperature in hot pressing are appreciably lower than those applied in the conventional press-and-sinter process. Hot pressing can be considered as the heating of a powder to such a temperature that under externally applied pressure, the yield point at the contact areas between the particles of powder is exceeded and plastic flow results. Diffusion may also play a role in the densification, but the mechanism is predominantly one of plastic flow.

The temperature limit for steel dies is approximately 1000°C (1832°F), above which one is limited to graphite, oxides, or uncemented carbides or borides. Among these, the carbides and borides are expensive and difficult to prepare. Oxides have the disadvantage of poor thermal shock resistance, poor thermal conductance, and very low electrical conductivity. Graphite is the die material most often selected for hot pressing at high temperatures. It is necessary, however, to use a high-density grade, free from volatile material, in order to have high temperature strength. The bore of the die and the surface of the plunger must be machined to have a smooth surface finish and to meet the dimensional tolerances.

The graphite die itself often acts as a furnace tube, heated either directly by electric current or as a susceptor for an induction current. High frequency (1–4 kHz) induction is generally adopted for large installations. An induction-heated hot-pressing assembly is shown in Fig. 4.24 (White and Jurkowitz, 1963). A graphite mold (12) and inner sleeve (13) and pistons (2), (4), and (6) are all made of graphite. The induction coil is wound around an asbestos sleeve, between which the die piston is packed with carbon black for insulation. A pressure of 70 kg/cm² (1000 psi) is maintained during heating, and it reaches 176 kg/cm² (2500 psi) at 1750°C. The temperature is measured with a micropyrometer through a sight tube. The tungsten
is protected from oxidation during pressing by the evolution of carbon monoxide gas from the mold material. A thin carbide skin is formed at the surface of the compact and is removed by machining. It is reported that the thickness of the carbide film is no greater than 1 mm after 1 hr of heating (Karpinos et al., 1970).

In their work on tungsten, White and Jurkowitz (1963) conclude that densities above 95% can be obtained by hot pressing in graphite dies at temperatures from 1500 to 1800°C and at pressures from 350 to 560 kg/cm² (5000 to 8000 psi) with fine powders of less than 5 μm average particle size. There is very little benefit obtained by going over the temperatures and pressures mentioned above. For coarser particle size powders, the maximum density obtained may be less than 85%. In these cases, hot pressing is desirable only to have a sintered body with interconnected porosity for specific applications such as transpiration-cooled structures. The disadvantage of hot pressing is that graphite die life is relatively short. Furthermore, uniform heating of large dies by induction is difficult to achieve, and for large production runs, hot pressing with graphite dies becomes too expensive.

4.4.2. Isostatic Hot Pressing

Isostatic hot pressing is also called gas pressure bonding and is a logical development of the well-known isostatic cold-pressing technique. In the latter
process, powder contained in a rubber bag is consolidated by hydrostatic pressure applied to the bag in a pressure vessel filled with a fluid. In isostatic hot pressing, the rubber bag is replaced by a thin-walled metal can, which is sealed by welding, and the pressure vessel now contains a furnace, separated from the vessel wall by powdered insulation so that the vessel itself is not heated. The sealed can is placed in the furnace and under a pressure exerted by an inert gas such as argon or helium.

The general construction of a hot-pressure vessel is shown schematically in Fig. 4.25 (Long and Snowden, 1969). Since the hot furnace is surrounded by the cold walls of the vessel, convection loops tend to develop. Convection originates from changes in density resulting from changes in temperature, and the magnitude of the density changes depends on the volumetric thermal-expansion coefficient of the fluid used. Heat transfer depends, further, on the density of the fluid. Bett and Saville (1965) have demonstrated the superiority of helium to gases of higher densities.

Commercial tungsten powder can be hot isostatically pressed to full theoretical density, although the densification temperature varies with the pretreatment. If the pretreatment is explosive impaction, the temperature needed for hot pressing is 1150°C (2100°F), while 1370–1595°C (2500–2900°F) are required to bond compacted if it is cold compacted. The time and temperature can be controlled to yield a product having a finer grain size and better ductility than the conventional pressed-and-sintered material (Hodge, 1964). The pressure used at maximum sintering temperature is between 7 and 14 kg/mm² (10 and 20 ksi) with detention times of 1–5 hr.

Spherical powder obtained by the vapor deposition process as developed by the Allied Chemical Company (1963) cannot be cold compacted readily but can be readily hot isostatically pressed into finished shapes without pretreatment. The
large-particle powder (40–650 μm) will pour-pack to a density of 60–70% and can be bonded to full theoretical density at 1595°C (2900°F) at 10.6 kg/mm² (15 ksi). If this powder is pretreated by explosive compaction, the full density can be achieved at 1150°C (2100°F) under the same pressure. Because of the nature of the process and the spherical shape of the particles, the shrinkage of the tungsten powder is very uniform and predictable, and good dimensional control can be exercised. The sheet material produced by this process has better properties than commercial sheet materials (see Sec. 6.3).

4.4.3. Explosive Compacting

There are essentially two major types of press for explosive compaction (Cooley, 1961). In the first type, the metal container of the powder is directly surrounded by the explosive. The detonation of the explosive is usually at one end of the press so that the detonation front travels along the length of the tube. The pressure generated in this fashion is of the order of several thousand kilograms per square millimeter at the interface between the explosive and the metal container. The disadvantage of this type of press is that when the explosive pressure is released, the elastic energy in the material tends to revert the material back to its original state. If the resulting tensile stress exceeds the dynamic fracture strength of the metal, both the compact and the container tend to disintegrate in tension.

In the second type of press, the explosive pressure acts with or without a buffer plate on a piston, which mechanically or hydraulically transmits the pressure to the metal powder. Using this type of press, Propellec Chemical Division of Chromalloy Corporation has compacted high-purity tungsten powder into pellets, 19-mm diameter × 38 mm long (0.75-in. diameter × 1.5 in. long), with a density of 14.6 g/cm³ (Cooley, 1961).

4.4.4. Slip Casting

Slip casting is a method of pressureless consolidation that is adapted from the ceramic industry for powder metallurgy applications. Finely divided tungsten powder is suspended in a liquid medium and poured into plaster of Paris molds. A common liquid vehicle for the metal powder slip is an aqueous solution containing a few percent (2.5–4%) of ammonium alengate, which is sold under the trade name of Marex (Kleco Company). This material performs the threefold purpose of (1) deflocculation of the particles, (2) a suspension agent, and (3) binding agent to impart green strength to the casting when the liquid is absorbed by the porous mold. Electrolytes such as hydrochloric acid, sulfuric acid, and sodium and ammonium hydroxides are used to adjust the pH of the slip. One important function of the binder deflocculant added to the vehicle is its ability to maintain a good fluidity, or viscosity, and a reasonably high powder-to-liquid slip ratio. Slip viscosity is dependent on the powder-to-liquid ratio as well as on the pH of the slip. A desired ratio is about 10:1 or higher (Hay et al., 1964; Hausner and Poster, 1961). As a rule, a spherical powder with high apparent density is the most difficult to slip form and should be avoided.
After removal from the mold, the slip-formed metal is heat treated in a hydrogen atmosphere at approximately 1400° C (2550° F) for 2 hr. The heat treatment serves the following purposes: (1) the binder is burnt off, (2) tungsten oxide formed during processing of slip is reduced to metal, and (3) sufficient bonding develops at the metal particle interfaces to strengthen the part. The heat-treated slip-cast material may be further machined and sintered as required for higher density and strength.

4.4.5. Plasma Spraying

Plasma may be defined as a mass of gas in which enough atoms are ionized so that it becomes a quasineutral collection of electrons, positive ions, uncharged atoms, and molecules. It is an electrical conductor and may be influenced by magnetic and electrical fields. By supplying a gas to an electric arc between a solid rod and a nozzle, the gas will be dissociated, ionized, and effaced through the nozzle as a high-temperature jet. The temperature and velocity obtained by the arc plasma jet are unusually high (Thorpe, 1961).

A typical arc torch consists of an arc between a cathode and a water-cooled copper nozzle, which is the anode. These are positioned in an insulated body through which gas is fed under pressure. When a short nozzle is used, the arc is actually blown through it together with the associated plasma jet. When a long nozzle is used, the arc is contained within the nozzle bore and only a plasma jet is projected.

The choice of the plasma-forming gas is important, because it affects the electric field of the arc and, thus, the maximum temperature and enthalpy. In general, a monatomic inert gas, argon, is preferred.

There are three basic types of substrates onto which deposits may be sprayed: expendable, reusable, and permanent. The expendable substrate may be removed by selective chemical etching, melting, or other means. When identical spray-formed objects are to be manufactured in quantity, consideration should be given to reusable substrates, such as those that shrink away from the deposit due to difference in thermal expansion. Permanent substrates are intended to be used in such a manner that they become an integral part of the completed article. The sprayed material is deposited so that a sound bond or fusion is obtained. Plasma spraying is mainly used for producing intricate shapes of tungsten objects, which cannot be otherwise manufactured. The internal thread in the unalloyed tungsten bush-spacer shown in Fig. 4.26 is in the as-sprayed condition. The contoured bore of the expansion nozzle was sprayed to close tolerance and the external thread was machined from strategically deposited W–5% Cu alloy (Moss and Young, 1964).

![Fig. 4.26. An as-sprayed internal thread (left) and a machined external thread (right) in plasma-sprayed-formed W–5% Cu alloy (Moss and Young, 1964).](image-url)
The density of the plasma-sprayed tungsten layer ranges from 50 to 95% of the theoretical. The conditions leading to highest densities are high and uniform substrate temperature and a low rate of deposition. As-sprayed tungsten may be hydrogen sintered to increase its density and strength (Hay et al., 1964).

The maximum particle diameter $d_{\text{max}}$ of particular material for essentially complete melting during plasma spraying can be calculated from the equation (Mash et al., 1961)

$$d_{\text{max}} = 2 \left( \frac{\alpha \theta}{0.3} \right)^{1/2}$$

(4.4)

where $\alpha$ is the diffusivity (cm$^2$/sec) and $\theta$ is the dwell time (sec). Taking 0.63 cm$^2$/sec as the diffusivity of tungsten and assuming a constant dwell time of 100 $\mu$sec, the $d_{\text{max}}$ is 290 $\mu$m.

4.4.6. Chemical Vapor Deposition

Chemical vapor deposition (CVD) of tungsten on some substrate is generally used to prepare intricate forms such as rocket nozzle inserts and some electronic devices (Hoertel, 1964; Huegel and Holman, 1970). It is also used to prepare tungsten whiskers with high purity and high strength, e.g., 2109–2812 kg/mm$^2$ (3000–4000 ksi) ultimate tensile strength (Starliper and Kenworthy, 1968).

The process falls into one of the following three categories of reaction: (1) pyrolysis of organometallic compounds of tungsten, e.g., W(CO)$_6$ $\rightarrow$ W + 6CO; (2) thermochemical reduction of tungsten halides by hydrogen, e.g., WX$_6$ + 3H$_2$ $\rightarrow$ W + 6HX, where X is a halide; and (3) pyrolysis of a tungsten halide, e.g., WX$_6$ $\rightarrow$ W + 3X$_2$. A typical setup for vapor deposition of tungsten is shown in Fig. 4.27 (Holman and Huegel, 1967), where the thermochemical reduction reaction (2) is used.

Advantages of vapor-deposited tungsten over that produced by other processes are:

1. The product is of exceptionally high purity; this is illustrated in Table 4.3.

2. It is resistant to grain growth. This resistance is probably related to low-energy grain boundaries and the absence of stored strain energy. It has been shown that the material has remarkable resistance to grain growth up to 2500°C (Weinberg et al., 1964).

3. Near-theoretical density is obtainable by this process (Hoertel, 1964).

4.4.7. Powder Rolling

Tungsten powder can be consolidated by hot rolling within a sheath (Williams, 1958) or by direct cold rolling (Ern, 1962; Evans and Smith, 1959). Lenz and Peterson (1961) has revealed that powders with an average particle size of 3 $\mu$m and less were not suitable for rolling, while coarser powders averaging from 3 to 10 $\mu$m tended to cohere well and yielded higher as-rolled densities. Maximum thickness
attained in 63-mm (2\(\frac{1}{2}\)-in.)-wide strips were in the range of 1.5–1.7 mm (0.059–0.067 in.) with green densities of 80–85\%. After sintering at 1700°C (3092°F) for a period of time, the density of consolidated tungsten ranged from 90 to 95\% of the theoretical.

### 4.4.8. Electron-Beam Melting

When exceptionally high-purity tungsten is desired, an ingot can be prepared by electron-beam melting. The construction and operating procedures for such a furnace can be found in a textbook relative to this subject (e.g., Bunshah, 1958). It is characterized by a high vacuum, in the range of 10\(^{-6}\) Torr, which is achieved by a system comprising a diffusion pump backed up by a diffusion ejector, a Roots-type blower, and a mechanical pump. The electron gun may be of the ring type, traverse type, or other complicated forms (Gruber, 1961). The electron beam is focused onto the tip of a consumable tungsten bar, which melts and drips into a water-cooled cylindrical copper mold with a retractable copper stool at the bottom. The top layer of the ingot in this mold is kept molten by directing part of the electron beam into the mold with magnetic deflectors. As the ingot solidifies at the bottom, it is retracted gradually with the stool so as to maintain a constant depth of molten pool at the top. The power capacity of the furnace ranges from 100 to 600 kW.

Witzke et al. (1963), Klopp et al. (1965), and Klopp and Witzke (1966) have melted ingots of 57–63 mm (2.25–2.50 in.) in diameter and up to 686 mm (27 in.) in length. Using high-purity pressed and sintered tungsten as well as arc-melted ingot as melt stock, the final electron-beam-melted ingots are of very high purity (Table 4.5). The grains are columnar in structure and considerably larger than those found in arc-melted ingots, which may be indirect evidence of their purity, for it suggests that few impurities were present to act as nucleation sites for new grains during the freezing of the molten metal.

These ingots can be successfully extruded in a low-velocity hydraulic press as well as in a high-velocity (Dynapak) press. The test results (see Section 6.3) show that the tensile strength of the electron-beam-melted material is lower than that of arc-melted and powder metallurgy material. The ductile–brittle transition temperature for electron-beam-melted tungsten, determined in tension and in bending, is similar or slightly higher than those for arc-melted and powder metallurgy materials in the worked condition. In the recrystallized condition the transition temperatures for electron-beam- and arc-melted tungsten are similar, both being lower than that for powder metallurgy material of similar grain size. In the range of 1370–1930°C (2500–3500°F), the electron-beam-melted material shows better ductility than either arc-melted or powder metallurgy material. All these data suggest that electron-beam-melted tungsten is of higher purity than arc-melted or powder metallurgy material. In addition, as a further indication of purity, electrical resistivity ratios (resistivity at 42 K/resistivity at 300 K) determined on single crystals increase from 734 for the first melt to 2930 for the seventh melt of electron-beam ingots (Klopp et al., 1965). The reason no significant difference is observed in chemical analyses between electron-beam- and arc-melted tungsten as shown in Table 4.5 is probably the fact that most impurities of both materials approach or exceed the detectable limits of present sampling and analytical techniques.
4.5. PREPARATION OF SINGLE CRYSTALS

Due to the high grain boundary brittleness of tungsten, efforts were made early in the history of the industry to produce some tungsten wire of single crystals. It is no surprise that tungsten was the first metal which single crystals were obtained. The earliest of these methods are Tammann's (1914) method, Czochralski's (1918) method, the Carpenter and Elam (1920) process, the Pintsch (1913, 1914) process, and a process developed independently by Goucher (1920) and by Jacoby (1925). All these have been reviewed by Smithells (1953). The present-day technique of growing single crystals is described below.

4.5.1. Electron-Beam Zone Melting

Electron-beam zone melting of tungsten yields the most ductile material currently obtainable. This is due to the following two factors: (1) a single crystal can be grown by this method that is free from grain boundaries, which are the cause of brittleness; (2) the highest vacuum can be achieved among all melting apparatus, which tends to eliminate most of the interstitial and metallic impurities.

The general construction of the apparatus consists of four components — vacuum system, power supply, anode support, and traversing cathode (Carlson, 1959). A schematic drawing of this equipment is shown in Fig. 4.28 (Reed, 1970). The housing is generally a Pyrex bell jar and the vacuum system includes an ion pump or

![Fig. 4.28. Schematic drawing of an electron-beam zone-melting apparatus (Reed, 1970).](image-url)
a diffusion pump backed up by blowers and mechanical pumps with cold traps in the vacuum line. The anode, a tungsten rod, is stationary and supported by molybdenum holders and tungsten shims. The cathode consists of a tungsten filament that emits electrons and a molybdenum concentrator that directs the flow of the electron beam to the workpiece anode. The cathode traverses by means of a screw drive mechanism.

During zone melting, the cathode traverses repeatedly in one direction, and so does the molten zone in the tungsten rod. Solute elements that depress the melting point of tungsten are then concentrated in the terminal end of the rod; solute elements that increase the melting point, on the other hand, tend to concentrate at the starting end. Purification thus results from the process under a high-vacuum environment, that reaches $10^{-10}$ Torr. Metallic impurities are below the limit of spectroscopic analysis; carbon can be reduced to below 20 ppm, and other interstitials are essentially below 1 ppm (Schadler, 1960).

Since the molten zone is very narrow and the temperature gradient in its vicinity is great, solidification is essentially nucleated at one point and a single crystal results.

4.5.2. Strain–Anneal Method

The strain–anneal method for producing single crystals depends on the fact that the recrystallized grain size increases with decreasing amounts of prior strain (Aust, 1963). The starting material must be in a strain-free, uniform, and fine-grained state, which is needed to obtain homogeneous deformation during the critical straining. A critical strain is required just sufficient to obtain recrystallization in order to allow as few nuclei as possible to grow into the deformed material at the annealing temperature. The critical strain of a few percent is usually performed on a tensile machine, and a slow heating rate should be used in annealing. A few new crystal nuclei form at some temperature and then invade the strained matrix and consume it entirely before the temperature has risen high enough to generate more nuclei.

A more reliable procedure is to pass the critically strained specimen through a temperature gradient. In this way, only a small portion at one end of the specimen will be at the proper temperature for recrystallization. This allows nucleation to begin at one end of the specimen, and the temperature gradient insuresthat the nucleation does not occur ahead of the main growth front.

Maloof (1962) used electron-beam equipment similar in construction to that used for zone melting. The rod, 1.5 mm (0.059 in.), having a cold-worked structure was first recrystallized by moving it at 60 mm/min at a temperature of 1550°C, and then strained by about 5% in a tensile machine at 315–425°C (600–800°F). The slightly strained rod was heated by the electron beam to a temperature of 2100°C with a traverse speed of about 1 mm/min and a temperature gradient greater than 39°C/mm (1000°C/in.). Maloof successfully produced parasite-free single crystals without any well-defined substructure in 80% of his runs. He claimed that this method produced better-quality material than that grown by the floating-zone method as far as the absence of substructure was concerned.
Fabrication of Tungsten

5.1. GENERAL BACKGROUND

The objective of fabrication is twofold: (1) to convert the metal from the original massive form to a desired shape and (2) to improve certain properties of the product such as density, strength, and ductility, which are desired for service. The fabrication process is generally divided into primary reduction, or breakdown, and secondary fabrication. Extrusion and forging are the processes employed for primary reduction, while rolling, swaging, drawing, etc., are used for secondary fabrication.

Since powder metallurgy tungsten is characterized by its fine-grained structure, it may be forged directly without prior extrusion. However, for arc-cast or electron-beam-melted ingots, with large-grained structure (characterized by brittle constituents at the grain boundaries), extrusion is the preferred process. During extrusion, the billet is subjected to compressive forces only so that the tendency to initiate a crack at the grain boundary is reduced. After this, the brittle constituents are broken up and the material becomes sufficiently ductile for further fabrication.

As a rule of thumb, tungsten is generally worked below its recrystallization temperature, because the recrystallized structure with distinct grain boundaries imparts brittleness to the material. The time at that temperature needed to induce recrystallization depends upon the amount of work and structure of the material. The temperature of recrystallization decreases as the amount of work increases. Therefore, the fabrication process should be so programmed that the temperature employed for successive steps is gradually reduced. This will make the material both stronger and more ductile at low temperatures.

5.2. EXTRUSION

Extrusion processes are generally classified according to the direction of the extrusion as forward (direct), backward (indirect), and combination types (Fig. 5.1) (Wilkinson, 1970). Tungsten is generally extruded by the forward method. Extrusion presses used for tungsten fabrication are classified as conventional and high velocity.
5.2.1. Conventional Extrusion

Conventional extrusion employs hydraulic presses, either horizontal or vertical, depending upon the travel direction of the ram (Wilkinson, 1970). Vertical extrusion presses have the advantage of easier alignment between the ram and the tools and a more uniform temperature around the periphery of the billet chamber. On the other hand, the transfer of a billet from a heating furnace to the billet chamber is easier with a horizontal press. Vertical presses are mainly used for producing thin-wall tubing where uniform wall thickness and concentricity are paramount. Horizontal presses are used for bars and other forms of extrusions. The dies and tooling used in extrusion are made of highly alloyed tool steels that will withstand the high stresses and thermal shocks at operating temperatures.

The principal factors that affect the extrusion pressure are (1) the reduction ratio, i.e., the ratio of the cross-sectional area of the billet before and after extrusion; (2) the extrusion temperature; (3) the speed of deformation; and (4) the friction between the workpiece and the die and that between the workpiece and the container wall.

For direct extrusion, the metal begins to flow through the die at a maximum pressure, the breakthrough pressure. As the billet extrudes through the die, the pressure required to maintain flow progressively decreases as the frictional forces decrease with decreasing length of the billet in the container. The pressure required to maintain the flow of the billet, the running pressure, is fairly constant, and it reaches a minimum value at the end of the operation. The calculation of this value can be obtained from Sejournet’s (1956) equation:

$$P = K \ln R \exp \left(2fL/r\right)$$  \hspace{1cm} (5.1)
where \( r \) is the liner radius, \( f \) is the friction coefficient between the billet and the liner wall, \( L \) is the length of the billet in contact with the container, \( R \) is the reduction ratio, and \( K \) is the extrusion constant. When \( L = 0 \), then \( f = 0 \) and the extrusion pressure \( P \) is at a minimum. Thus,

\[
P_{\text{min}} = K \ln R
\]

(5.2)

and from the minimum pressure, the extrusion constant can be obtained. This constant is established experimentally for a special metal of a particular configuration at a definite extrusion speed and at a certain temperature. Before extrusion, the die and the container are usually heated to 370–482°C (700–900°F). A hot graphite following block is placed behind the billet before extrusion. The extrusion speed is of the order of 51–508 mm/sec (2–20 in./sec).

The billet can be extruded with or without canning. In the former case, the cladding material may be molybdenum, niobium, or stainless steel. A metal-clad tungsten billet can be extruded at a higher reduction ratio or at a lower temperature than an unclad billet, because less friction is encountered during extrusion. However, stainless steel jacketing is so soft at the extrusion temperature that the inside surface will be roughened by the penetration of tungsten grains into the steel. Niobium is more suitable for this reason, but it is more expensive. Molybdenum is a good substitute for niobium. When tungsten is extruded without canning, the billet should be machined to a conical nose having an included angle of from 90° to 120°. Heating of the billet is generally performed with an induction coil under an inert atmosphere at a temperature range from 1650°C (3002°F) to 2200°C (3992°F). If the temperature is too high, it causes excess wearing of the tooling and recrystallization and grain growth of the extrusion. If the temperature is too low, it will cause the extrusion press to stall or will result in a product with some internal and surface defects.

A common lubricant for tungsten extrusion is glass, which is applied by spraying on before heatup or by picking up while rolling the billet over the glass after a heatup. The glass should be sized to ~325 mesh. When the glass is applied by spraying, it is mixed with the following materials (1) glass, 56.5%, (2) ball clay, 3%, (3) methocell, 0.25%, (4) bentonite, 0.25%, (5) distilled water, 40% (Riesen et al., 1964). The transferring time from the induction furnace to the press container should be within 10 or 15 sec, because this will minimize the temperature drop and reduce the extent of oxidation.

Hostetter and Cook (1969) reported that based on lubricity, reactivity, insulation, and extrusion tests of some 470 lubricants, copper phthalocyanine was found to be an excellent lubricant for Mo–0.5% Ti extrusions; and another two lubricants, Cr₂O₃–graphite mixtures and waterglass–graphite combination, exhibited a capability for satisfactory service in the extrusion of refractory metals in the 1650–1970°C (3002–3580°F) range, which is comparable to the temperature used for tungsten extrusion. Haverstraw (1964) reported that a mixture of magnesium metaborate and graphite in water promotes relatively low extrusion pressures and superior control of extrusion dimensions and surface finish, and it is applicable to extrusion of 4340 steel at 980°C (1796°F) and Mo–0.5% Ti at 1920°C (3490°F). McDonald and Leitten (1967) suggested that no lubricant should be used,
since tungsten oxide forms naturally, and serves as a lubricant during extrusion.

The extrusion die may be coated with zirconia for high-temperature performance. The alternative to die coating is to build tungsten or chromium carbide inserts into steel dies. It has been reported that tungsten carbide insert type dies yield a significant increase in die life and an improvement in extrusion surface finish (Sandstrom and Hanks, 1966).

Tungsten extrusions of T shapes with flange thickness of 6.35 mm (0.250 in.) and length of about 3050 mm (120 in.) have been extruded at 2050°C (3720°F) with a reduction ratio of 19 : 1. Extrusion constants range from 45.3 to 49.2 kg/mm² (64.5 to 70 ksi) (Riesen et al., 1964). Tube extrusion techniques have been developed in recent years, and this subject will be treated in Sec. 5.8.

5.2.2. **High-Velocity Extrusion**

The construction of a high-velocity extrusion press and die is shown in Fig. 5.2. The high-pressure gas from the upper chamber activated by a triggering mechanism rushes through the orifice plate and forces the piston downward, which transfers the energy to the ram column and punch assembly. Due to the sudden release of the high-pressure gas, high-velocity of 7.5–90 m/sec (295–3540 in./sec) of the punch assembly results. As the ram accelerates downward, an equal and opposite reaction force causes an upward motion of the top plate of the upper chamber and the guide rods, which contain a recoil-shock absorber. In this type of extrusion press, the billet may or may not be extruded through the die depending on the setting of the initial gas pressure.

The billet is usually heated by an induction coil under an inert atmosphere, and it is then transferred to the press. Another technique (Foyle, 1963) is heating the billet inductively in line with the die, with the coil and the billet enclosed in an argon-filled polyethylene bag to minimize oxidation. The powder to the induction coil is cut off just before the press is fired. The billet is extruded, and the copper induction coil is smashed in position, resulting in no loss of temperature.

Deformation during high-velocity extrusion produces heat, which softens the metal under the adiabatic condition, and thus the metal is deformed more easily in spite of the higher strain rate. Therefore, the preheating temperature for the billet may be lower than that for conventional extrusion. The lower starting temperature and short contacting time between the hot billet and the tooling lessens tooling wear. On the other hand, the capacity of the high-velocity press is generally limited; it has so far been used in developmental work or small-scale production only. Rods and flat bars have been extruded at 1650–2095°C (3000–3800°F) with reduction ratios up to 45:1. The size of the products is usually limited to 645 mm² (1 in.²) in cross section, and 914 mm (36 in.) in length.

**5.3. FORGING**

For arc-cast or electron-beam-melted tungsten, extrusion is a preferred breakdown process, because, under the compressive stresses of extruding, the
Fig. 5.2. Dynapak extrusion press (courtesy of U.S. Bureau of Mines, Albany Research Center): (a) cross-sectional view of Dynapak extrusion press, (b) cross section of typical extrusion tooling.
material's tendency to crack is lessened. For powder metallurgy material, on the other hand, with its fine-grained structure and better fabricability, forging is used for breakdown. In some cases, forging is applied extensively in order to produce the particular desired shapes. A hammer or press type of forge is used in conventional forging practice, while a high-velocity forge is used when a short-duration blow has advantages. To shape a particular form of the product, a process of closed-die forging is sometimes employed.

For preparation of forging billets by the powder metallurgy technique, the first concern is the selection of the metal powder. The requirements are high purity, a medium average particle size of 3–5 μm, and a relatively wide range of particle size distribution, such as C-10 powder (see Sec. 4.2.1). A powder of this sort will usually have good compressibility during pressing and good densification characteristics during sintering (see Secs. 4.2.2 and 4.2.3). Forging billets are comparatively large in size and are generally compacted by hydrostatic rather than by mechanical means. The compacts are usually sintered in an indirect resistance furnace. For precautions during preparation and sintering of billets of these sizes and for details of sintering schedules, the reader is referred to Sec. 4.2.3.2.

After sintering, the billet should be inspected by repeated pickling and observation to ensure that it is free from imperfections or cracks. For light oxide removal, a pickling solution consisting of 40% HF, 40% HNO₃, and 20% H₂O by volume should be used. If heavy surface oxides are encountered, a pickling solution of hot caustic is required (see Sec. 5.9). The acid pickling is effective in revealing hidden imperfections of microcracks on the surface. Any such cracks or imperfections made visible must be removed by careful hand dressing. This may be accomplished by wheel grinding, belt sanding, or disk sanding, depending upon the nature and extent of the imperfections. For proper care in grinding, the reader is referred to Sec. 5.11.1. Furthermore, nondestructive testing (NDT) with dye or fluorescent penetrant and ultrasonic inspections should be applied before forging is employed. Any minor imperfections or microcracks that are not removed will result in severe cracks during forging.

5.3.1. Conventional Forging

Both forging hammers and presses are commonly employed (Wilkinson, 1970). In the former, the hammer is operated by compressed steam or air, which drives a piston, connected to the hammer, in a vertical (up or down) direction. Forging presses are of either mechanical or hydraulic design. Most mechanical presses are operated by an eccentric crank, and presses delivering loads up to 7300 mt (8000 tons) are commercially available. Hydraulic presses usually have the pressure chamber located on top of the press, and an intensifier, which builds up high pressure, is connected to the chamber. Hydraulic presses are built with ratings as high as 45,000 mt (50,000 tons).

The ram velocity of a conventional press ranges from 40 to 80 mm/sec (1.6–3.1 in./sec), while that for a drop hammer ranges from 4 to 8 m/sec (157–315 in./sec). Since the forging in the latter case is performed faster, temperature control is easier
and the risk of cracking is less. Hammer forging is therefore preferred for tungsten fabrication.

According to the direction of the force relative to the workpiece, the forging processes are classified as upset and drawing. In the former process, the force is directed along the longitudinal axis of the workpiece, while in the latter case, the workpiece is elongated by a series of transverse reductions along its length.

During primary forging, the furnace temperature is generally maintained at 1550–1650°C (2822–3002°F) for powder metallurgy material. A comparatively lower forging temperature may be used for hammer forging as compared to press forging. For arc-cast or electron-beam-melted material, forging temperatures may be as high as 1750°C (3182°F) in order to avoid cracking. In any event, the workpiece should be reheated after every blow. The reduction per blow ranges from 5 to 10% for large billets; it may be higher for small ones. During reheating, special caution should be exercised to prevent recrystallizing. Forging dies and tooling are generally made of AISI H-11, H-12, or H-13 type steel. During forging, tungsten oxides form on the surface of the workpiece and act as a lubricant.

Forging pressures depend upon the yield strength of the material, friction between contact areas, and undeformed regions of the workpiece. The forging pressure for a simple disk is formulated as (Parkins, 1968)

\[ P = \frac{2\sigma(M - 1/\mu)\rho^M}{M^2} \]  

(5.3)

where \( \sigma \) is the flow stress of the material; \( M = \mu D/t; \mu \) is the coefficient of friction between dies and the workpiece; \( D \) is the diameter of the forged disk; \( t \) is the thickness of the forged disk. As a general practice, the total reduction for an upset forging is limited to 50–60%.

5.3.2. High-Velocity Forging

The ram velocity of a high-velocity forging press is up to 40 m/sec (131 ft/sec). This type of forge probably delivers energy 500 times as fast as a conventional hammer forge. Since forging in this case is performed in very short duration of time, the temperature of the workpiece remains the same as that of the furnace or even increases to some extent due to the energy input of the blow. The tendency for cracking is reduced. The disadvantage of this type of forging is that the degree of deformation may vary from the surface to the interior of the workpiece. Since the energy required to forge tungsten billets is very large, it is impractical to use high-velocity forging operations commercially. The construction of the high-velocity forging press is similar to that of the high-velocity extrusion press mentioned in Sec. 5.2.2.

Using a Dynapak forging press, Parkinson (1964) has experimented with tungsten forgings. The starting materials were 184-mm (7.25-in.) diameter arc-cast ingots that were machined and extruded to 70-mm (2.75-in.) diameter rounds. After being annealed 1 hr at 1649°C (3000°F) for recrystallization and machined to 51-mm (2-in.) diameter × 45-mm (1.75-in.) length, they were upset forged at 1427°C (2600°F)
with fire pressure of 0.368–0.492 kg/mm² (523–700 psi) for a reduction of 60–70%. The resulting pancake shapes were recrystallized 1 hr at 1538°C (2800°F) and block forged to gear blanks. At this stage, they were further forged without recrystallization in a finish die at 1316°C (2400°F). The final forging, 10.2-cm (4-in.) diameter with a rim thickness of 2.22 cm (0.875 in.) and web thickness of 0.318 cm (0.125 in.), was essentially without cracks.

5.3.3. Closed-Die Forging

During free forging, the edge of a workpiece is generally under severe tensile stresses, and this results in cracking. Closed-die forging eliminates this problem by subjecting the workpiece to compressive forces in all directions. An example of closed-die forging is that used to produce rocket nozzle inserts. The first step of the nozzle insert fabrication is free upset forging, preferably with a hammer forge as mentioned in Sec. 5.3.1. The total reduction in this step ranges from 30 to 50%. Instead of free forging, a cup-shaped female die may be used so that the workpiece is formed into a pancake shape between the punch and the inside wall of the female die. This changes the internal stresses at the periphery of the billet from tension to compression and ensures the success of the process.

After upset forging, with or without a female die, the billet is generally recrystallized at 1550–1650°C, which is necessary to relieve the internal stresses developed during forging and to soften the material. Subsequently, extensive work is performed in the closed-die forging operation. This particular process of closed-die forging is termed backward extrusion, because in this operation when the punch pushes the workpiece inside the cup-shaped female die, tungsten flows backward between the punch and the side wall of the die and fills up the clearance (see Fig. 5.1).

Since contact area between the workpiece and dies is large in the case of closed-die forging, and since free flow of material is important, a lubricant is generally required. This typically consists of 30% graphite, 60% high-viscosity mineral oil, and the balance a thickening agent. A proprietary product, Thermex 8238 by D. A. Stuart Oil Company, is suitable for this application.

The starting temperature for closed-die forging is similar to that for free forging, i.e., in the range of 1550–1650°C (2822–3002°F), but decreasing temperatures are preferred during later stages of forging. This will generally improve mechanical properties and lower the ductile–brittle transition temperature. A typical sequential process for closed-die forging is exemplified in Table 5.1 (Evans and Tsung, 1962a).

After the final step of forging, a stress-relief anneal is required, the temperature of which depends upon the percentage of reduction performed. At about 90% reduction, an annealing temperature of 1150–1250°C (2102–2282°F) is recommended.

Closed-die forging is also used to fabricate a product with a complex configuration. In this case, a small workpiece is generally involved, and, hence, the temperature for the later stages of forging may be lowered more than that mentioned above. Using arc-cast unalloyed tungsten, W–2% Mo, and W–15% Mo extrusions as starting materials, Lake (1964) was able to fabricate a complex-shaped product with some thin web sections.
Table 5.1. Example of Closed-Die Forging Process*

1. Starting billet size: 98.3-mm (34 in.) diameter × 149-mm (54 in.) height
2. Preheat at 982°C (1800°F)
3. Upset forging
   a. Forging temperature: 1593°C (2900°F)
   b. Upset size: 124-mm (4\(\frac{3}{4}\) in.) diameter × 72.9-mm (54 in.) height
   c. Total reduction: 51% in four blows
4. Recrystallization
   1649°C (3000°F) for 5 min
5. Backward extrusion
   a. Upset preform size: 124-mm (4\(\frac{3}{4}\) in.) diameter × 72.9-mm (2\(\frac{7}{8}\) in.) height
   b. Extrusion process
      1st stage: After heating from 982°C to 1482°C (1800–2700°F) in 6 min, strike two blows with a punch travel of 42.2 mm (1.66 in.)
      2nd stage: After reheating to 1454°C (2650°F) in 5 min, strike three blows with a punch travel of 13.0 mm (0.51 in.)
      3rd stage: After reheating to 1399°C (2550°F) in 5 min, strike five blows with a punch travel of 14.0 mm (0.55 in.)
   c. Final extrusion configuration
      Bottom diameter 127 mm (5.00 in.) × bottom thickness 3.96 mm (\(\frac{3}{32}\) in.) × height 91 mm (3.6 in.)

* Evans and Tsung (1962a).

5.4. FLAT ROLLING

For arc-cast or electron-beam-melted tungsten, breakdown by extrusion or forging is generally required to impart moderate ductility to the material before flat rolling is employed. Powder metallurgy material, on the other hand, with its small grain structure, is usually prepared in the form of sheet bars of suitable size that can be flat rolled without previous working.

The degree of cold working varies depending upon the ultimate application of the material. Thin sheets are heavily worked so that a combination of high strength and low ductile–brittle transition temperature is obtained, while thick plates are cold worked to a lesser degree to allow further reduction in subsequent forming operations. The final wrought product is generally in a stress-relieved condition. In commercial production, flat tungsten mill products are generally rolled from powder metallurgy material to a thickness of 15.9–0.127 mm (0.625–0.005 in.). The availability of these plates and sheets and their dimensional tolerances are shown in Table 5.2.

A rolling mill consists essentially of rolls, bearings, and a drive for transferring power to the rolls and for controlling the speed of rolling. They are generally classified according to the number of rolls (Dieter, 1961). A two-high mill consists of only two rolls, which may be rotated in one direction or both directions. In a four-high mill, two small rolls are supported by large-diameter backup rolls. In this design, the power required is reduced and very thin sheets can be rolled to close tolerances. For tungsten, a two-high mill is generally used for high-temperature rolling and a four-high mill is used for rolling at lower temperatures. For high-
### Table 5.2. Commercially Available Tungsten Plates and Sheets

#### A. Dimensions

<table>
<thead>
<tr>
<th>Thickness [mm (in.)]</th>
<th>Minimum width [mm (in.)]</th>
<th>Maximum width [mm (in.)]</th>
<th>Maximum length [mm (in.)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.127 (0.005)</td>
<td>3.18 (0.125)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.279 (0.011)</td>
<td>3.18 (0.125)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.305 (0.012)</td>
<td>6.35 (0.250)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.432 (0.017)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.457 (0.018)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.610 (0.024)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.635 (0.025)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.737 (0.029)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.762 (0.030)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.864 (0.034)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>0.889 (0.035)</td>
<td>12.70 (0.500)</td>
<td>305 (12)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>1.270 (0.050)</td>
<td>12.70 (0.500)</td>
<td>610 (24)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>1.520 (0.060)</td>
<td>12.70 (0.500)</td>
<td>610 (24)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>1.780 (0.070)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>2.54 (0.100)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>3.18 (0.125)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>2438 (96)</td>
</tr>
<tr>
<td>4.06 (0.160)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>2134 (84)</td>
</tr>
<tr>
<td>4.76 (0.1875)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>1829 (72)</td>
</tr>
<tr>
<td>6.35 (0.250)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>1432 (56)</td>
</tr>
<tr>
<td>7.62 (0.300)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>1219 (48)</td>
</tr>
<tr>
<td>10.16 (0.400)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>914 (36)</td>
</tr>
<tr>
<td>12.70 (0.500)</td>
<td>25.40 (1.000)</td>
<td>610 (24)</td>
<td>710 (28)</td>
</tr>
<tr>
<td>15.88 (0.625)</td>
<td>25.40 (1.000)</td>
<td>508 (20)</td>
<td>610 (24)</td>
</tr>
</tbody>
</table>

#### B. Dimensional tolerances

<table>
<thead>
<tr>
<th>Thickness [mm (in.)]</th>
<th>Thickness tolerance [mm (in.)]</th>
<th>Width tolerance [mm (in.)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.127 (0.005)</td>
<td>$\pm 0.0178$ (± 0.0007)</td>
<td>$\pm 0.254$ (± 0.010)</td>
</tr>
<tr>
<td>0.178 (0.007)</td>
<td>$\pm 0.0178$ (± 0.0007)</td>
<td>$\pm 0.254$ (± 0.010)</td>
</tr>
<tr>
<td>0.254 (0.010)</td>
<td>$\pm 0.0254$ (± 0.001)</td>
<td>$\pm 0.254$ (± 0.010)</td>
</tr>
<tr>
<td>0.381 (0.015)</td>
<td>$\pm 0.0254$ (± 0.001)</td>
<td>$\pm 0.254$ (± 0.010)</td>
</tr>
<tr>
<td>0.457 (0.018)</td>
<td>$\pm 0.0254$ (± 0.001)</td>
<td>$\pm 0.381$ (± 0.015)</td>
</tr>
<tr>
<td>0.508 (0.020)</td>
<td>$\pm 0.0381$ (± 0.0015)</td>
<td>$\pm 0.787$ (± 0.031)</td>
</tr>
<tr>
<td>0.635 (0.025)</td>
<td>$\pm 0.0381$ (± 0.0015)</td>
<td>$\pm 0.787$ (± 0.031)</td>
</tr>
<tr>
<td>0.762 (0.030)</td>
<td>$\pm 0.0381$ (± 0.0015)</td>
<td>$\pm 0.787$ (± 0.031)</td>
</tr>
<tr>
<td>0.889 (0.035)</td>
<td>$\pm 0.0432$ (± 0.0017)</td>
<td>$\pm 0.787$ (± 0.031)</td>
</tr>
<tr>
<td>1.020 (0.040)</td>
<td>$\pm 5%$</td>
<td>$\pm 1.600$ (± 0.063)</td>
</tr>
<tr>
<td>1.140 (0.045)</td>
<td>$\pm 5%$</td>
<td>$\pm 1.600$ (± 0.063)</td>
</tr>
<tr>
<td>1.270 (0.050)</td>
<td>$\pm 5%$</td>
<td>$\pm 1.600$ (± 0.063)</td>
</tr>
<tr>
<td>2.030 (0.080)</td>
<td>$\pm 5%$</td>
<td>$\pm 1.600$ (± 0.063)</td>
</tr>
<tr>
<td>4.763 (0.1875)</td>
<td>$\pm 4%$</td>
<td>$\pm 1.600$ (± 0.063)</td>
</tr>
<tr>
<td>15.875 (0.625)</td>
<td>$\pm 4%$</td>
<td>$\pm 3.18, -0.025$ (± 0.025, -0)</td>
</tr>
</tbody>
</table>
temperature rolling, rolls are preheated by a gas torch so as to maintain the workpiece at a desired rolling temperature.

In the strict sense of the definition, tungsten is not usually hot rolled, because it is always rolled below its recrystallization temperature. The aim, however, is to work the metal at a temperature high enough to obtain deformation at low stress yet low enough to prevent recrystallization and excess oxidation. Rolling at a temperature above that of recrystallization would cause brittle fracture of the material.

5.4.1. Primary Rolling

In this section, emphasis will be placed on powder metallurgy material. A comparable process may be applied to arc-cast or electron-beam-melted tungsten after initial breakdown by extrusion or forging. To select a powder for this purpose, just as for other mill products, purity, particle size distribution, and the average particle size should be considered. A typical C-10 powder with an average particle size of 5–6 μm, a relatively wide range of particle size distribution, good compressibility during pressing, and good densification characteristics during sintering (see Sec. 4.2) is most desirable. Experience indicates that a density of 93.5% of the theoretical for the sintered material is desired to ensure successful rolling. For a slab of the size 145 × 125 × 38 mm (5.600 × 4.920 × 1.500 in.), sintering at 2300–2400°C (4148–4352°F) for 10 hr is necessary to reach a sintered density of the above-mentioned level. For a detailed sintering schedule, the reader is referred to Sec. 4.2.3. The ordinary powder metallurgy tungsten slabs for rolling are of the dimension, 18–50.8 × 203–254 × 254–508 mm (0.71–2.0 × 8–10 × 10–20 in.).

The conventional process for primary rolling of tungsten thicker than 25.4 mm (1 in.) is to preheat the sintered slab to 1550–1650°C (2822–3002°F) and employ a 20–30% reduction for the first pass. The slab is then reheated to the same temperature for a certain length of time, which depends essentially upon the judgment of the operator. The slab is then given a second pass of a similar percentage of reduction. Difficulties are usually encountered, and cracking of the slab results.

When a pressed and sintered slab is rolled to different percentages of reduction and then annealed at 1600°C (2912°F) for 15 min, the hardness at the edge and at the center of the slab differs, depending on the percentage of the reduction (see Fig. 5.3). It is noted that the spread of hardness variation is the greatest near 20%, while the variation is within a narrow range of 5 VHN (Vickers hardness number) at a reduction of 70%. There are two major factors contributing to the variation of hardness. The first factor is the microstructure, and the second is the densification of the material. At the center of the sheet, the actual percentage of reduction is higher than that at the edge. After annealing, the center is fully recrystallized while the edge remains in a stress-relieved condition; hence, the hardness is higher at the edge than that at the center. It is only after larger percentages of reduction that the difference in reduction and therefore in hardness between the edge and the center becomes insignificant. Another striking phenomenon is that the hardness at the center increases with increasing percentages of reduction after annealing. This apparently indicates that the increasing hardness is due to increasing density imparted by the
increased degree of working. The densification should also play a role in the variation of hardness between the edge and the center; however, this is not apparent from Fig. 5.3.

Since uniformity of microstructure and properties is achieved only after a reduction of 70% or greater followed by proper annealing, it is fair to state that a flat product with a total reduction of 60–80% is desirable. On the other hand, the worst results are obtained by a single pass of 20–30% reduction followed by annealing. Further rolling of this material will result in cracking. It is therefore suggested that for breakdown rolling of tungsten two passes of 20–30% reduction per pass should be employed consecutively before reheating. This can be easily performed, because the plate is usually thick and the heat loss during the first pass is not severe.

After about 50% reduction has been employed, tungsten is usually rolled at temperatures about 150–200°C lower than the breakdown temperature. The pitfall here again is the inadvertent recrystallization during reheating. Figure 5.4 is a plot of hardness versus time at the annealing temperature after the plate has been rolled at 1600°C (2912°F) for two passes of 30% reduction each, while Fig. 5.5 shows a similar plot, except that the plate is stress-relieved at 1250°C (2282°F) for 75 min prior to reheating. The worked plate, at least at the center, is softened or recrystallized within 4 min at a furnace temperature of 1600°C (2912°F) or 1450°C (2642°F) if no previous heat treatment is employed. On the other hand, after a heat treatment of 1250°C (2282°F) for 75 min, the plate remains in a wrought structure with a hardness level of 430–450 VHN, even it is annealed at 1450°C (2642°F) for 18 min. The reason is that when the plate is stress-relieved at 1200–1250°C (2192–2282°F), the driving force for recrystallization is lowered. This leads to the recommendation that, after tungsten plates have been rolled to about 50% reduction, they should be heat treated at 1200–1250°C (2192–2282°F) prior to further reheating. This will avoid the
potential of damage due to inadvertent recrystallization through misjudgment of the operator in selecting an unnecessarily long annealing time.

Another practice used in the industry to avoid inadvertent recrystallization
during reheating for fabrication is to add carbon to the tungsten powder before sintering. This intentional addition of carbon increases the recrystallization temperature of the material, and the potential for damage due to recrystallization is lessened. The drawback of this practice is that carbon diffusion out of the sintered billet tends to be nonuniform, especially for those billets with diameters greater than 127 mm (5 in.). Thus, a billet with nonuniformity in mechanical properties is obtained, and difficulties will be encountered during fabrication.

Tungsten slabs may be clad or sprayed with a layer of molybdenum, about 0.51 mm (0.020 in.) thick, before rolling. This usually will impart better fabricability to the slab and create less tendency for cracking at the surface. After 50% reduction or just before the final rolling, the molybdenum coating can be removed by pickling in a solution of water–nitric acid–sulfuric acid with a volume ratio of 2 : 2 : 1 at 55°C (131°F).

5.4.2. Secondary Rolling

With increasing amounts of work, the temperature of recrystallization decreases continuously. After a total reduction of about 70%, the reheating temperature should be decreased to 1050–1250°C (1922–2282°F). When the total reduction reaches 95% and the sheet is less than 1 mm (0.040 in.) in thickness, the temperature may be lowered to 250–425°C (482–797°F). This low-temperature rolling gives a better surface finish and dimensional control. The reduction per pass ranges from 10 to 25% at thick gauges and decreases to a few percent at thin gauges. When the rolled sheet shows end cracks or splits, it indicates that the reduction for the pass was too great, whereas if laminations appear at the end of the sheet, it is an indication that the reduction for the pass was too light.

Typical wrought structures of rolled tungsten are shown in Fig. 5.6. Since rolling in one direction of the sheet develops a fibrous structure in that direction only, the mechanical properties of the sheet will differ in the longitudinal as compared to the transverse directions. Cross rolling is always preferred, and furthermore, the rolling schedule should be so designed that the total percentages of reduction in either direction in the final sheet should be roughly equal to each other, when this is possible.

Tungsten may be pack-rolled between molybdenum sheets during final passes, and thus the surface finish and dimensional control will be improved. This technique may be carried out at high temperatures, 1050–1250°C (1922–2282°F), or low temperatures, 250–425°C (482–797°F), depending upon the final thickness of the sheet. After final rolling, tungsten sheets should be stress relieved by annealing at 950–1150°C (1742–2102°F).

Rolling of tungsten plates to thin sheets, say, 0.254–0.508 mm (0.010–0.020 in.), usually presents no difficulties if the size is relatively small, e.g., within a width of 305 mm (12 in.) and a length of 610 mm (24 in.). However, when rolling larger sizes of tungsten sheet, either from powder metallurgy or from arc-cast material, cracking or other difficulties may occur.

Using powder metallurgy material, Bodnie (1963) investigated the possibility of producing high-quality large tungsten sheet and plate with gauges ranging from
Fig. 5.6. Typical wrought microstructure of rolled tungsten sheets: (a) 1-mm (0.040-in.)-thick, longitudinal cross section, 250 x; (b) 2.54-mm (0.100-in.)-thick, longitudinal cross section, 250 x.
0.25 to 6.35 mm (0.010 to 0.250 in.) and width up to 457 mm (18 in.) and length up to 1219 mm (48 in.). His sheet-rolling evaluations indicated:

1. A rolling temperature in the range of 1150–1450°C (2102–2642°F) resulted in material with the most uniform structure and best surface finish.
2. All material that was recrystallized after the completion of intermediate rolling split during later rolling.
3. Highest yields and lowest bend transition temperature were favored for sheet that received no in-process heat treatments.
4. Lowest bend transition temperature occurred with a 1 : 1 ratio between cross-rolling directions, whereas the highest occurred for straight-rolled material.

An example of the optimized method of producing of tungsten sheet was outlined as follows (Bodine, 1963):

1. Isostatically press 25.4 × 152 × 330 mm (1 × 6 × 13 in.) bars under 24.6 kg/mm² (35,000 psi) pressure.
2. Induction sinter according to the following schedule: raise the temperature to 1700°C (3092°F) in 4 hr, hold at temperature for 1 hr, and then raise to 2300°C (4172°F) in 4 hr, hold for 9 hr.
3. The rolling schedule for 1.57-mm (0.062-in.) sheets are shown in Table 5.3.

<table>
<thead>
<tr>
<th>Pass number</th>
<th>Thickness after pass [mm (in.)]</th>
<th>Preheating temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.3 (0.8)</td>
<td>1450 (2642)</td>
</tr>
<tr>
<td>2</td>
<td>15.9 (0.625)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>3 (Cross roll)</td>
<td>12.7 (0.5)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>4</td>
<td>10.2 (0.4)</td>
<td>1400 (2552)</td>
</tr>
</tbody>
</table>

Anneal 5 min at 1300–1350°C

<table>
<thead>
<tr>
<th>Pass number</th>
<th>Thickness after pass [mm (in.)]</th>
<th>Preheating temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.26 (0.325)</td>
<td>1350 (2462)</td>
</tr>
<tr>
<td>6</td>
<td>6.86 (0.270)</td>
<td>1300 (2372)</td>
</tr>
<tr>
<td>7 (Cross roll)</td>
<td>5.46 (0.215)</td>
<td>1300 (2372)</td>
</tr>
<tr>
<td>8</td>
<td>4.45 (0.175)</td>
<td>1300 (2372)</td>
</tr>
</tbody>
</table>

Anneal 5 min at 1250–1300°C; caustic pickling and condition

<table>
<thead>
<tr>
<th>Pass number</th>
<th>Thickness after pass [mm (in.)]</th>
<th>Preheating temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>3.51 (0.138)</td>
<td>1250 (2282)</td>
</tr>
<tr>
<td>10</td>
<td>2.82 (0.111)</td>
<td>1200 (2192)</td>
</tr>
<tr>
<td>11</td>
<td>2.26 (0.089)</td>
<td>1200 (2192)</td>
</tr>
<tr>
<td>12</td>
<td>1.80 (0.071)</td>
<td>1150 (2102)</td>
</tr>
<tr>
<td>13</td>
<td>1.63 (0.064)</td>
<td>1150 (2102)</td>
</tr>
</tbody>
</table>

Anneal 5 min at 1150°C (2102°F); caustic pickling and acid etching

Another investigation on the rolling of large sheets, 914 x 2400 mm (36 x 96 in.), to 0.51, 1.02, or 1.52 mm (0.020, 0.040, or 0.60 in.) for thickness, using arc-cast material was unsuccessful (Schwertz et al., 1967).

5.5. ROD ROLLING AND SWAGING

Rod rolling and swaging are the fabrication processes for producing tungsten rods used principally for electrical contacts, glass-to-metal seals, filament supports, and electrodes of various kinds. Because of high melting point, low vapor pressure, good thermal conductivity, and hardness, tungsten electrical contacts display minimal wear under heavy contact pressures and exhibit outstanding resistance to arc erosion, welding, and pitting. Tungsten rods are used extensively for glass-to-metal seals in hard-glass lamps and electronic applications due to the fact that its coefficient of expansion approximates that of hard glass. For this application, it is necessary to produce nonporous and split-free rod with no surface imperfections. Tungsten rod is also used as the electrode for inert-gas arc welding, resistance welding, vacuum arc melting, electrodischarge machining, etc. For these applications, both pure and thoriated or zirconiated tungsten are employed. Thoriated and zirconiated tungsten rod and wire will be discussed in Sec. 5.6.3. Rod rolling and swaging also serves as preliminary steps to produce wire before drawing.

Large sintered bars of round cross section, up to 63.5 mm (2.5 in.) in diameter, or the equivalent in square cross section may be rolled down to about 25.4 mm (1 in.) with grooved rolls. In a row of grooves on a roll, the size decreases from one end to the other, so that when the bar is rolled from one pass to the next its cross section will be reduced. In any one pass, the metal is usually compressed in one direction only. On the next pass it is rotated 90° and then compressed in the direction perpendicular to the previous one.

The starting temperature for rod rolling is about 1700°C (3092°F) and is gradually decreased to 1450°C (2642°F). The reduction per pass is between 10 and 15%, the rod should be reheated after every pass. After rod rolling, the material should be stress-relieved at a temperature ranging from 1450 to 1500°C (2642 to 2732°F), for 15–30 min, depending upon the degree of work hardening and the size of the rod.

After rod rolling, the bar is further reduced by swaging. Sintered bars with cross sections less than 25.4 mm (1 in.) in diameter or the equivalent are reduced by swaging without rod rolling. Swaging machines are generally classified into two types. The first type is the rotating die swage, which consists of a spindle assembly driven by a flywheel, and a heavy steel housing. At one end of the spindle is a roller cage with 10 to 12 loosely fitted rollers, which surround two or four hammer blocks. As the spindle revolves, centrifugal force throws the hammers outward against rollers. Each time the hammers strike diametrically opposed the rollers, the rollers are driven inward, causing the die to close and compress the workpiece. As the hammers pass out from under the rollers, the die is then thrown open. The die assembly may consist of either two or four dies comparable with the number of hammer blocks. Higher-tensile-materials can be swaged with a four-die machine,
since there are twice as many blows doing the work and each blow strikes a smaller area as compared to a two-die machine. Greater reduction per pass and a steeper angle of reduction can also be achieved.

The second type of swaging machine is the stationary-die type. In this swage, the spindle assembly remains stationary while the roller cage rotates. This method is used mainly to make precision parts of complicated cross section other than rounds. Since tungsten is swaged hot as a breakdown or as an intermediate step for wire drawing, the stationary die machine is of little practical importance for this application.

In the following, the use of the first type of swaging machine will be discussed. Machine speeds vary from about 200 to 1500 rpm, depending upon the size of the machine. Swaging dies are generally made of tungsten or molybdenum high-speed tool steels. Cemented tungsten carbide or titanium carbide is also used as a die material or for die inserts. Particular attention should be paid to the manufacture and maintenance of the dies to retain their size and shape. Reduction in area per die step usually ranges from 10 to 15%. The ideal length of the working face of the dies in relation to the feed speed of the rod is such that no part of the rod receives more than one blow during each pass. If dies continue hammering after the temperature has fallen considerably, the workpiece will crack.

Pressed and sintered tungsten bars with a cross section of 25.4 × 25.4 mm (1 × 1 in.) are generally heated in a hydrogen furnace at a temperature of 1550–1600°C (2822–2912°F) and then swaged by hand feeding. For the first few passes, the rod is swaged for only half its length; then the rod is reversed, reheated, and the other half swaged in the same die. When it is reduced to less than 8.89 mm (0.350 in.) in diameter, the rod is usually heated by gas manifold burners at temperatures of 1200–1400°C (2192–2552°F) (Fig. 5.7). It is fed through the gas manifold burner into the

![Fig. 5.7. Tungsten swage machine with gas manifold burners. (Courtesy of Teledyne Wah Chang Huntsville, Alabama.)](image)
Table 5.4. Swaging Schedule for Tungsten Rod Production*

<table>
<thead>
<tr>
<th>Rod diameter [mm (in.)]</th>
<th>Temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.30 (0.800)</td>
<td>1600 (2912)</td>
</tr>
<tr>
<td>17.8 (0.700)</td>
<td>1600 (2912)</td>
</tr>
<tr>
<td>15.2 (0.600)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>12.7 (0.500)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>11.2 (0.440)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>9.91 (0.390)</td>
<td>1400 (2552)</td>
</tr>
<tr>
<td>8.89 (0.350)</td>
<td>1200 (2192)</td>
</tr>
<tr>
<td>8.00 (0.315)</td>
<td>1200 (2192)</td>
</tr>
<tr>
<td>7.11 (0.280)</td>
<td>1200 (2192)</td>
</tr>
<tr>
<td>6.35 (0.250)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>5.59 (0.220)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>4.95 (0.195)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>4.57 (0.180)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>4.19 (0.165)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>3.81 (0.150)</td>
<td>950 (1742)</td>
</tr>
<tr>
<td>3.38 (0.133)</td>
<td>950 (1742)</td>
</tr>
</tbody>
</table>

* Courtesy of Teledyne Wah Chang Huntsville, Alabama.

swaging machine, picked up by a pair of rolls at the back of the machine, and pulled through the dies at a constant speed, usually 2–4 m (78.7–157 in.) per min. No protective atmosphere is used with this type of gas heating, but the rod may be coated with graphite, which serves the double purpose of reducing the die wear and protecting the metal against oxidation. An example of a swaging schedule for tungsten rod production is shown in Table 5.4. Typical wrought structures of swaged tungsten rods are shown in Fig. 5.8. Swaging may be done at the lower range of temperatures mentioned above to a size of about 1 mm (0.039 in.).

In the early stages of swaging, the rod is reheated to 1550–1600°C (2822–2912°F) and recrystallization may occur, particularly near the surface of the rod, which may be transformed into a fibrous structure during later stages of working. However, special caution must be taken in the later stages of swaging to prevent recrystallization. A recrystallized equiaxed rod breaks transversely, and the fracture follows the grain boundaries. Rods with a fibrous structure are ductile and will split longitudinally only when they are swaged at too low a temperature.

5.6. WIRE FABRICATION

Tungsten wire is generally classified into three categories—pure or unalloyed, doped or nonsag, and thoriated or zirconiated tungsten. The major applications of different types of wire are:
Fig. 5.8. Typical wrought microstructure of swaged tungsten rods: (a) 4.06 mm (0.160 in.) diameter, as swaged, 250 x; (b) 3.38 mm (0.133 in.) diameter, as swaged, 250 x.
(1) Lamp filaments for incandescent and fluorescent lamps. In most of these applications, the nonsag property is paramount, and hence, doped tungsten wire is extensively employed.
(2) Lamp support wire, which is also a major application for doped tungsten.
(3) Electronic filament and heater wire. In this application, a nonsag property is also required. However, in the case of direct cathode electronic filaments, an increased electron emissivity is required, and hence, thoriated tungsten is employed.
(4) Electronic grid wire. Nonsag tungsten is used in this case, and special requirements for maximum ductility, straightness, and controlled tensile strength are imposed.
(5) Vacuum metallizing wire in the form of single- or multiple-strand filaments. A special nonsag, highly formable tungsten wire is employed.
(6) Heating elements for furnaces and other uses in which the nonsag property is not important. In this case, pure tungsten wire is employed.

To ensure good fabricability, the starting powder for tungsten wire should be of high purity, 99.95% minimum, excluding the additives in the case of doped, thoriated, and zirconiated tungsten. After compacting, the sintering and fabrication processes for different types of wire differ in only a few details.

5.6.1. General Fabrication Process

Tungsten wire may be fabricated from large bars with square or round cross sections of arc-cast, electron-beam-melted, or powder metallurgy material. Since powder metallurgy material has better fabricability and is less expensive to prepare, it is preferred as a general practice in the industry. The as-sintered bar, usually with a cross section of 20 × 20 mm (0.787 × 0.787 in.) is swaged down to about 2.54 mm (0.1 in.) in diameter and then reduced by drawing. The exact gauge of the wire at which drawing starts after swaging depends upon the following two factors: (1) The wire should have been worked more than 97% by swaging from the original sintered bar so that it is ductile enough for handling on the drawing machine. (2) A minimum of some ten drawing passes should be given to develop a satisfactory surface and a uniform diameter to assure the quality of the final product.

The general arrangement of a tungsten wire-drawing machine is shown in Fig. 5.9. The wire is released from a take-off drum, which is controlled by a brake, brought through a lubricant pot, gas burners, and the die; and then wound on a drawing drum. The lubricant is a mixture of fine graphite, a colloid to hold it in suspension, sugar or syrup, zinc oxide, a preservative, a froth preventative, and water. The colloid to be used may be agar-agar or gracilaria gum, the preservative is generally formaldehyde, and the froth preventative Ocenol. The purpose of the sugar or syrup is to make the lubricant adhere better to the wire. The function of the zinc oxide is to prevent acids formed by decomposition from corroding the copper pipeline of the lubricant circulating system.

The procedure to prepare the lubricant is as follows: To 72 liters (19 gal) of hot water at 60–70°C (140–158°F) in a steam-jacketed kettle is added one of the
following alternative colloids: (a) 2.84 kg of agar-agar, (b) 1.85 kg of gracilaria gum. The mix is heated with agitation until the colloid is completely formed. Boiling should be avoided. In the meantime, 13.6 kg of graphite in flake form has been put in a ball mill, to which is now added the above colloid solution, using 7.75 liters of water as a wash. The mill is run for 20 hr, during which time the temperature of the mix will rise due to energy absorption. Next, 62 liters of cold water is added and the mill is run for another hour. Now 6.8 kg of brown sugar or an alternative is added; 1 liter of formaldehyde, 150 g of zinc oxide, 113 g of Ocenol, and 113 of Tergitol are also added. The mill is then tumbled for an additional 2–3 hr for mixing, and the lubricant is then ready for use.

The method of heating the wire depends mainly on the size of the wire being drawn. For large sizes, high-pressure gas burners with flames directed onto the wire may be used, while for fine wires, a gas-heated trough shielding the wire from the direct flame is employed.

Large-size drawing dies are made of cemented tungsten carbide, but for finishing dies and all sizes of dies below 0.25 mm (0.010 in.), diamond is the preferred material because of its superior wear resistance. Dies are mounted in steel cases with a brazing alloy that will hold them securely at service temperature. Average die life is about 8 hr, after which time the die surface should be repolished in the tool shop. A general sketch of the wire drawing die is shown in Fig. 5.10. In their investigation of tungsten wire drawing to 0.3–2.5 mm (0.012–0.098 in.) with carbide dies at 800 ± 50°C (1472 ± 90°F), Bryskin et al. (1970) reported that there is an optimum zone of die angles, which varies from 10 to 15°, depending upon the percentage of reduction of the drawing pass. Optimum angles are indicated in Fig. 5.11. For large-size wire, the die is mounted in a water-cooled block to prevent overheating, but in
Fig. 5.10. Sketch of diamond die for drawing tungsten.

Fig. 5.11. Variation of drawing stresses with the reduction angle of the die for various percent reductions. The area between dashed lines designates the zone of optimum angles (Bryskin et al., 1970).
the later stages of drawing it is necessary to use a heated die block to keep the die from cooling off.

Before drawing, the wire is usually pointed by first heating to 900°C (1625°F) and then dipping into sodium nitrate powder so that the wire can be threaded through the die. During the early stages of drawing, the wire tends to initiate splits and cracks, which tendency can be minimized by heating the wire to 1000–1100°C (1832–2012°F). The temperature is gradually reduced to 600–700°C (1112–1292°F) when the wire is below 0.1 mm (0.004 in.) in diameter; for the final few passes, the temperature is even lower. The wire may be handled on a draw bench to avoid bending when the wire is large, after which the wire is wound into progressively smaller drums or spools after passing through the die.

The reduction in area for each pass is of the order of 10–15°. The speed of drawing is gradually increased from about 3 m/min (118 in./min) to 100 m/min (3940 in./min), and the speed is again reduced for fine wires of less than 0.02 mm (0.008 in.) diameter. During the process of drawing, the metal becomes work hardened, and it is necessary to anneal it to restore its ductility before further drawing.

Starting with Avitzur’s (1967, 1968) theoretical equation for wire drawing, Mullendore (1971) reached a simple die-line equation:

\[
\ln \frac{D_1}{D_2} = \frac{q(1+\theta) - B}{2A}
\]  

(5.4)

where \(D_1\) and \(D_2\) are the initial and final wire sizes, respectively; \(q\) is the ratio of the draw stress to the flow stress of the wire, which depends on the degree of diametral uniformity, ranging from 0.60 to 0.85; and \(\theta\) is the temperature coefficient of the flow stress and can be evaluated experimentally. For tungsten wire drawn from 1.65 to 1.00 mm (0.065–0.039 in.) at 900°C (1652°F),

\[
\theta = 0.064 \frac{900 - T_2}{100}
\]  

(5.5)

where \(T_2\) is the temperature (in degrees Celsius) of the wire at the exit of the die. In general, \(T_2\) is about 200°C (360°F) lower than the entrance temperature. The values for \(A\) and \(B\) can be calculated for the Avitzur’s equation for different angles of dies. These values are shown as in Table 5.5. According to Mullendore (1971), the calculations show that the industry die lines, for the most part, are in fact the correct

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(A)</th>
<th>(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6°</td>
<td>1.785</td>
<td>0.132</td>
</tr>
<tr>
<td>8°</td>
<td>1.565</td>
<td>0.186</td>
</tr>
<tr>
<td>10°</td>
<td>1.395</td>
<td>0.243</td>
</tr>
</tbody>
</table>

ones. For certain passes where the calculated die lines differed from that being used, there had been troubles over the years.

Tungsten wire is not generally drawn to size below 0.01 mm diameter, due to the difficulties in handling the wire and in die preparation. Finer wire can be produced by etching in alkaline potassium ferricyanide or ammonium persulfate. An alternative method is electrolytic etching using a dilute solution of sodium hydroxide as the electrolyte. The wire, being the anode of the cell, is passed continuously through the solution over pulleys of hard rubber at some 30 m/min (1181 in./min). A third method of reducing the diameter of fine wires is to subject them to cathodic thinning in an argon discharge. This last method gives the best results for uniform reduction, but it is only applicable to short lengths of wire.

The diameter of tungsten wire above 0.5 mm (0.020 in.) can be measured accurately with a micrometer, but for finer sizes, the measurement is usually made in terms of milligrams per 200 mm length of wire. The diameter $D$ in microns is calculated from the weight $W$ in milligrams per 200-mm length according to the equation (Espe, 1950)

$$D = KW^{1/2}$$

(5.6)

where $K$ is 18.138 for pure tungsten, 18.212 for doped tungsten, 18.313 for wire with 1% ThO$_2$, and 18.390 for wire with 2% ThO$_2$.

Drawn tungsten wire appears black owing to an adherent layer of graphite on the surface with some oxides and contaminants. Since graphite is insoluble in practically all reagents, chemical cleaning processes depend essentially upon dissolving the tungsten oxides and removing the now loosely adherent graphite. For large wires with heavy oxide coating on the surface, fused sodium or potassium hydroxide should be used; for small wire with light oxide coating, a boiling solution of 40% concentration of the same reagents may be applied. After thoroughly washing with water, the wire is passed between felt pads to remove the graphite.

Electrolytic methods may also be used, and the electrolyte may be an aqueous solution of caustic soda or a saturated solution of sodium sulfate. Tungsten wire can also be cleaned by heating to an incandescent temperature, say 1500–1600°C (2732–2912°F) under either a slightly oxidizing or reducing atmosphere, e.g., hydrogen or commercial nitrogen containing less than 1% of oxygen.

5.6.2. Pure (Unalloyed) Tungsten Wire

A production schedule for pure tungsten wire starts with a compacted bar, usually of the size $20 \times 20 \times 1000$ mm ($0.787 \times 0.787 \times 39.4$ in.), which is presintered in a hydrogen furnace at 1250–1400°C (2282–2552°F) for about 60 min. This produces a bar with a density of about 68–70% of the theoretical and sufficient strength to withstand clamping and handling for direct sintering (see Sec. 4.2.3.1). At the beginning of direct sintering, the indicated voltage is high, due to the high resistance of the bar, which is in turn caused by a large void volume between the compacted particles. The current is increased to a maximum value and held at 2550–
2600°C (4622–4712°F) for some 30–60 min, during which time the voltage drops, indicating that the density of the material is increasing. The desired density is generally 93% of the theoretical.

The sintered bar is then swaged at 1550–1650°C (2822–3002°F) and then at gradually decreasing temperatures to a size of about 2.54 mm (0.100 in.). The swaged rod should be reheated after every pass, but no in-process annealing is required.

After swaging, the wire is drawn through different-sized dies as detailed in Sec. 5.6.1 until the final size is obtained. At certain stages of drawing, the wire is annealed by passing electricity through a section of the wire in a hydrogen atmosphere. This is effected by utilizing mercury contacts as electrical leads. The wire length between the mercury contacts is some 200 mm (8 in.), and the speed of the wire running through the annealing zone ranges from 10 to 30 m/min (394 to 1181 in./min), depending upon the size of the wire. Since the oxide and lubricant coating is removed in a hydrogen atmosphere, the wire is lubricated again for further drawing.

When a lamp filament made from pure tungsten is heated to an operating temperature of about 2000°C (3632°F), the wrought fibrous structure is transformed into minute equiaxed grains that continue to grow on further heating until the grain size becomes comparable to the wire diameter. These filaments are subject to “offsetting” due to motion on the crystal boundaries that are lying in planes steeply inclined to the wire axis. This “offsetting” causes a local reduction in area and leads to overheating and failure of the filament. This effect can be prevented by either of two methods — (1) introducing into the metal small amounts of finely divided refractory oxides, such as thoria or zirconia, which restrain the grain growth; (2) adding some volatile material, such as the oxides of potassium, silicon, or aluminum, which promotes the interlocking grain growth.

Since the introduction of gas-filled incandescent lamps in 1913, coiling the filament into a helix has been a common practice, for it reduces the cooling of the filament by conduction and convection. The single-coil filaments are made by winding the filament on mandrels of molybdenum or steel wire of larger diameter than the tungsten wire. These coils may be wound again on a larger mandrel to form a secondary coil. The steel mandrels are dissolved in hydrochloric acid, and molybdenum mandrels in a solution containing 50 vol % HNO₃, 30 vol % H₂SO₄, and 20 vol % H₂O at 90°C (194°F). The tungsten filament is not attacked by either of these solutions.

Although offsetting does not occur in coiled filaments, the pitch of the coil increases under the influence of gravity, and the filament sags. Great stability of the wire is required to prevent short circuiting between turns. This stability is achieved by either doping or by the addition of refractory oxides, as mentioned above for straight filaments.

5.6.3. Doped (Nonsag) Tungsten Wire

The original doping process was discovered at Battersea, England (Smithells, 1953), when tungstic oxide was heated in a fire clay crucible at 1200°C (2192°F) for several hours. This resulted in the introduction of some 0.1% of Al₂O₃ and 0.1% of SiO₂ into the material. The addition of certain oxides, which are mainly volatilized
during sintering, has a marked effect on the crystal growth in the drawn wire, which promotes an elongated, interlocking grain growth. The effect is greater when a second, less volatile oxide is also present. Comparison of pure tungsten wire and doped wire when heated at elevated temperatures is shown in Fig. 5.12.

Various conjectures exist in the literature on the effect of doping on tungsten wire. Early observations (Kopelman and Gregg, 1948) examined the pore size of hydrogen-reduced tungsten powder and speculated that the pores in the doped tungsten trapped the dopant until high temperatures were reached and thus aided grain size control. Other investigations (Meijering and Rieck, 1957; Rieck, 1958, 1961) have proposed that the dopant exists as a second phase in the form of thin tubes parallel to the wire axis. Recent studies by transmission electron microscopy have unambiguously identified stringers of the dopant several angstroms in diameter in annealed doped wire. One explanation is that they are particles of mullite (Walter, 1967), and the other is that they are bubbles developed by volatilization of the dopant upon annealing (Das and Radcliffe, 1968; Koo, 1967).

Moon and Koo (1971) concluded that during the working of a sintered ingot, the bubbles became elongated; those with a length-to-width ratio of less than 10 spheroidize, while bubbles with a length-to-width ratio greater than 20 ovulate and break up into a row of bubbles (Fig. 5.13). Yamazaki et al. (1974) further studied the mechanism and stated that $K_2O$ and $SiO_2$ doped before reduction cause potassium and silicon to be included in tungsten particles. With the addition of $Al_2O_3$, the potassium concentration in tungsten increases proportionally. During sintering, aluminum and silicon volatilize easily and remain at less than 0.003% in sintered billets. Only potassium remains at about 55–70% of its original content. With an increasing potassium content, the density of rows of bubbles in the annealed wire increases, promoting the formation of interlocking elongated recrystallized grains.

Fig. 5.12. Comparison of pure tungsten wire (top) and nonsag wire (bottom) when heated to 100°C, 1800°C, and 2300°C (left to right), 250× (Davison and Neleker, 1966).
The doping solution used in today's industry is an aqueous solution of potassium silicate, K₂Si₂O₅, and aluminum chloride, AlCl₃, or nitrate, Al(NO₃)₃. Depending upon the reduction process used, it is blended with the yellow, blue, or brown oxide; then air dried; and then reduced by hydrogen as described in Chapter 3. The metallic tungsten powder is then leached with concentrated hydrochloric and hydrofluoric acids and water-washed and air-dried. The final powder usually contains about 0.05% each of K₂O, SiO₂, and Al₂O₃.

Since some residual impurities of doped tungsten should be removed during sintering, and since the doped tungsten is stronger than tungsten, the compacted bar of the former is generally made smaller than that of the latter. The presintering temperature and time are the same as that for pure tungsten. The maximum temperature and the desired density in direct sintering are also the same as that of pure tungsten, but the heating time and holding time at the maximum temperature is usually shorter due to the fact that densification of the doped material is comparatively easily achieved.

The swaging and drawing processes for doped tungsten are not much different from those for pure tungsten, with the exception that in-process annealing is required more often for the doped material. This is due to the fact that the rate of work hardening is higher for doped tungsten than for the pure metal. The annealing temperature is generally higher to assure full recrystallization, and the interlocking crystal structure obtained will prevent failure during the subsequent working processes. A complete processing schedule for nonsag tungsten wire is shown in Fig. 5.14.

For vacuum metallizing applications, nonsag tungsten wire is widely used, because it is able to withstand repeated heatings at very high temperatures without noticeable deflection or distortion. Also, most metals used for metallizing wet the
DOPED TUNGSTEN POWDER

- Press to 55% theoretical density
- Compact, 14 mm x 14 mm x 600–800 mm
  - Press and sinter (see Sec. 4.2.3.2)
  - Swage at 1650°C, 20% red./pass

SINTERED BAR, 7.6 mm dia. x length

- Pickle and condition, anneal at 2150°C, 300 mm/min
- Swage at 1350°C, 25% red./pass (4 passes)

SWAGED ROD, 4.3 mm dia. x length

- Anneal at 2000°C, 250 mm/min
- Tandem (2-die) swage at 1300°C,
  - 28% red./pass, 3 m/min

SWAGED ROD, 2.9 mm dia. x length

- Tandem (2-die) swage at 1250°C,
  - 26% red./pass, 3 m/min

SWAGED ROD, 2.0 mm dia. x length

- Draw at 1050°C (3 passes)
  - 40% red./pass, 4.8–8.5 m/min

WIRE, 1.19 mm dia. x length

- Draw at 1000°C (1st pass), drop 50°C every pass
  - 35% red./pass (4 passes), 8.5–11.3 m/min

WIRE, 0.58 mm dia. x length

- Draw at 450°C (14 passes)
  - 15% red./pass, 12.5–27.7 m/min

WIRE, 100 mg/200 mm length

- In-line anneal (constant current)
  - Draw at 350°C (16 passes),
  - 15% red./pass, 40–68 m/min

WIRE, 7.0 mg/200 mm length

- In-line anneal (gas), no die in series
  - Draw at 300°C (14 passes),
  - 13% red./pass, 91–99 m/min

WIRE, 1.0 mg/200 mm length

- Draw at room temp. (10 passes)
  - 10% red./pass, 120 m/min

WIRE, 0.340 mg/200 mm length

- Fig. 5.14. Typical nonsag tungsten wire processing schedule.

nonsag wire easily and produce uniform coatings. The wire is usually a strand of from two to seven individual wires of 0.38–1.02 mm (0.015–0.040 in.). The stranding machine consists of a large-diameter metal tube, inside of which are stationary cradles for holding wire spools (Davison, 1972). While the tube is rotating at a speed of 750–1700 rpm, the cradles and spools remain stationary. The tungsten wires are fed from the spools through guides along the inside diameter of a large rotor, a collecting plate, then through bunching dies, and finally onto a take-up capstan, where they are evenly twisted. Multiple strand wire with a designation of 3 × 3 × 0.5 mm (0.020 in.) can also be produced by twisting three wires of 0.5-mm (0.02-in.) diameter together followed by stranding three such sections together. In addition to an all tungsten strand, other varieties of strand, incorporating one or more wires of other metals, are also employed.
5.6.4. *Thoriated and Zirconiated Tungsten Wires*

Thorium and zirconia are very refractory oxides and will remain in tungsten products through the high-temperature sintering process, and will restrain grain growth during heating at the operating temperature of the lamp filament. For thoriated tungsten wire, the grain size after heating for 1000 hr is comparable to that developed in pure tungsten after a few minutes (Smithells, 1953). Although there is a much smaller distortion of the filament than with pure tungsten, a progressive increase in grain size does occur, and it is therefore less effective for lamp applications than nonsag wire. The thoriated wire, therefore, is used mainly for lamps and electronic applications when high electron emission is required and where filament hot strength is more important than nonsag characteristics.

The major use for zirconiated rod or wire and the other use for thoriated material is for tungsten inert-gas arc-welding electrodes. Thoriated tungsten carries 50% more current than pure tungsten; it starts easier, gives a stable arc, and is less likely to sputter tungsten into the deposit. It is recommended for use with dc, but not ac welding, such as for welding aluminum (Blucker, 1972). Zirconia-doped tungsten starts well, has a stable arc, and resists arc sputtering. It can carry slightly more current than thoriated tungsten and is recommended for welding aluminum in order to get extremely pure weld deposits.

Thorium or zirconia is added as a nitrate or chloride to the tungsten oxide, whether yellow, blue, or brown, depending upon the reduction process used. The amount of thorium or zirconia may be up to 4 or 5% of the calculated final weight of tungsten metal powder to be reduced. After blending, the tungsten oxide is air dried and reduced in a hydrogen furnace as described in Chapter 3. The reduced product is screened and blended with pure tungsten powder in order to obtain a powder with 1 or 2% of the refractory oxide, as required.

Since the thoriated tungsten is stronger than pure tungsten (King and Sell, 1965), the compact bar for sintering is generally smaller for the former than the latter. The sintering temperature is usually in the range of 2600–2800°C (4712–5072°F), which is comparatively higher than that for pure tungsten, and the time for sintering is also longer. The rate of densification for the thoriated or zirconiated tungsten is lower than that of pure tungsten. The final density is 92–93% of the theoretical.

The swaging and drawing procedures are the same as for pure tungsten, except that in-process annealing is required more often, because the rate of work hardening for thoriated or zirconiated tungsten is higher. A typical wrought structure of thoriated tungsten wire as compared to unalloyed tungsten wire is shown in Fig. 5.15.

Thoriated tungsten filaments used for high electron emission purpose require a special treatment. It is first flashed for a minute or so at temperatures above 2000°C (3632°F) followed by activation at lower temperatures. Alternatively, the activation process is replaced by carburization from gaseous medium (Schneider, 1958). For best results, a standard process used today is as follows (Longhurst, 1974): Flash the thoriated tungsten wire at 2100–2200°C (3812–3992°F) in a vacuum of 10⁻⁷ Torr and then introduce pentane or benzene to a pressure of 50 × 10⁻³ Torr followed by
Fig. 5.15. Typical wrought microstructures of thoriated and unalloyed tungsten wire: (a) W-2ThO$_2$ wire, 2.4 mm (0.093 in.) diameter, longitudinal cross section, 250 ×; (b) unalloyed tungsten wire, 24-mm (0.093 in.) diameter, longitudinal cross section, 250 ×.
heating the wire to 1950–2100°C (3542–3812°F) for 1–5 min or until the wire current drops by about 11%. At the completion of the process, 15–30% of the cross-sectional area of the wire should have been transformed into carbides.

The activation process is based on the fact that higher electron emission is obtained due to a lower work function of metallic thorium formed at the surface of the tungsten wire. The reason for the formation of thorium at the surface is not fully understood. Langmuir (1923) suggests that a certain amount of the chemical reduction of thoria by tungsten may occur due to the volatility of the oxides of tungsten. Ackermann et al. (1963) believe that thoria is reduced by carbon, which is present as an impurity in tungsten, at about 2000°C (3141°F). On the basis of a series of experiments, Sell et al. (1964) argue that thoria may volatilize via two possible paths according to the equations

\[ \text{ThO}_2(s) = \text{ThO}_2(g) \]  
\[ \text{ThO}_2(g) = \text{ThO}_2(g) + \text{O}_2(g) \]

They also state that thoria is not reduced by carbon to thorium, but to carbides according to the reactions

\[ \text{ThO}_2 + 3\text{C} = \text{ThC} + 2\text{CO} \]  
\[ \text{ThO}_2 + 4\text{C} = \text{ThC}_2 + 2\text{CO} \]

The thoria volatilization starts at 1850–2000°C (3362–3632°F), which is about the same temperature range in which Schneider (1958) first found free thorium in thoria-activated tungsten wire. This suggests that thorium may form via some reaction in which one of the gaseous phases of thorium oxide plays an important role.

Sell et al. (1964) also suggest that thoria reacts with tungsten carbide to form thorium monocarbide, which, in turn, reacts with tungsten to form metallic thorium:

\[ \text{ThO}_2 + 3\text{WC} = 3\text{W} + \text{ThC} + 2\text{CO} \]  
\[ \text{ThC} + 2\text{W} = \text{W}_2\text{C} + \text{Th} \]

5.7. METAL FORMING

Tungsten in the pressed-and-sintered condition or as wrought structure, especially in sheet form, can be further formed by special processes into final shapes. Examples are solid-fuel rocket nozzle liners and some other parts for which the refractory property combined with light weight are essential. The forming processes are generally ring rolling, spinning, and sheet forming, which will be described in the following subsections.
5.7.1. Ring Rolling

This process usually requires starting preforms in cylindrical form. A ring mill consists essentially of a pressure roll and a bearing column (Evans and Tsung, 1962a). During rolling, one roll bears on the inner surface of the thick-walled cylindrical workpiece, and the other bears on the opposite side of the same section. The preforms are usually pressed and sintered to a density above 93% of theoretical with some grain refiners such as alkali-silicate doping agents. Either straight-walled cylinders or rings having a curved wall with a convergent-divergent configuration can be rolled into shapes. Upsetting the rings between ring rolling operations is helpful to flatten the end surfaces and prevent cracking. The processing temperature ranges from 1427 to 1649°C (2600 to 3000°F). The microstructure of the ring-rolled nozzle liners, not like that of forged ones, is generally of the fibrous wrought structure.

5.7.2. Spinning and Shear Forming

Spinning is a process in which a metal sheet is fixed to and rotated with a mandrel. A roller applies pressure to one side of the sheet, which is then formed into a conical shape according to the shape of the mandrel (Wilkinson, 1970). The formability of the sheet depends largely on its ability to withstand bending stresses, since there is little reduction in thickness. During spinning, torch heat at a temperature of 800–1100°C (1472–2012°F) is generally required. The starting material should have a small-grained wrought structure, and after every 4% reduction, an intermediate anneal is necessary for stress relief (Henning and Strohecker, 1966).

Another sheet-forming process is shear forming, which is also called power spinning, flow turning, roll forming, compression spinning, or rotary extrusion. In shear forming (Wilkinson, 1970), the metal sheet is not only to conform to the shape of rotating mandrel, but it is also thinned by the pressure applied by the roller head. Some machines have one power-fed forming roller, others may have three, which are 120° apart from each other. The radial pressure applied by the rollers against the metal sheet over the mandrel is as high as 141 kg/mm² (200 ksi). In the forming of tungsten, one may use enamel frits, metal, or glass coatings as lubricants. Since shear forming, just like spinning, must be performed above the ductile–brittle transition temperature, local heating with a gas torch flame just ahead of the roller is necessary during the operation.

The starting material for shear forming may be pressed-and-sintered or as-wrought by forging, extrusion, and rolling. The reduction in thickness ranges from 20 to 25% and the shapes of 90° cones, truncated cones, and cylinders can be made. The operating temperature is between 800 and 1150°C (1472 and 2102°F). High-purity arc-cast and rolled tungsten sheet is more amenable to shear forming than sheet rolled from powder metallurgy bars (Boulger and Sabroff, 1964).

Starting with ring-rolled powder metallurgy material, 0.5-mm (0.020-in.)-thick wall × 305-mm (12-in.)-I.D. cylinders were produced by shear spinning (Worcester,
1965). It was noted that maintaining a uniform temperature through the thickness of the sheet during spinning was essential to achieving good gauge tolerance. An intricate form of convergent–divergent rocket nozzle liner has been produced by a combination of spinning and shear forming with total thickness reduction of 75% (Banta, 1961).

5.8. TUBE FABRICATION

Tungsten tubing has been in demand because of its high-temperature strength and corrosion-resistant properties, and small-diameter thin-wall tubes have special applications in nuclear reactors. The fabrication of such seamless tubing is one of the most formidable problems for metallurgists, not only because of the unusually high strength, but also because of the high ductile–brittle transition temperature of tungsten.

The starting material for unalloyed tungsten may be pressed and sintered, arc cast, or vapor deposited. Vapor-deposited tungsten is more fabricable than others, and it may be worked without primary breakdown. Pressed-and-sintered tungsten, however, is generally used in production because of its lower cost and its better fabricability than arc-cast material.

Tungsten alloy W–25 Re is preferable over unalloyed tungsten for tube fabrication, mainly because of the better ductility of the alloy. However, due to the very high cost of rhenium, the application of W–25 Re alloy is rather limited. W–30 at % Re–30 at % Mo ("at %" designates atomic percent; this alloy expressed in weight percent is W–33.3 Re–19.2 Mo) being more ductile, but of lower strength than unalloyed tungsten, is also used in the tube fabrication. However, due to the difficulties in separating the molybdenum core material from the tube after fabrication, as described below, the ternary alloy is less desirable. The primary fabrication process is either single or double extrusion, and the second fabrication process consists of drawing and/or tube reduction.

5.8.1. Tube Extrusion

The extrusion press used is the same as that for rod or bar extrusion as mentioned in Section 5.2. Extrusion temperature ranges from 1000 to 2000°C (1832 to 3632°F), but 1020–1200°C (1866–2192°F) is preferred. The tube blank thus produced should be annealed at 1450°C (2642°F) for 1 hr for full recrystallization before secondary fabrication. Extrusions performed at 1800°C (3272°F) or above can be drawn in the as-extruded condition without annealing (Iserow et al., 1965). The full recrystallization temperature for W–25 Re and W–30 at % Re–30 at % Mo ranges from 1500 to 1700°C (2732 to 3092°F).

Extrusion dies may be machined from cast H-12 tool steel and hardened to Rockwell C47–52. At extrusion temperatures above 1200°C (2192°F), it is necessary to coat the die with zirconia or to place a molybdenum alloy, TZM (MO–0.5Ti–0.08 Zr–0.02 C), insert in order to prevent serious die wash. The plasma-sprayed zirconia-coated dies usually will last two extrusions, after which the die should be recoated.
The steel die bodies require rehardening after three to five extrusions.

The starting tungsten sleeve size ranges from 63.5 to 12.7 mm (2.5 to 0.5 in.) O.D. with wall thickness about 10% of the diameter and with a length of 102–203 mm (4–8 in.). A molybdenum core is generally placed inside the sleeve, both of which are sealed inside a steel or molybdenum can. A more sophisticated billet is comprised of a tungsten sleeve, inner and outer molybdenum fillers, a graphite core, and a steel can. The outer molybdenum filler should have a wall thickness at least twice that of the tungsten sleeve. The steel can, comprising about 30% of the billet cross-sectional area, is made thick enough to reduce the overall stiffness of the billet. However, a steel can without the molybdenum outer filler is too soft at 1200°C (2192°F), which results in failure during extruding.

A standard process reported by Isserow et al. (1965) is operated at 1200°C (2192°F) with a reduction ratio of 16:1 and a ram speed of 51–107 mm/sec (2–4.2 in./sec) with an extrusion constant \( K = 28.1–50.6 \text{ kg/mm}^2 \) (40–72 ksi), where

\[
K = \frac{P}{A \ln R}
\]

(5.13)

where \( R \) is the reduction ratio, \( P \) is the running extrusion force, and \( A \) is the liner area. Lubrication may be provided by a copper can with a 1.6-mm (0.063-in.) wall coated with aquadag, which is placed in the liner prior to extrusion. Glass or mica pads may be used as die lubricant.

W–25 Re can be extruded at temperatures 1400–2000°C (2552–3632°F) without noticeable difference in subsequent drawing behavior. In this case, sheaths made of TZM should be used rather than steel. \( K \) ranges from 16.9 to 43.6 kg/mm² (24 to 62 ksi) as extrusion speed ranges from 51 to 279 mm/sec (2 to 11 in./sec). Note that the extrusion constant for W–25 Re is generally less than that for unalloyed tungsten; this is attributed to the fact that the alloy is extruded at higher temperatures.

The steel sheath is removed by pickling in a hot solution composed of equal volumes of water and concentrated nitric acid. The TZM can and the molybdenum filler can be dissolved in a solution of water–nitric acid–sulfuric acid with a volume ratio of 2:2:1 at 55°C (131°F). Alloy W–30 at % Re–30 at % Mo may be extruded at 1100°C (2012°F). However, this alloy is strongly attacked by aqua regia and other acids used for filler pickling and consequently is not generally used for tube extrusion. Graphite cores can be drilled out mechanically to expose the molybdenum inner filler for acid leaching. For small extrusions with diameters near 2.54 mm (0.1 in.), the graphite core is no longer practical, since it cannot be removed mechanically. Calcium carbide or hafnium cores have been used, although no standard technique has been established. The final extruded tubing size ranges from 3.18 to 21.3 mm (0.125 to 0.840 in.) O.D. with 10% wall thickness.

### 5.8.2. Tube Drawing

After extrusion and annealing, the second fabrication process — either tube drawing or tube reducing — is employed. The equipment and dies for tube drawing
are similar to those for rod and wire drawing. The various techniques of tube drawing are deformable mandrel, moving mandrel, stationary mandrel (plug), and drawing without a mandrel (sinking) (Isserow et al., 1965).

The deformable mandrel process is generally preferred, because it reduces both the diameter and the wall thickness, while the deformable core provides internal support and prevents cracking and folding at the inner surface. It also allows higher reductions between anneals than is possible with stationary-mandrel drawing. This process also gives a rather uniform diameter, but the wall becomes more irregular than that produced by either stationary- or moving-mandrel methods. The molybdenum core left from coextrusion of the “filler billet” may be used as the mandrel; otherwise, a molybdenum or TZM core should be inserted for this purpose. Starting with a tube diameter ranging from 6.35 to 10.20 mm (0.250 to 0.400 in.) with wall thickness 8 to 12% of the diameter, the drawing temperature is best performed at 570–580°C (1058–1076°F). A reduction per pass ranging from 6.0 to 24.4%, with a cumulative reduction of 38.2%, can be achieved. The drawing speed ranges from 838 to 940 mm/min (33 to 37 in./min), with a \( K \) value ranging from 49.2 kg/mm² to 112.5 kg/mm² (70 to 160 ksi), where

\[
K = \frac{P}{\ln R}
\]  

(5.14)

where \( R \) is the reduction ratio, obtained by dividing the finished length by initial length of the tube, and \( P \) is the average drawing force per unit cross-sectional area.

For W–25 Re, drawn at the same temperature as that for unalloyed tungsten, the reduction is about 3% per pass at a speed of 762 mm/min (30 in./min), with \( K \) values being about 633 kg/mm² (900 ksi). The high drawing force and low reduction obtained are due to the high strength of the alloy. The core or the mandrel are removed by techniques previously mentioned for tube extrusions.

For moving-mandrel drawing, hardened M-1, M-2, M-3, or T-1 tool steel mandrels can be used satisfactorily up to 650°C (1200°F). The mandrel is usually gripped and pulled through the die until it engages an internal shoulder on the tungsten tube, which is then also pushed through the die. Since the mandrel does not deform, control of wall thickness and inside diameter with concurrent surface smoothing can be accomplished.

This process is performed at 580°C (1076°F), with a reduction ranging from 5.0 to 46.2% per pass. The \( K \) value ranges from 141 to 506 kg/mm² (200 to 720 ksi) with a speed of 76–1524 mm/min (3–60 in./min). Using the same temperature for W–25 Re, the reduction ranges from 20.6 to 28.1% per pass, with a \( K \) value of 176–457 kg/mm² (250–650 ksi).

The mandrel can be removed by reeling or pickling. In a two-roll reeling machine, one roll is mounted on a cross-feed slide, which permits adjustment of roll spacing and pressure. The axes of two rolls are set at an angle to each other, and the angular settings are variable in parallel planes, thus permitting adjustment in the rate of translation of the tube and in the roll contact area. During operation, the rolls rotate the tubing while squeezing the wall between the rolls and the mandrel. This squeezing thins the wall slightly and increases the circumference, thus loosening the contact between the mandrel and the tube.
In stationary-mandrel drawing, the tip of the mandrel is fixed in the die land and the tube is drawn through the annular clearance between the mandrel and the die. Wall thinning with improvement of the inner surface results as in the moving mandrel process and the problem of mandrel removal is avoided. The mandrel material is the same as that used for moving mandrel drawing. Although requiring a large draw force, which often causes breakage of the tubing, this technique shows the most promise for producing long lengths of precision tubing. Tubes about 711 (28 in.) long have been produced thus.

At a drawing temperature of 580°C (1078°F), a reduction ranging from 4.4 to 18% per pass with a total reduction of up to 43.2% can be achieved. The K value ranges from 148 to 752 kg/mm² (210 to 1070 ksi) as the speed ranges from 432 to 1016 mm/min (17 to 40 in./min). For W–25 Re tubing, reduction per pass ranges from 1.8 to 12.5% with a total reduction of 41.0% can be performed. The K value ranges from 148 to 2461 kg/mm² (210 to 3500 ksi) with a drawing speed of 762 to 1016 mm/min (30 to 40 in./min).

When the tube is drawn without a mandrel, the diameter of the tube is reduced while the wall thickness remains the same or increases to some extent. This may cause heavy surface striations, which act as stress risers and result in cracking of the tube. After each pass, a stress relief annealing at 940 to 1100°C (1724 to 2012°F), for half an hour is necessary. For unalloyed tungsten drawn at 580°C (1076°F) the reduction per pass ranges from 1 to 6% with which a total reduction of 51.5% can be achieved. The K value ranges from 28.1 to 485 kg/mm² (40 to 690 ksi) as the drawing speed ranges from 102 to 1524 mm/min (4 to 60 in./min).

For W–25 Re tubing extruded at the same temperature as that for unalloyed tungsten, the reduction ratio per pass ranges from 0.8 to 6.6%, with which a total of 42%, reduction can be accomplished. The K value ranges from 309 to 2109 kg/mm² (440 to 3000 ksi) as the drawing speed ranges from 508 to 1016 mm/min (20 to 40 in./min).

For all drawing processes mentioned above, a satisfactory operation depends largely on a successful pointing technique for the tube end. Because of the brittleness of tungsten, swage-pointed tubing cannot be gripped directly for drawing. Instead, molybdenum alloy TZM is used as an insert inside the tube. For W–25 Re, the insert is left inside after extrusion and the end is gripped during drawing. For unalloyed tungsten, a protruding TZM insert is brazed into the swaged end and the protrusion is gripped. During drawing, a lubricant (generally a mixture of graphite powder, sugar, and methanol) is applied to the inner and outer surfaces of the tube. Aquadag may be used as a final coating.

5.8.3. Tube Reduction

Tube reduction is generally an intermediate step between extrusion and drawing in the tube fabrication process. However, due to the special behavior of tungsten as mentioned above, this intermediate step is not applicable. On the other hand, it may be used as a method for producing final sizes of tubing. A Pilger tube reducer consists of two rolls with tapered grooves (Geleji, 1967). With the tube blank on the mandrel, the feeder pushes the mandrel slowly toward the rolls. When the
tube reaches the rolls, a part of the tube is gripped and reduced by the working portion of the groove. After half a revolution of the rolls, the tube is released by the rolls and the mandrel suddenly jumps forward while it rotates around its axis. Because of the rotation of the mandrel and the tube, the concentricity of the tube is maintained during reduction.

Another type of tube reducer, called a rocker, consists of two cam-shaped rolls situated in a saddle that moves forward and backward while the rolls rotate so that the diameter of the groove matches that of the tapered mandrel. The tube advances a definite distance after each stroke while it rotates around its axis through a predetermined angle.

A newly developed Argonne three-roll tube reducer (Mayfield and Brak, 1967) consists of a reciprocating housing with three tapered guide tracks. A carrier for the three rolls is attached to a piston plate, which is driven by a mechanical linkage at half the reciprocating speed of the housing. The tube to be reduced is slipped over the mandrel, whose opposite end is held in a feed-index mechanism. The rolls travel along the tapered tracks so that the tube is reduced. After each pass, the tube is simultaneously advanced and rotated.

Tubing is subject to lower tensile stresses by tube reduction methods than by drawing. Tubes of tungsten and its alloys should be reduced at temperatures comparable to that for drawing. The reduction method should help to remove surface striations from the extrusion operation, eliminate lubrication problems, and avoid the swage-point failures that occur during preparation of the tube end for the drawing operation.

5.8.4. Chemical Vapor Deposition

Chemical vapor deposition (CVD) processes for the consolidation of tungsten have been described in Sec. 4.4.6. Because of the high costs and difficulties encountered in producing seamless tubing by the reduction and drawing methods described above, the CVD process for tube production has drawn much attention in the industry in recent years. CVD tungsten tubing in the as-deposited condition is more ductile than either arc-cast or powder metallurgy tungsten, so that it may be used as the end product. In addition, it can be extruded, reduced or drawn to final size with further improved properties.

During deposition, thin-wall stainless steel tubing may be used as the mandrel with a thermocouple installed inside the tube for temperature monitoring. The power supply should be controlled to maintain the desired deposition temperature. Uniformity of deposition is enhanced by the electrical resistance behavior of the tube substrate. Areas that are low in tungsten have a higher current density, which raises the temperature locally and thus increasing the rate of deposition at the area. For a 5.1-mm (0.2-in.)-I.D. tube deposited at 650°C (1202°F), 100 cm³/min. (6.1 in.³/min.) WF₆ with 2100 cm³/min (128 in.³/min.) hydrogen at a pressure of 10 Torr will give a deposition rate of 0.14 mm/hr (0.0055 in./hr) along a 231-mm (9.1-in.) length at an efficiency greater than 90%. At this deposition rate, 1016 mm (40 in.) of tubing can be produced per day with a wall thickness of 0.76 mm (0.030 in.) (Martin et al., 1967). Due to the difference in coefficient of expansion between the stainless steel mandrel
and the tungsten deposit, the tungsten tube can be removed readily from the stainless steel mandrel after cooling. The inner surface is generally very smooth, and the outer surface may be ground in order to improve the surface finish.

For a process aiming at a wrought structure, a heavy-wall starting CVD tube shell may be used. A 7.6-mm (0.3-in.)-thick layer may be deposited inside a TZM sleeve or on the outside of a molybdenum core. This deposited product together with the core or sleeve may be extruded and drawn to final size. The microstructure in the as-deposited condition is generally columnar; in the extruded condition, partially recrystallized; and, after drawing, it is a completely wrought structure.

In order to improve the as-deposited structure, a rubbing or brushing device may be installed in the deposition chamber. This is usually accomplished with a small water-cooled rod having a tungsten carbide face or with a small brush of tungsten bristles that are blanketed with hydrogen to avoid deposition (Holman and Huegel, 1967). The local deformation along the path of rubbing or brushing causes nucleation of new crystalline sites, resulting in randomly oriented crystals. Using ring specimens for testing, Holman and Huegel (1967) reported that the tensile properties of the brushed CVD tungsten are comparable to those of wrought tungsten. The CVD process can also be applied to W–Re and W–Re–Mo alloys.

5.8.5. Comparison of Tube Fabrication Processes

An alternative to seamless tubing is welded tubing. The starting billets are extruded into sheet bars and then rolled into thin sheets, which are then formed and welded into tubing. The tubing is further worked by drawing to convert the welded area from a recrystallized into a wrought structure. Normally, welded tubing thus produced is 20% to 30% less expensive than seamless tubing.

The major cost of any mechanically formed tubing is due to the many fabrication steps. However, tubing can be made by the CVD process with relatively inexpensive equipment and with few mechanical steps. Tungsten as WF₆ costs two to three times more than tungsten powder, but the higher cost is offset by the lower costs of CVD than the operations of melting, sintering, extrusion, and drawing. If CVD is used to produce tube shells that are then extruded, drawn, etc., then the total cost increases and approaches that of the conventionally fabricated products (Martin et al., 1967).

5.9. DESCALING AND CLEANING

During the process of fabrication, one should remove grease, oxides, and contaminants by degreasing and pickling. In general, heavy oxide layers for most metals are so dense that they can only be removed by mechanical means, such as abrasive blasting, belt grinding, or wire brushing. Since tungsten oxides are porous, they can be removed by pickling alone. If mechanical means are used, however, special precautions are required. For example, when a tungsten plate is subjected to abrasive blasting on one side for an extended length of time without changing to the other side, the thermal stress caused by the temperature gradient across the thickness of the plate may be so severe that cracking or breaking may result.
For heavy oxide layers, a two-step pickling process is employed. The first pickling solution is molten sodium hydroxide, used either alone or with an addition of 10% NaNO₃ or NaNO₂ or with 0.5–2.5% NaH (Gurklis and McGraw, 1961). The operating temperature is usually 343–399°C (650–750°F), and the immersion time is from 5–20 min or until the bubbling reaction stops. When the workpiece is removed from the caustic, it is immediately rinsed with a jet of hot water in order to blast off the dissolved material and attached caustic soda.

The second step of pickling is usually performed in an acid mixture of 70 vol % of concentrated HNO₃, 10 vol % of concentrated HF and 20 vol % of water, although it has been reported that the most effective acid mixture is 40 vol % HNO₃ and 60 vol % HCl (Robbins, 1957). The mechanism of acid pickling is that the metal surface is first oxidized by the nitrogen dioxide generated by HNO₃, and then the oxide is dissolved in HF. For thin films of oxide or “blue stains,” only acid pickling is required.

Electrolytic etching may be used instead of the chemical pickling mentioned previously; this is usually useful for the preparation and activation of tungsten before electroplating. The electrolytes and processes employed are generally as follows: (1) acid electrolyte, aqueous solution of 5–50 % HF, using 5 V, 60 Hz alternating current (Cannizzaro, 1948); (2) caustic electrolyte, aqueous solution of 1–10% NaOH or KOH, preferably in the range of 2–4%, with a nickel cathode, using a current density of 0.023 A/mm² (15 A/in.²) (ASM, 1973).

When grease is the contaminant during fabrication, it may be cleaned by an ordinary solvent such as methylene chloride or 1,1,1-trichloroethane. After cleaning or pickling, surface or edge cracks may appear, and they should be removed by grinding or cutting before further working.

5.10. JOINING

Difficulties encountered in the forming of tungsten increase the need for joining techniques in order to produce tungsten parts. On one hand, parts used at elevated temperatures, such as rocket nozzles and leading-edge components, require joining seams that withstand the high service temperature without failure; on the other hand, for parts such as thermionic emitters, which are used at lower temperatures, elevated temperature failure is not expected, but low-temperature ductility is crucial.

Before joining, the first step is degreasing, as mentioned in Sec. 5.9; the second step is cleaning to remove any oxide films or layers. This is done using the pickling methods mentioned previously or by heating the workpiece in a hydrogen atmosphere at 538°C (1000°F) or above. Joining methods include mechanical joining, fusion welding, resistance welding, brazing, diffusion bonding, vapor deposition, and combination of these.

5.10.1. Fusion Welding

Fusion welding may be performed using either tungsten arc or electron beam. In the former case, a vacuum chamber evacuated and backfilled with helium or
argon is generally used. Thermal shock during welding will often cause fractures, which can be avoided by preheating above the ductile–brittle transition temperature, approximate 150°C (302°F). For small welds, 3.05 mm (0.120 in.) wide in a 3.18-mm (0.125-in.)-thick sheet, a speed of 381 mm/min (15 in./min) is generally satisfactory. For large welds, the welding speed should be slower (Lesmann and Gold, 1969). Welds in arc-cast tungsten are generally free from porosity, while welds in powder metallurgy material are characterized by gross porosity, particularly along the fusion line. Welds in chemical-vapor-deposited (CVD) tungsten show an unusual heat-affected zone due to the grain structure of the base metal (see Sec. 4.4.6), and cracks are usually found in the columnar grain boundaries in the heat-affected zone. This is probably caused by rapid formation and growth of bubbles due to fluorine impurities (Cole et al., 1971). In mechanically worked CVD material, the heat-affected zone of the weld has the normal recrystallized grain structure that is also typical of other materials.

W–25 Re or W–26 Re can be arc welded without preheating, and, again, the powder metallurgy material exhibits some weld porosity. W–25 at% Re–30 at% Mo can also be welded without preheating, but a high-temperature stress relief near the recrystallization temperature is needed before welding. Without a sufficient stress relief, severe cracking may occur at the center line. Powder metallurgy products of this ternary alloy also show weld porosity.

The ductile–brittle transition temperature of the arc welds of unalloyed tungsten range from 325 to 385°C (617 to 725°F), as compared with 150°C (302°F) for the base metal. A stress-relief anneal at 1000–1800°C (1832–3272°F) after welding will reduce the ductile–brittle transition temperature substantially.

The equipment used for electron-beam welding is similar to that used for electron-beam melting (see Sec. 4.4.7), except that the gun is simpler and the size and power of the beam are generally smaller. The welding is usually carried out at 100–200 kV with 10–40 mA of current in a vacuum of 10⁻⁵ Torr or better. Electron-beam welding gives a higher ratio of depth to width and a narrower heat-affected zone than does arc welding.

Unalloyed tungsten may be electron-beam welded with or without preheating, although preheating to the ductile–brittle transition temperature is generally recommended. W–Re and W–Re–Mo alloys can be welded without preheating. Electron-beam welds in alloyed or unalloyed powder metallurgy products show some porosity, as do the arc welds mentioned above.

### 5.10.2. Resistance Welding

In the resistance welding process, the two sheets to be joined are placed between two electrodes and a current is passed through the electrodes. Because the resistance is highest at the contact point between the sheets, the material at the interface reaches the melting temperature first and forms the weld after solidification. An alternative method is to heat to a temperature below the melting point and to effect a pressure through the electrodes.

Resistance spot welding has been used to join tungsten parts for electron tubes. A common practice is to make use of interlayer metal foils or of plating of
columbium, titanium, iron, or nickel, to ease the joining problems. High electrode pressures are recommended to alleviate the problem of electrode-to-work sticking. Resistance spot welding is limited to very thin sheets or wires.

A newly developed method, called fiber metal resistance welding, is accomplished by placing a piece of fiber metal sheet between the surfaces to be welded. The fiber metal sheet is prepared by suspending short lengths of metal fibers in glycerine and felting to produce a porous body. The body is then pressed and sintered (Schwartzbart, 1961). The fibrous mat presents a multiplicity of contact resistances, and the metal in the mat can reach its melting point while the base metal remains relatively cold. For tungsten, it is advantageous to formulate the mats of dissimilar metal fibers in the desired proportions to yield a filler alloy of lower melting point than that of the base metal. Thus, tungsten can be joined below its recrystallization temperature. In a strict sense, this process should be called a fiber metal resistance brazing.

5.10.3. Brazing

In conventional brazing practice, a low melting point metal or alloy is used as the filler material and various means such as gas–tungsten–arc or electron beam are used to supply the necessary heat. A list of brazing filler metals is shown in Table 5.6 (Griffing, 1971). Selection of appropriate filler metals is based on their wettability to the base metal. The melting temperature of the filler metal should also be considered, because a relatively long time at the brazing temperature may alter the grain structure and, hence, the properties of the base metal adjacent to the brazed joint. The disadvantage of the conventional brazing method is that the service temperature of the joint is limited to the melting temperature of the filler material.

For high-temperature applications, alloys of molybdenum, rhenium, rhodium, osmium, ruthenium, iridium, tantalum, tungsten, etc., may be used for filler materials. It is found that the W–2 Os, W–50 Mo–3 Re, and Mo–5 Os are suitable for brazing tungsten for thermal nuclear-reactor service to 2500°C (4532°F) in a hydrogen atmosphere (Moore et al., 1967).

Some parts, such as the ion emitter module for space vehicles, operate at a very high temperature, and a leak-free bond between a porous tungsten ionizer and a refractory metal plenum chamber present special problems in joining. A porous structure is metastable at elevated temperatures and densification may result at 1100°C (2012°F) by the addition of a small percentage of nickel or palladium (see Sec. 4.2.3.3). It has been found that brazing with rhodium or its alloys, e.g., Mo–40 Rh, results in a sharp interface between the brazing material and the porous tungsten and a lack of infiltration by liquid rhodium. This is attributable to the fact that the rapid reaction between tungsten and liquid rhodium causes the formation of a solid solution with high melting point, which resolidifies immediately.

5.10.4. Diffusion Bonding

In the strict sense, diffusion bonding is a process in which high pressures are applied to the metal pieces to be joined during heating. Because of the tungsten's
**Fabrication of Tungsten**

Table 5.6. *Brazing Filler Materials for Refractory Metals*

<table>
<thead>
<tr>
<th>Brazing filler metal</th>
<th>Liquidus temperature [°C (°F)]</th>
<th>Brazing filler metal</th>
<th>Liquidus temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cb</td>
<td>2416 (4380)</td>
<td>Co–Cr–Si–Ni</td>
<td>1899 (3450)</td>
</tr>
<tr>
<td>Ta</td>
<td>2996 (5425)</td>
<td>Co–Cr–W–Ni</td>
<td>1427 (2600)</td>
</tr>
<tr>
<td>Ag</td>
<td>960 (1760)</td>
<td>Mo–Ru</td>
<td>1899 (3450)</td>
</tr>
<tr>
<td>Cu</td>
<td>1082 (1980)</td>
<td>Mo–B</td>
<td>1899 (3450)</td>
</tr>
<tr>
<td>Ni</td>
<td>1454 (2650)</td>
<td>Cu–Mn</td>
<td>871 (1600)</td>
</tr>
<tr>
<td>Ti</td>
<td>1816 (3300)</td>
<td>Cb–Ni</td>
<td>1191 (2175)</td>
</tr>
<tr>
<td>Pd–Mo</td>
<td>1571 (2860)</td>
<td>Pd–Ag–Mo</td>
<td>1316 (2400)</td>
</tr>
<tr>
<td>Pt–Mo</td>
<td>1774 (3225)</td>
<td>Pd–Al</td>
<td>1177 (2150)</td>
</tr>
<tr>
<td>Pt–30W</td>
<td>2299 (4170)</td>
<td>Pd–Ni</td>
<td>1204 (2200)</td>
</tr>
<tr>
<td>Pt–50 Rh</td>
<td>2049 (3720)</td>
<td>Pd–Cu</td>
<td>1204 (2200)</td>
</tr>
<tr>
<td>Ag–Cu–Zn–Cd–Mo</td>
<td>618–702 (1145–1295)</td>
<td>Ag–Cu–Zn–Mo</td>
<td>718–788 (1325–1450)</td>
</tr>
<tr>
<td>Ag–Cu–Mo</td>
<td>779 (1435)</td>
<td>Au–Cu</td>
<td>885 (1625)</td>
</tr>
<tr>
<td>Ag–Mn</td>
<td>971 (1780)</td>
<td>Au–Ni</td>
<td>949 (1740)</td>
</tr>
<tr>
<td>Ni–Cr–B</td>
<td>1066 (1950)</td>
<td>Au–Ni–Cr</td>
<td>1038 (1900)</td>
</tr>
<tr>
<td>Ni–Cr–Fe–Si–C</td>
<td>1066 (1950)</td>
<td>Ta–Ti–Zr</td>
<td>2093 (3800)</td>
</tr>
<tr>
<td>BNI–I</td>
<td>1038 (1900)</td>
<td>Ta–V–Ti</td>
<td>1760 (3200)</td>
</tr>
<tr>
<td>Ni–Cr–Mo–Mn–Si</td>
<td>1149 (2100)</td>
<td>Ti–V–Cr–Al</td>
<td>1649 (3000)</td>
</tr>
<tr>
<td>Ni–Ti</td>
<td>1288 (2350)</td>
<td>Ti–Cr</td>
<td>1482 (2700)</td>
</tr>
<tr>
<td>Ni–Cr–Mo–Fe–W</td>
<td>1304 (2380)</td>
<td>Ti–Si</td>
<td>1427 (2600)</td>
</tr>
<tr>
<td>Ni–Cu</td>
<td>1349 (2460)</td>
<td>Ti–Zr–Be</td>
<td>1066 (1950)</td>
</tr>
<tr>
<td>Ni–Cr–Fe</td>
<td>1427 (2600)</td>
<td>Zr–Cb–Be</td>
<td>1066 (1950)</td>
</tr>
<tr>
<td>Ni–Cr–Si</td>
<td>1121 (2050)</td>
<td>Ti–V–Be</td>
<td>1249 (2280)</td>
</tr>
<tr>
<td>BNI–4</td>
<td>1066 (1950)</td>
<td>Ta–V–Cb</td>
<td>1871 (3400)</td>
</tr>
<tr>
<td>Mn–Ni–Co</td>
<td>1021 (1870)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


unique high melting point and high strength at elevated temperature, this technique has hardly met with any success at all for the metal.

However, there is another kind of diffusion bonding in the loose sense, called diffusion brazing, which is applicable to tungsten. Generally, nickel or palladium is electroplated or vapor deposited on the tungsten sheet. Another sheet of tungsten or molybdenum to be joined is held against the plated sheet by means of a vise or by spot welding and is then heat treated at 900–1100°C (1652–2012°F). Starting with 0.127-mm (0.005-in.) tungsten sheet and an electroplated film $2.54 \times 10^{-4}$ to $2.54 \times 10^{-5}$ mm ($10^{-3}$ to $10^{-6}$ in.) thick, the heat treatment to develop optimum bond strength has been found to be 90 min at 1000°C (1832°F) or 15 min at 1100°C (2012°F). Such diffusion joints, however, are inevitably accompanied by at least partial recrystallization of the base metal (Brophy et al., 1962).

### 5.10.5. Other Joining Techniques

Chemical vapor deposition can be used for the joining of tungsten. Since the operating temperature is low, from 538 to 760°C (1000 to 1400°F), recrystallization
and embrittlement of the base metal is avoided. Also, since there is no low-
temperature brazing metal used for bonding, the service temperature of the product
may be very high. It has been found that a sound joint can be made readily with
deposition from both sides onto a joint geometry having a double V shape (Disckind,
1966). The ductile–brittle transition temperature of CVD joints stress-relieved at
1000°C (1832°F) is found to be 200°C (392°F) (Cole et al., 1971).

Screws, bolts, and rivets are difficult to make from tungsten and, once made, are
very sensitive to fracture. In some instances, if their use is permissible, molybdenum
rivets may be employed. A simple but acceptable all-tungsten mechanical joint may
be made by clamping. In this method, tungsten sheets to be joined are drilled and
then clamped together with tungsten wire, which is bent into place.

5.11. MACHINING AND GRINDING

The conventional machining operations consist of turning, boring, milling,
drilling, etc. Unalloyed tungsten machining behavior varies according to its
fabrication history and density. Some tungsten alloys, such as thoriated tungsten
and W–Mo, have characteristics similar to unalloyed tungsten during machining,
while other alloys, such as copper- or silver-infiltrated tungsten are rather easily
machined. Electrical discharge machining is an alternative method to conventional
machining, especially for fragile parts. In addition to these methods, abrasive
grinding, cutting, and sawing will also be discussed in the following sections.

5.11.1. Machining

In general, when tungsten and tungsten alloys are machined, the feed should be
heavy enough to cause the chips to turn dark red; however, a preferred practice is to
heat the workpiece to 343–371°C. Presintered tungsten, heavy alloys, and copper-
or silver-infiltrated tungsten (see Sec. 8.4) can be machined without applying heat.

In machining tungsten, the possibility of chipping or cracking is high in any
discontinuous cutting operation such as milling. During drilling and tapping, the
high axial and radial forces generated tend to produce spalling and radial cracking.
In a continuous cutting process, such as turning, heat is generated due to chip
formation, and the metal immediately in front of the tool reaches a semiplastic state
that will partially overcome the difficulties mentioned above. Therefore, the turning
process is a more successful method than are other machining processes (Arzt and
Stewart, 1966).

As the turning speed is increased to a proper rate, the chips change from a short
granular shape to a continuous chip, whereupon an optimum tool life is realized.
The machine finish that can be produced by turning is never better than 1.6 μm
(63-μin. RMS). If a smoother finish is desired, the workpiece should be ground or
sanded after machining. Cutting fluids are generally not required, although they help
to cool the tool inserts and increase the tool life somewhat. Due to an extremely high
radial force generated when turning tungsten, the criteria for operation are use of low
feeds, light cuts, and high positive-rake tools.
Pressed and sintered tungsten with porosity less than 93% of the theoretical is easier to machine than the higher-density material. A green compact or presintered tungsten is even easier to machine, giving much longer tool life, as compared with that for high-density material. If applicable, powder metallurgy tungsten should be machined after presintering but before final sintering.

The machinability of commercial silver- or copper-infiltrated tungsten is better than most refractory metals and even better than mild steel. Both carbide and high-speed steel tools may be used, but the cutting speed for the latter, 91.4 m/min (300 ft/min), is slower than that for the carbide tool, which ranges from 305 to 579 m/min (1000 to 1900 ft/min). When high-speed steel tools are used, force fluctuations and vibrations are observed. When carbide tools are used, cutting forces and power requirements are low, and a surface finish of 0.406 μm (16-μin. RMS) can be obtained. At a cutting speed of 305 m/min (1000 ft/min), the tool life is around 30 min, and the tool life decreases as the cutting speed increases. Positive-rake tools are preferred for infiltrated tungsten as well as for unalloyed tungsten, because the cutting force is substantially lower and the surface finish is superior to that when negative rake is applied.

Because light metals, e.g., copper or silver, act as an excellent lubricant during machining, a patented process for machining of powder metallurgy tungsten involves the addition of copper or silver by infiltration (The Iron Age, 1964). With the sintered tungsten density of 70–80% of the theoretical, copper is infiltrated into the billet at 1343°C (2450°F) for 10 min or longer, depending upon the billet size, under a hydrogen atmosphere. After machining, the billet is heated in a vacuum furnace at 1802–1899°C (3275–3450°F) to evaporate the copper. This method is suitable for making parts for furnaces, rocket and ion engines, and plasma devices.

A deep-freeze treatment is also helping to tame tungsten to the point that it can be machined much more easily (Ziegelmeier, 1969). The best coolant is found to be a 25% by volume solution of trichlroethylene in Stoddard solvent, which is maintained at -40°C (-40°F) by dry ice or by mechanical refrigeration. The machine is protected from the coolant by a sheet of polyethylene over it. This process is applied to turning, boring, drilling, and threading, but not milling due to its intermittent cutting operations. When turning high-density tungsten, the following cutting tool geometry is recommended: back rake angle, 0°; end relief angle, 8–10°; side rake angle, 0°; side cutting edge angle, 45°; end cutting edge angle, 10°; side relief angle, 20°; nose radius when roughing, 0.381 mm (0.015 in.); nose radius when finishing, 0.127 mm (0.005 in.). Cutting speed 6.1–7.62 m/min (20–25 sfpm) is employed with a feed of 0.102–0.203 mm/rev (0.004–0.008 in./rev) for roughing, 0.025–0.051 mm/rev (0.001–0.002 in./rev) for finishing. The depth of cut is 0.635–1.27 mm (0.025–0.050 in.) for roughing and 0.127 mm (0.005 in.) for finishing.

The machinability of thoriated tungsten is superior to that of unalloyed tungsten, while the machinability of tungsten–molybdenum alloys, such as W–2 Mo and W–15 Mo, are similar to that of the unalloyed metal. The ternary alloy, W–25 at % Re–30 at % Mo, is easier to machine than unalloyed tungsten; but W–25 Re is more difficult to machine than unalloyed tungsten. This is attributable mainly to the high hardness of the binary alloy. General machining data for tungsten and its alloys are shown in Table 5.7 (Udolf, 1974).
<table>
<thead>
<tr>
<th>Operation</th>
<th>Material</th>
<th>Tool material carbide grade</th>
<th>Tool geometry</th>
<th>Depth of cut [mm (in)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turning, roughing</td>
<td>Unalloyed tungsten, &gt;96% density</td>
<td>C-2 (K-6)</td>
<td>BR: 0–5°</td>
<td>1.52–3.18 (0.060–0.125)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Unalloyed tungsten, &gt;96% density</td>
<td>C-3 carbide (K-68, K-8)</td>
<td>BR: 25–30°</td>
<td>0.25–0.38 (0.010–0.015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 25°</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>Unalloyed tungsten, &lt;93% density</td>
<td>C-2 carbide (K-6)</td>
<td>BR: 0–5°</td>
<td>?–6.35 (0.125–0.250)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Unalloyed tungsten, &lt;93% density</td>
<td>C-3 carbide (K-68)</td>
<td>BR: 0–5°</td>
<td>&gt;0.51 (0.020)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>Unalloyed tungsten, green or presintered</td>
<td>C-3 (K-68) carbide</td>
<td>BR: 0–5°</td>
<td>3.18–12.70 (0.125–0.500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NR &lt;1.59 mm</td>
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</tr>
<tr>
<td>Turning, finishing</td>
<td>Unalloyed tungsten, green or presintered</td>
<td>C-3 (K-68)</td>
<td>BR: 0–5°</td>
<td>&gt;0.51 (0.020)</td>
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<tr>
<td></td>
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<td>ER: 10°</td>
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<td>ECEA: 0–30°</td>
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<td></td>
<td></td>
<td>NR &lt;1.59 mm</td>
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</tr>
<tr>
<td>Turning, roughing</td>
<td>Thoriated tungsten, W-2 ThO₂</td>
<td>C-3 (K-68)</td>
<td>BR: 5–7°</td>
<td>3.18–6.35 (0.125–0.250)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5–10°</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
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<td></td>
<td></td>
<td>ECEA: 85–90°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Thoriated tungsten, W-2 ThO₂</td>
<td>C-3 (K-68)</td>
<td>BR: 5–7°</td>
<td>0.13–0.38 (0.005–0.015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5–10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 85–90°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>Unalloyed tungsten, or W-2 Mo, arc cast</td>
<td>C-3 (K-68) carbide</td>
<td>BR: 25–30°</td>
<td>1.60–3.18 (0.063–0.125)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 15°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0–15°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 75–80°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Unalloyed tungsten, or W-2 Mo, arc cast</td>
<td>C-3 (K-68) carbide</td>
<td>BR: 25–30°</td>
<td>0.25–0.51 (0.010–0.020)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 15°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0–15°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 75–80°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>W-25 Re</td>
<td>C-3 (K-68)</td>
<td>BR: 0°</td>
<td>1.52–3.18 (0.060–0.125)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 75°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>W-25 Re</td>
<td>C-3 (K-68)</td>
<td>BR: 0°</td>
<td>0.25–0.51 (0.010–0.020)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 75°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>Heavy alloy, W-3.5% Ni–1.5%Fe</td>
<td>C-3 (K-68)</td>
<td>BR: 0°</td>
<td>3.18–12.70 (0.125–0.500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5–10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 85–90°</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Heavy alloy, W-3.5% Ni–1.5%Fe</td>
<td>C-3 (K-68)</td>
<td>BR: 0°</td>
<td>0.13–0.38 (0.005–0.015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 5–10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SR: 0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 85–90°</td>
<td></td>
</tr>
<tr>
<td>Turning, roughing</td>
<td>Ag- or Cu-Infiltrated tungsten</td>
<td>C-2 (K-6, K-68)</td>
<td>BR: 0°</td>
<td>3.18–12.70 (0.125–0.500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NR: 0.80 mm</td>
<td></td>
</tr>
<tr>
<td>Turning, finishing</td>
<td>Ag- or Cu-Infiltrated tungsten</td>
<td>C-3 (K-68) carbide</td>
<td>BR: 0°</td>
<td>0.05–0.25 (0.002–0.010)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ER: 10°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ECEA: 0–30°</td>
<td></td>
</tr>
</tbody>
</table>

* Udolf, 1974.

* All operations may be performed dry or using heavy-duty soluble oil as cutting fluid.

* Carbide grade designations are in accordance with the Joint Industrial Council Codes. C-2 and C-3 are straight carbide abrasive resistance grades. For C-2: hardness, 92 Rockwell A; transition rupture strength (TRS), 176 kg/mm² (220 ksi). For C-3: Hardness, 92.5 Rockwell A; TSR, 141 kg/mm²
for Tungsten and Its Alloys

<table>
<thead>
<tr>
<th>Feed [mm/rev (in./rev)]</th>
<th>Cutting speed [m/min (ft/min)]</th>
<th>Surface finish, RMS [μm (μin.)]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25–0.38 (0.010–0.015)</td>
<td>42.72–91.44 (150–300)</td>
<td>3.18 (125)</td>
<td>Feed heavy enough to cause the chips to turn dark red or heat to 343–371 °C (650–700 °F)</td>
</tr>
<tr>
<td>0.18–0.23 (0.007–0.009)</td>
<td>60.96–91.44 (200–300)</td>
<td>2.54 (100)</td>
<td>Sand and polish to improve surface finish</td>
</tr>
<tr>
<td>0.38–1.27 (0.015–0.050)</td>
<td>121.92 (400)</td>
<td>3.18 (125)</td>
<td>Sand and polish to improve surface finish</td>
</tr>
<tr>
<td>0.10–0.30 (0.004–0.012)</td>
<td>274.32 (900)</td>
<td>2.54 (100)</td>
<td>Sand and polish to improve surface finish</td>
</tr>
<tr>
<td>0.15–0.30 (0.006–0.012)</td>
<td>30.48 (100)</td>
<td>3.18 (125)</td>
<td></td>
</tr>
<tr>
<td>0.08–0.15 (0.003–0.006)</td>
<td>121.92 (400)</td>
<td>0.41 (16)</td>
<td></td>
</tr>
<tr>
<td>0.18–0.30 (0.007–0.012)</td>
<td>30.48 (100)</td>
<td>1.60 (63)</td>
<td></td>
</tr>
<tr>
<td>0.08–0.18 (0.003–0.007)</td>
<td>91.44 (300)</td>
<td>0.81 (32)</td>
<td></td>
</tr>
<tr>
<td>0.18–0.30 (0.007–0.012)</td>
<td>30.48 (100)</td>
<td>—</td>
<td>Heat to 593–816 °C (100–1500 °F) during machining</td>
</tr>
<tr>
<td>0.076–0.18 (0.003–0.007)</td>
<td>60.96 (200)</td>
<td>1.78–2.03 (70–80)</td>
<td></td>
</tr>
<tr>
<td>0.18–0.31 (0.007–0.012)</td>
<td>12.19 (40)</td>
<td>—</td>
<td>Heat to 260 °C (500 °F) during machining</td>
</tr>
<tr>
<td>0.08–0.18 (0.003–0.007)</td>
<td>24.38 (80)</td>
<td>3.18 (125)</td>
<td></td>
</tr>
<tr>
<td>0.15–0.25 (0.006–0.010)</td>
<td>60.96 (200)</td>
<td>1.60 (63)</td>
<td></td>
</tr>
<tr>
<td>0.076–0.18 (0.003–0.007)</td>
<td>128.02 (420)</td>
<td>0.81 (32)</td>
<td></td>
</tr>
<tr>
<td>0.64 (0.025)</td>
<td>109.73 (360)</td>
<td>1.60 (63)</td>
<td>High-speed steel tool may be used for speed of 300 ft/min</td>
</tr>
<tr>
<td>0.03–0.13 (0.001–0.005)</td>
<td>597.12 (1900)</td>
<td>0.41 (16)</td>
<td>Sand to 8-μin. finish</td>
</tr>
</tbody>
</table>

(200 ku). The designation in the parenthesis is a Kennametal grade.

The abbreviations used in this column are designated as follows: BR, back rake; ER, end relief; SR, side rake; ECEA, end cutting edge angle; NR, nose radius.
5.11.2. Abrasive Grinding and Cutting

Abrasive wheels are used in one of the following operations: (1) hand grinding, which is used to remove spot or edge cracks formed during metal working; (2) surface grinding, which is applied to a billet or plate to improve the surface finish or to meet the dimensional requirements; (3) cylindrical or centerless grinding, applied to rods or tubes to remove cracks or to improve the surface finish; (4) cutoff, for cutting of rods, plates, or other shapes.

For unalloyed tungsten, chip removal is accomplished largely by a brittle fracture mechanism similar to what occurs when glass is cut. Imbedded thermocouples have measured temperatures reaching 1093°C (2000°F) just below the surface during grinding (Richards, 1965). If excessive heat is generated by chip removal, it will cause compressive flow, which changes to tensile stress during cooling, resulting in surface fissures or cracks, which usually propagate during further grinding.

Unalloyed tungsten with high density, above 93% of theoretical, whether produced by arc melting, sintering, or mechanical working, is the most difficult material to grind. To avoid excessive heat and consequent chipping, a rather soft grade of grinding wheel with open structure is used and a rather slow speed should be employed. Silicon carbide wheels cause less damage than aluminum oxide wheels, but produce lower reduction ratio (the ratio of the volume of stock removed to wheel wear). A hardness grade up to P with resinoid or rubber bond may be used for cutoff. This bond is preferred because of its ability to withstand bending, as opposed to the vitrified bond, which is used for other operations. Tungsten of low density, less than 90% of the theoretical, is easier to deal with. Higher hardness grade and ruby abrasive wheels may be used in some instances. For the grinding of W–25 Re, wheels with a higher hardness grade but lower feed speed are employed. This is because of the alloy’s tougher and harder properties than unalloyed tungsten.

For silver-infiltrated tungsten, it is recommended that aluminium oxide abrasive and medium hardness grade wheels be used. A typical selection of wheels and operation data for grinding are shown in Table 5.8 (Udolf, 1974).

The coolant used for grinding should provide good lubrication but should not be flooded so as to chill the workpiece. As a rule, highly chlorinated or sulfurized oil is preferred.

5.11.3. Electrical Discharge Machining and Grinding

When difficulties are encountered in conventional machining, especially in milling, the electrical discharge machining method may be used. In the electrical discharge machining process, material is removed by a series of electrical discharges (sparks) that occur in the machining gap between the electrode and the workpiece. The dielectric fluid creates a path for the discharge as the fluid becomes ionized. The small area in which the discharge occurs is heated to an extremely high temperature, so that the workpiece material is locally melted and removed. The electrode materials may be graphite, copper, brass, unalloyed tungsten, or copper- or silver-infiltrated tungsten. The dielectric fluids have traditionally been petroleum products
<table>
<thead>
<tr>
<th>Operation</th>
<th>Material</th>
<th>Abrasive</th>
<th>Grit</th>
<th>Hardness grade</th>
<th>Bond</th>
<th>Structure</th>
<th>Wheel speed [m/min (sfpm)]</th>
<th>Work speed [m/min (ft/min)]</th>
<th>In feed [mm/pass (in./pass)]</th>
<th>Cross feed [mm/pass (in./pass)]</th>
<th>G ratio</th>
<th>Surface finish [μm (μin.)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>Tungsten, high-density ²</td>
<td>Al₂O₃</td>
<td>46–60</td>
<td>G-J</td>
<td>Vitrified</td>
<td>5–8</td>
<td>610 (2000)</td>
<td>12.2–18.3</td>
<td>0.0127</td>
<td>1.27 (0.050)</td>
<td>1.5–2.5</td>
<td>0.20–0.25</td>
</tr>
<tr>
<td>Cylindrical, roughing</td>
<td>Tungsten, high-density ²</td>
<td>Al₂O₃</td>
<td>46</td>
<td>K-N</td>
<td>Vitrified</td>
<td>5</td>
<td>290 (950)</td>
<td>(40–60)</td>
<td>0.152</td>
<td>(0.0005)</td>
<td>(32–50)</td>
<td>(8–10)</td>
</tr>
<tr>
<td>Cylindrical, finishing</td>
<td>Tungsten, high-density ²</td>
<td>SiC</td>
<td>100</td>
<td>K</td>
<td>Vitrified</td>
<td>290</td>
<td>2.4 (950)</td>
<td>(4–8)</td>
<td>0.025</td>
<td>(0.1001)</td>
<td>0.10–0.15</td>
<td>0.81</td>
</tr>
<tr>
<td>Cylindrical, roughing</td>
<td>Tungsten, low-density ²</td>
<td>Ruby</td>
<td>60</td>
<td>K</td>
<td>Vitrified</td>
<td>290</td>
<td>2.4 (950)</td>
<td>(4–8)</td>
<td>0.102</td>
<td>(0.0004)</td>
<td>(4)</td>
<td>0.15</td>
</tr>
<tr>
<td>Cylindrical, roughing</td>
<td>SiC</td>
<td>W-25 Re</td>
<td>60</td>
<td>L</td>
<td>Vitrified</td>
<td>290</td>
<td>1.3–2.4 (950)</td>
<td>(4–8)</td>
<td>0.023</td>
<td>(0.0001)</td>
<td>(6)</td>
<td>0.10</td>
</tr>
<tr>
<td>Cylindrical, finishing</td>
<td>SiC</td>
<td>Ag-infiltrated tungsten</td>
<td>60</td>
<td>J</td>
<td>Vitrified</td>
<td>290</td>
<td>0.37 (950)</td>
<td>(1.2)</td>
<td>0.0025</td>
<td>(0.0001)</td>
<td>(4)</td>
<td>0.05–0.15</td>
</tr>
<tr>
<td>Cut off</td>
<td>Tungsten, high-density ²</td>
<td>SiC</td>
<td>60–120</td>
<td>K-P</td>
<td>Resinoid</td>
<td>732</td>
<td>1.5–2.4 (950)</td>
<td>(5–8)</td>
<td>0.023</td>
<td>(0.0001)</td>
<td>(2–6)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

¹ Udoff, 1974.
² High-density refers to as-cast or wrought material; generally greater than 93% of the theoretical.
³ Low-density refers to as-sintered material; usually less than 93% of the theoretical.
such as kerosene and S.A.E. 50 viscosity hydrocarbon oil. However, with metallic electrodes, the hydrocarbon fluids do not break down easily to assure the formation of an electrical discharge at each charging pulse. In this case, triethyleneglycol plus water is a preferred dielectric fluid (Springborn, 1967).

Commercial electrical discharge machining equipment with a dc power source up to 400 V and 300 A is usually equipped with a servomechanism to control the movement of the electrode. In general practice, a tolerance of $\pm 0.051$ mm (0.002 in.) can be attained.

To calculate the metal removal rate, an empirical equation may be used (Berghausen et al., 1963):

\[
R_w = 39821M_w^{-1.23} \quad \text{(5.15)}
\]

\[
V = 2.2286M_w^{-1.43} \quad \text{(5.16)}
\]

where $R_w$ is the average metal removal rate from workpiece (mm³/A-min $\times 10^4$), $M_w$ the melting point of workpiece (°C), and $V$ the average volume/discharge (mm³). A practical removal rate ranges from 16.4 to 1966 mm³/hr (0.001 to 0.120 in.³/hr).

An electrical discharge grinding machine uses a conducting grinding wheel, which is made the negative electrode. For the purpose of sawing, a saw blade is used as the negative electrode in a dielectric fluid. The principle of operation for both grinding and sawing is the same as for electrical discharge machining.

5.12. PROTECTIVE COATING

In addition to its very high melting point, tungsten also has a very high modulus of elasticity, extraordinary elevated temperature strength, and the lowest vapor pressure of all metals. One of the most serious disadvantages of tungsten is the low resistance to oxidation in air at temperatures above 1121°C (2050°F). During the initial stage of oxidation the parabolic law holds for the growth of the oxide film. For a longer duration in an oxidizing medium, there is a transition from the parabolic law to a linear one; the time for this transition depends on the temperature (see Sec. 7.2). The cause of the transition is probably due to the appearance of microscopic cracks in the oxide layer (Gulbransen and Andrew, 1960).

In order for tungsten and its alloys to operate at high temperatures, protective coatings are required. These applications include furnace components, thermocouple housings, melting equipment, plasma equipment, rocket nozzles and components, reentry nose cones and structures. The requirements imposed on materials to be used for these coatings are high resistance to oxidation, thermal stability, self-healing ability, low diffusivity of the gaseous medium in the coating material, good adhesiveness with tungsten, absence of eutectic formation and brittle intermetallic compounds with tungsten, resistance to erosion and mechanical impact, and the matching of the thermal expansion coefficient with that of the tungsten substrate, etc.
The method of applying the coating plays a significant role. It should guarantee high density, flawless coatings, and strong adhesion to the substrate. Contamination and excessive heating above the recrystallization temperature should be avoided. The methods most widely used include electrolytic deposition, plating, precipitation from the vapor-gas phase, flame and plasma spraying, and vacuum metallizing.

In general, coatings of the metals of the platinum group protect tungsten satisfactorily from oxidation for a relatively long time at temperatures up to 1650°C (3002°F). At higher temperatures up to 1950°C (3542°F), tungsten disilicide and oxide coatings of the type Ti–Zr–(Si–W)–O may be used. At even higher temperatures, brief protection is achieved with coatings of complex oxides or multiple layers of metals and oxides. These will be discussed separately in the following sections. For a more detailed review of this topic, readers are referred to Ivanov et al. (1969), Huminik (1963), and Hausner (1966).

5.12.1. Metal Coating

The principal advantages of metal coatings are their ductility and good adhesion with tungsten because of the formation of intermediate diffusion zones at the interface. The disadvantage is that few metals have a sufficiently high resistance to oxidation at elevated temperatures. The method applied here is generally electrolytic deposition.

Nickel–chromium coatings are generally used at 1000–1400°C (1832–2552°F), and noble metal coatings may be used at temperatures up to 1650°C (3002°F). A disadvantage of the latter is the high rate of interdiffusion of tungsten, platinum, and rhodium. The solid solution and intermetallic compounds obtained as the result of diffusion are characterized by brittleness and low heat resistance. The deposition of barrier layers of rhenium, ruthenium, and iridium is effective in preventing the interdiffusion from taking place (Pentecost, 1963). For even higher service temperatures, hafnium–tantalum coatings are generally used. Table 5.9 gives some details of the applied methods and service temperatures of metal coatings.

5.12.2. Refractory Oxide Coating

Refractory oxides are very stable at high temperatures in an oxidizing medium and therefore are the natural choice of coatings for tungsten. The criteria for selection are high melting point, high thermal conductivity, and low vapor pressure at the service temperature. The oxides generally used for coating are shown in Table 5.10.

The method of slurry application with subsequent sintering or fusion is usually used for oxide coatings. A disadvantage of this method is that a very low adhesive strength is obtained. The coefficient of thermal expansion of the coating material must match the substrate to prevent spalling. However, the thermal expansion coefficients of all the oxides listed in Table 5.10 except ZrO₂ are not sufficiently close to that of tungsten. Furthermore during the sintering required for this application process, tungsten may be recrystallized.
### Table 5.9. Metal Coatings for Tungsten

<table>
<thead>
<tr>
<th>Coating alloy</th>
<th>Application method</th>
<th>Temperature [°C (°F)]</th>
<th>Life (hr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–22Cr</td>
<td>Electroplating</td>
<td>900–1200 (1652–2192)</td>
<td>—</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Au+(Ni–Cr)</td>
<td>Electroplating</td>
<td>1095–1375 (2033–2507)</td>
<td>500</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Ni–Si–B–Cr</td>
<td>Electroplating</td>
<td>1095–1375 (2033–2507)</td>
<td>1–200</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Ni–Cr–P</td>
<td>Electroplating</td>
<td>1095–1375 (2033–2507)</td>
<td>1–200</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Al–Si</td>
<td>Immersion of W into melts at 1300°C (2372°F)</td>
<td>—</td>
<td>—</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Pt(127 μm thick)</td>
<td>Electroplating from cyanides</td>
<td>1650 (3002)</td>
<td>5</td>
<td>Withers, 1963</td>
</tr>
<tr>
<td>Pt–30 Rh</td>
<td>Electroplating from cyanides</td>
<td>1650 (3002)</td>
<td>5–10</td>
<td>Pentecost, 1963</td>
</tr>
<tr>
<td>Rh–Cr–Si–Cr layers</td>
<td>Electroplating (Rh), vapor deposition (Cr, Si)</td>
<td>1640 (2984)</td>
<td>1</td>
<td>Goetzal et al., 1959</td>
</tr>
<tr>
<td>HF–27 Ta</td>
<td>Electroplating, plasma spraying, etc.</td>
<td>2095 (3803)</td>
<td>—</td>
<td>Marnoch, 1965; Materials Advisory Board, 1965</td>
</tr>
<tr>
<td>HF–20 Ta</td>
<td>Electroplating, plasma spraying, etc.</td>
<td>2095 (3803)</td>
<td>—</td>
<td>Marnoch, 1965; Materials Advisory Board, 1965</td>
</tr>
<tr>
<td>HF–20 Ta–2 Mo</td>
<td>Electroplating, plasma spraying, etc.</td>
<td>2095 (3803)</td>
<td>—</td>
<td>Marnoch, 1965</td>
</tr>
<tr>
<td>Sn–25 Al, Sn–30 Al</td>
<td>Electroplating, dipping</td>
<td>1895 (3443)</td>
<td>1</td>
<td>Krier and Baginski, 1965</td>
</tr>
</tbody>
</table>

The other method of application is flame or plasma spraying, but precautions should be made to keep porosity below a limit of 5–10% of the oxide coating. When the porosity is high, the coating cannot serve as an effective barrier to prevent the substrate from oxidizing. The coatings obtained by plasma spraying have less porosity than those obtained by flame torch. Moreover, the plasma-sprayed coatings have better adhesive strength to the substrate.

### Table 5.10. Refractory Oxide Coatings for Tungsten

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting point [°C (°F)]</th>
<th>Thermal Conductivity at 1205°C (cal/cm·sec·°C)</th>
<th>Vapor pressure at 1730°C (3150°F) (atm)</th>
<th>Maximum temperature (0–100 hr) [°C (°F)]</th>
<th>Thermal expansion 25–1500°C (77–2732°F) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>2045 (3720)</td>
<td>0.013</td>
<td>5.7 x 10⁻⁸</td>
<td>1980 (3600)</td>
<td>1.37</td>
</tr>
<tr>
<td>BeO</td>
<td>2570 (4660)</td>
<td>0.041</td>
<td>~1.2 x 10⁻⁷</td>
<td>2100 (3800)</td>
<td>1.52</td>
</tr>
<tr>
<td>CeO₂</td>
<td>2645 (4800)</td>
<td>—</td>
<td>—</td>
<td>2100 (3800)</td>
<td>—</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2340 (4250)</td>
<td>~0.030</td>
<td>1.2 x 10⁻⁷</td>
<td>1800 (3272)</td>
<td>—</td>
</tr>
<tr>
<td>HfO₂</td>
<td>2805 (5090)</td>
<td>—</td>
<td>—</td>
<td>2100 (3800)</td>
<td>0.93</td>
</tr>
<tr>
<td>MgO</td>
<td>2800 (5070)</td>
<td>0.013</td>
<td>~5 x 10⁻⁶</td>
<td>1980 (3600)</td>
<td>2.23</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1730 (3140)</td>
<td>—</td>
<td>—</td>
<td>1600 (2900)</td>
<td>—</td>
</tr>
<tr>
<td>ThO₂</td>
<td>3200 (5800)</td>
<td>0.005</td>
<td>1.3 x 10⁻¹⁸</td>
<td>2280 (4150)</td>
<td>1.50</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>2410 (4370)</td>
<td>—</td>
<td>—</td>
<td>1980 (3600)</td>
<td>—</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2685 (4870)</td>
<td>0.005</td>
<td>~1 x 10⁻⁸</td>
<td>1900 (3450)</td>
<td>0.79</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1838 (3340)</td>
<td>0.008</td>
<td>—</td>
<td>1800 (3230)</td>
<td>—</td>
</tr>
<tr>
<td>Mg₂Al₂O₄</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1980 (3600)</td>
<td>—</td>
</tr>
<tr>
<td>W</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.75</td>
</tr>
</tbody>
</table>

* Pentecost, 1963.
* a The method of slurry application with subsequent sintering or fusion is usually used.
The diffusional limitation on the choice of potential oxides for oxidation protection above 2000°C (3632°F) is very severe. Of the simple refractory oxides, only alumina and magnesia are known to exhibit sufficiently restricted mobilities to qualify as protective in terms of the criterion of less than 0.254 mm (0.010 in.) growth of oxide thickness in an hour. Alumina melts at 2050°C (3722°F), and magnesia vaporizes at an enormous rate in this temperature range, sharply limiting their potential usefulness. The rare earth sesquioxides comprise the largest group of refractory oxides whose diffusive properties are known. Marker movement experiments and measurements of the growth of layers of complex oxides in diffusion couples composed of reacting simple oxides, suggest that there may be some complex oxides wherein the mobility of the diffusing species is depressed (Breet and Seigle, 1965).

Complex oxides such as SrZrO$_3$, Nd$_2$Zr$_2$O$_7$, and Yb$_{0.5}$Zr$_{5.5}$O$_2$ have been studied to determine their potential as protective coatings for tungsten at 1927°C (3500°F) (Phalen et al., 1968). These oxides are prepared by solid state synthesis. Vaporization rates at 1949°C (3540°F) are highest (10$^{-5}$ to 10$^{-6}$ g/sec-cm$^2$) in vacuum and decrease to nearly zero in oxygen or argon. The oxygen diffusion rate at 1949°C (3540°F) in SrZrO$_3$ is found to be 10$^{-6}$ cm$^2$/sec, which is considered to be a factor of 10 too high for protection of tungsten in air. These oxides will require some modification in composition or structure that will reduce the oxygen-diffusion rate even further. However, the structural stability, vaporization, and cation-diffusion properties of these oxides are satisfactory for protective coating purposes.

Multiple layer of metal oxide coatings are developed mainly in order to overcome such disadvantages of oxides as low adhesive strength, high rate of oxygen diffusion and unsatisfactory thermal stability. The coating systems identified as W+(Si–W)–O, W+Ti–Zr(Si–W)–O, and W+Ti–(Zr–B)–(Si–W)–O have good oxidation resistance. These coatings are usually applied by a pack cementation process similar to that used for silicides (see Sec. 5.12.3) and their service temperature under cyclic conditions goes to 1954°C (3550°F) (Nolting and Jefferys, 1963).

Coatings obtained by plasma spraying that consist of W and HfO$_2$ stabilized by 5% Y$_2$O$_3$ can be used at 1980–2315°C (3596–4199°F) under oxyhydrogen heating (Space Aeronautics, 1964). Coatings made of W–HfO$_2$–SrZrO$_3$, W–ThO$_2$, and Cr–HfO$_2$ are also used in an oxidizing atmospheres at temperatures up to 2760°C (5000°F) for the purpose of protecting tungsten nozzles of liquid fuel rockets or rocket noses during reentry performance (Jaffee, 1964; Rausch, 1965). Simultaneous electrolytic deposition of nickel, chromium, platinum, rhodium, and Co–W with Al$_2$O$_3$, ZrO$_2$, and SiO$_2$ in various compositions may be used for protective coatings for tungsten at 1375°C (2507°F) for 15 hr (Pentecost, 1963).

5.12.3. Carbides, Nitrides, Borides, and Silicides

As a group, the carbides, borides, nitrides, and silicides exhibit low electrical resistance, high thermal conductivity, high hardness, and high mechanical strength at elevated temperatures. They oxidize more slowly than tungsten, but not sufficiently so as to provide the desired protection, with the exception of some silicides that form a protective coating of SiO$_2$ upon oxidation. Coatings consisting
of tungsten carbide and 8% cobalt or the carbide with aluminum oxide can be used for protective purposes (Frantsevich et al., 1963).

Since the ratio between the atomic radius of silicon and tungsten, 0.84, greatly exceeds Hagg’s ratio (0.59), the compound tungsten disilicide is a substitutional phase instead of an interstitial phase, as is the case for carbides or nitrides of tungsten (Samsonov, 1959). Tungsten disilicide is generally used for protective coatings in the temperature range of 1300–1800°C (2372–3272°F), where a film of amorphous silica is formed. During the initial oxidation period, oxides of the metal and of silicon are formed on the surface of the disilicide. Some of the WO₃ dissolves in SiO₂, and a vitreous protective layer is formed. Subsequently, the access of oxygen to the surface of the disilicide is practically eliminated, and the rate of oxidation is determined by the rate of diffusion in the oxide layer. The disilicide expands below the SiO₂ film, and the lower silicide W₅Si₃ is formed with the liberation of silicon. The liberated silicon interacts with oxygen, which brings about a gradual increase in the thickness of the silica layer (Ivanov et al., 1965). The brittleness of tungsten disilicide and the continuous diffusion occurring during utilization and the conversion of the disilicide to the lower silicide limits the usefulness of WSi₂ coating applications.

A method for application of the silicide coating on a tungsten substrate is the hydrogen reduction of silicon halides on a hot surface of tungsten. The temperature ranges from 1100 to 1800°C (2012 to 3272°F) with a total pressure of 1 atm (Prokoshkin and Arzamasov, 1962). The process can be carried out more rapidly by using a glow discharge in a medium of SiCl₄ + H₂ at a temperature of 1000°C (1832°F) (Prokoshkin et al., 1965).

The method of silicification in a fluidized bed is widely used on an industrial scale (Wood, 1964). The advantages of this process are the increased growth rates of the layer and the economy thus achieved. Another method, called pack cementation, is widely used on both research and commercial scales. It consists of packing the substrate in a retort with a powder mixture of the coating element, silicon, an inert powder such as Al₂O₃ in order to prevent sintering of the pack, and an activator such as NH₄Cl or NaF. The activator reacts with silicon to form a volatile compound, which is transferred to the surface of the substrate and deposits the coating material. The process is generally performed at a temperature of 982–1204°C (1800–2200°F) under vacuum or in an inert or reducing atmosphere for 2–16 hr (Payne, 1964).

A phenomenon called “pest behavior” (an analogy with the low-temperature decomposition of tin) has been observed for silicides, as well as for aluminides and beryllides. At high and low temperatures, these materials have excellent oxidation resistance. However, in the intermediate temperature region, they disintegrate in air but not in vacuum nor in an inert atmosphere (Rausch and Simcoe, 1961). The cause of the “pest behavior” is probably due to the presence of pores and cracks. In the intermediate temperature range, the oxidation products are nonvolatile and accumulate in the pores and cracks. The formation of the oxide is accompanied by an increase in volume by a factor of 2–3, and this brings about an increase in internal stress, which, in turn, causes a rapid growth of the cracks and, ultimately, disintegration of the material (Nechiporenko et al., 1965). The “pest” phenomenon can be prevented by increasing the purity and homogeneity of the coating, and this
can be achieved by the siliconization of metals under vacuum (Sinel'nikov et al., 1956).

5.12.4. Intermetallic Compounds

Compounds in the W–Be system—WBe₂, WBe₁₂, WBe₅, and WBe₂₂—have been tested at temperatures of 1260 and 1595°C (2300 and 2903°F) (Arzhanyi et al., 1962; Pentecost, 1963). However, there are no data on the properties of the beryllide coatings on tungsten. In general, the limitations for beryllides are the high values of their coefficients of thermal expansion and the high rate of diffusion of beryllium in tungsten.

Of the aluminides, Ni₃Al shows good oxidation resistance and strength only up to 1099°C (2010°F). TiAl has been reported to have a 70.3 kg/mm² (100 ksi) strength in bending at 999°C (1830°F) and fair oxidation resistance. TaAl₃ and NbAl₃ have been observed to form a thin tough oxide scale at 1260°C (2300°F). However, the aluminides generally show poorer oxidation resistance above 1371°C (2500°F) than beryllides or silicides (Westbrook, 1960).
Physical and Mechanical Properties of Tungsten

6.1. THE ELEMENT

The properties of the nucleus and its electron cloud are discussed in this section.

6.1.1. The Nucleus

Tungsten is defined as the element whose nucleus contains 74 protons \((z = 74)\), with as few as 99 and as many as 115 neutrons. The five stable isotopes of tungsten occurring in nature are listed in Table 6.1, where atomic mass units (amu) are shown on the physical scale in which carbon isotope 12 is defined as 12.00000 amu. The

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Number of protons</th>
<th>Number of neutrons</th>
<th>Weight of atom (a.m.u.)</th>
<th>Natural abundance ((%))</th>
<th>Weight of nucleus (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{180}\text{W})</td>
<td>74</td>
<td>106</td>
<td>179.9470</td>
<td>0.14</td>
<td>179.9068</td>
</tr>
<tr>
<td>(^{182}\text{W})</td>
<td>74</td>
<td>108</td>
<td>181.9483</td>
<td>26.41</td>
<td>181.9081</td>
</tr>
<tr>
<td>(^{183}\text{W})</td>
<td>74</td>
<td>109</td>
<td>182.9503</td>
<td>14.40</td>
<td>182.9101</td>
</tr>
<tr>
<td>(^{184}\text{W})</td>
<td>74</td>
<td>110</td>
<td>183.9510</td>
<td>30.64</td>
<td>183.9108</td>
</tr>
<tr>
<td>(^{186}\text{W})</td>
<td>74</td>
<td>112</td>
<td>185.9543</td>
<td>28.41</td>
<td>185.9141</td>
</tr>
</tbody>
</table>

Weighted average: 183.8415 amu

Standard value\(^{c}\): 183.85 amu

\(^{a}\) Heath, 1969.

\(^{b}\) Calculation of nuclear mass per Thomas–Fermi model (Evans, 1955):

\[
M' = M - [Zm_e - B_z(Z)]
\]

\[
M' = M - [Zm_e - (15.73)Z^{7/3}] \text{ eV}
\]

where \(m_e = 5.110034 \times 10^{-3} \text{ eV}\) is the electron rest mass for tungsten, \(Z = 74\). Let \(\varepsilon = 1.07354 \times 10^{-9}\) [conversion factor to atomic mass units (amu/eV)]. Then

\[
M' = M - [74 \times 5.110034 \times 10^{-3} - (15.73)74^{7/3}] \text{ eV}
\]

\[
M' = M - 0.0402069 \text{ amu}
\]

\(^{c}\) 1966 international atomic weight (Weast, 1969).
atomic weight of tungsten in the older chemical scale (in which naturally occurring oxygen is defined as 16.00000 amu) is 183.86. For a complete list of tungsten isotopes and their properties, the reader is referred to Heath (1969).

6.1.2. The Atom

The energy states of electrons in the unexcited tungsten atom are shown in Table 6.2.

6.1.2.1. X-Ray Absorption Spectrum

The mass absorption coefficient for x-rays in tungsten is given as a function of wavelength in Fig. 6.1 (Cauchois and Hulubei, 1947). The intensity of the transmitted beam I after passing through a thickness t (cm) of tungsten absorber is

\[ I = I_0 \exp \left[ -\rho t \left( \frac{\mu}{\rho} \right) \right] \]  \hspace{1cm} (6.1)

where \( \mu/\rho \) can be obtained from Fig. 6.1, density \( \rho = 19.3 \text{ g/cm}^3 \) for tungsten, \( t \) is the thickness of the tungsten absorber in centimeters, and \( I_0 \) is the intensity of the incident beam.

The absorption edges in Fig. 6.1 are at 1.21552 Å for the L-series, and at 0.17838 Å for the K-series. These wavelengths represent the minimum energy required to completely remove an electron from the second orbital shell and the first

<table>
<thead>
<tr>
<th>Energy States of Electrons in the Unexcited Tungsten Atom*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron shell</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>M</td>
</tr>
<tr>
<td>M</td>
</tr>
<tr>
<td>M</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>P</td>
</tr>
</tbody>
</table>

* Cauchois and Hulubei, 1947.
orbital shell, respectively. The complete set of x-ray absorption wavelengths for tungsten is shown in Table 6.3.

6.1.2.2. X-Ray Emission Spectrum

The strongest lines of the x-ray spectrum from the International Tables for X-Ray Crystallography (Lonsdale, 1962) are shown matched with the term scheme of the energy levels of tungsten in Table 6.4. Note that the selection rules limit the possible transitions from $p$ to $s$; from $d$ to $p$; from $s$ to $p$; and from $f$ to $d$. For a complete list of all x-ray emission wavelengths of tungsten, the reader is referred to Cauchois and Hulubei (1947).

6.2. PHYSICAL PROPERTIES OF TUNGSTEN

6.2.1. Structure Properties

6.2.1.1. Crystal Structure and Lattice Constants

Alpha-tungsten is the stable form of body-centered cubic structure of type A2 or Im3m with two atoms per cell at (0, 0, 0) and $(1/2, 1/2, 1/2)$. The lattice constant is
Table 6.3. X-Ray Absorption Wavelengths for Tungsten

<table>
<thead>
<tr>
<th>Series</th>
<th>Name</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>—</td>
<td>1.7838</td>
</tr>
<tr>
<td>L</td>
<td>I\textsubscript{I}</td>
<td>1.02452</td>
</tr>
<tr>
<td></td>
<td>I\textsubscript{II}</td>
<td>1.07465</td>
</tr>
<tr>
<td></td>
<td>I\textsubscript{III}</td>
<td>1.21553</td>
</tr>
<tr>
<td>M</td>
<td>M\textsubscript{I}</td>
<td>43.74</td>
</tr>
<tr>
<td></td>
<td>M\textsubscript{II}</td>
<td>48.10</td>
</tr>
<tr>
<td></td>
<td>M\textsubscript{III}</td>
<td>54.41</td>
</tr>
<tr>
<td></td>
<td>M\textsubscript{IV}</td>
<td>65.00</td>
</tr>
<tr>
<td></td>
<td>M\textsubscript{V}</td>
<td>67.16</td>
</tr>
</tbody>
</table>

* Data from Cauchois and Hulubei, 1947. Units converted from \(kX\) to Å using the conversion factor, \(kX = 1.0020771\) Å (Cohen and Taylor, 1973).

\[ a = 3.16522 \pm 0.00009\,\text{Å} \text{ at } 25°C. \text{ The corresponding shortest interatomic distance is } 2.74116\,\text{Å}. \]

Beta-tungsten occurs only in the presence of oxygen and is probably \(W_3O\). It is stable below 630°C and is of type A15 or Pm3n with eight atoms per cell in the following positions: \(I: (0, 0, 0), (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}); II: (0, \frac{1}{4}, \frac{1}{4}), (0, \frac{3}{4}, \frac{3}{4}), (\frac{1}{4}, 0, \frac{1}{4}), (\frac{1}{4}, \frac{3}{4}, 0), (\frac{3}{4}, \frac{1}{4}, 0), (\frac{3}{4}, \frac{3}{4}, 0). \)

The lattice constant is \(a = 5.046\,\text{Å}\), with the shortest interatomic distance of \(a/2 = 2.52\,\text{Å}\).

Table 6.4. Strongest Lines of X-Ray Emission Spectrum of Tungsten\(^a\)

<table>
<thead>
<tr>
<th>Energy state change</th>
<th>Spectral line name</th>
<th>Wavelength in air (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>From (n , k_j)</td>
<td>To (n , k_j)</td>
<td></td>
</tr>
<tr>
<td>2 2\textsubscript{1}</td>
<td>1 1\textsubscript{1}</td>
<td>(K_{x_1})</td>
</tr>
<tr>
<td>2 2\textsubscript{2}</td>
<td>1 1\textsubscript{1}</td>
<td>(K_{x_2})</td>
</tr>
<tr>
<td>3 2\textsubscript{1}</td>
<td>1 1\textsubscript{1}</td>
<td>(K_{p_1})</td>
</tr>
<tr>
<td>3 2\textsubscript{2}</td>
<td>1 1\textsubscript{1}</td>
<td>(K_{p_2})</td>
</tr>
<tr>
<td>3 3\textsubscript{2}</td>
<td>2 2\textsubscript{2}</td>
<td>(L_{x_1})</td>
</tr>
<tr>
<td>3 3\textsubscript{3}</td>
<td>2 2\textsubscript{2}</td>
<td>(L_{x_2})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(L_{y_1})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(L_{y_2})</td>
</tr>
</tbody>
</table>

\(^a\) Data from Cauchois and Hulubei, 1947. Units converted from \(kX\) to Å using the conversion factor, \(kX = 1.0020771\) Å.

\(^*\) This line is a doublet with 0.179604 and 0.179421 Å components.
6.2.1.2. Density and Lattice Defects

The calculated density from x-ray diffraction lattice constant spacings is \( D_x = 19.254 \, \text{g/cm}^3 \) (or 0.69559 lb/in.\(^3\)) (Rieck, 1967). The energies of vacancy formation, migration, and annihilation in tungsten are shown in Table 6.5. Dislocation densities that have been observed range from \( 10^8/\text{cm}^2 \) for annealed rods to \( 10^{12}/\text{cm}^2 \) for as-worked foil (Rieck, 1967).

6.2.1.3. Diffusion

Since grain boundary diffusion may be much larger than diffusion through the grain, particularly at lower temperatures, observed rates of volume diffusion will depend on the microstructure of the specimen involved. At constant temperature, Fick’s second law of diffusion is

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

where \( c \) is the concentration (g/cm\(^3\)); \( t \) is the time (sec); \( x \) is the distance (cm); \( D \) the diffusion constant is equal to \( D_0 e^{-Q/RT} \), where \( D_0 \) the frequency is a constant (cm\(^2\)/sec); \( T \) is the Kelvin temperature; \( R \) is the gas constant (1.9872 cal/°C-mole); and \( Q \) is the activation energy of diffusion (cal/mole).

When single-crystal and grain boundary self-diffusion are both present, the effects are additive, since the diffusion paths are parallel. Therefore, at a given temperature, the self-diffusion coefficient for a given isotropic single-crystal material will be less than that for the polycrystalline case. Figure 6.2 shows the values for some typical cases. Bulk diffusion of thorium and carbon in tungsten are also shown in Fig. 6.2. The surface diffusion coefficients for some metals in tungsten are shown in Table 6.6.

<table>
<thead>
<tr>
<th>Property</th>
<th>Energy ( \text{ kcal/mole} )</th>
<th>Energy ( \text{ eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of formation of vacancies</td>
<td>80.0(^a)</td>
<td>3.4(^b)</td>
</tr>
<tr>
<td>Energy of migration of a vacancy</td>
<td>40.0(^c)</td>
<td>1.7(^c)</td>
</tr>
<tr>
<td>Energy of annihilation of a vacancy</td>
<td>40.0(^d)</td>
<td>1.7(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Danneberg, 1961.
\(^b\) Schultz, 1964.
\(^c\) Schultz, 1959.
\(^d\) Thompson, 1958; Schultz, 1959; Neimark and Swalin, 1960; Koo, 1961.
Fig. 6.2. Self-diffusivity of tungsten and bulk diffusivity of carbon and thorium in tungsten; (1) Andelin et al. (1965), (2) Danneberg, 1961, (3) Langmuir, 1934, (4) Samsonov, 1953, Zwikker, 1927.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$D_0$, cm$^2$/sec</th>
<th>$Q$, kcal/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium</td>
<td>0.47</td>
<td>66.4</td>
<td>Langmuir, 1934</td>
</tr>
<tr>
<td>Cerium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First atomic layer</td>
<td>0.2</td>
<td>14.0</td>
<td>Langmuir and Taylor, 1932</td>
</tr>
<tr>
<td>Second atomic layer</td>
<td>0.016</td>
<td>2.3</td>
<td>Taylor and Langmuir, 1933</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.43</td>
<td>15.2</td>
<td>Bosworth, 1936</td>
</tr>
</tbody>
</table>


6.2.2. Thermal Properties

6.2.2.1. Melting and Boiling Points, Heats of Fusion and Sublimation, Vapor Pressure, and Critical Points

The melting point of tungsten is $3410 \pm 20^\circ$C (Cezairliyan, 1972) and the boiling point is $5700 \pm 200^\circ$C (Rieck, 1967). The critical temperature, 23,000 K, is obtained by calculation, assuming that the critical pressure is 10,000 atm. The heat of fusion is $9.6 \pm 1.6$ kcal/mole, which covers a range of values found in the literature (Rieck,
1967). The heat of sublimation is \(205.5 \pm 1.1\ \text{kcal/mole}\) (Plante and Sessoms, 1973).

The vapor pressure, for the temperature range 2600–3100 K, is given by the equation (Plante and Sessoms, 1973)

\[
\log_{10} P = \frac{-45385}{T} + 7.871
\]  

(6.3)

where \(P\) is the pressure in atmospheres and \(T\) is Kelvin temperature.

The rate of vaporization in argon is exponentially related to temperature with an activation energy of 190 kcal/mole and is inversely proportional to total pressure to the 0.87 power. Figures 6.3 and 6.4 (Harvey, 1972) illustrate this relationship.

### 6.2.2.2. Thermal Expansion and Thermal Conductivity

The thermal expansion of tungsten has been investigated at low, medium, and high temperatures. At low temperatures, 40–180 K, the coefficients of linear thermal expansion of tungsten are shown in Table 6.7.

Thermal expansion at intermediate temperatures, 298–2773 K (25–2500°C), can be calculated by the equation (Conway and Losekamp, 1966)

\[
\frac{L-L_{25^\circ C}}{L_{25^\circ C}} \times 100 = A_0 + A_1 T + A_2 T^2
\]  

(6.4)
Fig. 6.4. Rate of vaporization of tungsten \( \dot{m} \) vs. reciprocal argon pressure \( P_{\text{argon}} \) at 2875 and 3015 K (Harvey, 1972).

### Table 6.7. Coefficient of Linear Thermal Expansion of Tungsten at Low Temperatures

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Data from x-ray spacings (( \alpha \times 10^6 ))</th>
<th>Data from linear expansion (( \alpha \times 10^6 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>3.7</td>
<td>3.9\textsuperscript{b}</td>
</tr>
<tr>
<td>140</td>
<td>3.2</td>
<td>3.4\textsuperscript{b}</td>
</tr>
<tr>
<td>100</td>
<td>2.3</td>
<td>2.7\textsuperscript{b}</td>
</tr>
<tr>
<td>80</td>
<td>1.8</td>
<td>2.2\textsuperscript{c}</td>
</tr>
<tr>
<td>60</td>
<td>1.1</td>
<td>1.5\textsuperscript{c}</td>
</tr>
<tr>
<td>40</td>
<td>0.4</td>
<td>0.6\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Shah and Straumanis, 1971.
\textsuperscript{b} Nix and McNair, 1942.
\textsuperscript{c} Corruccini and Gniewek, 1961.

where \( T \) is the Celsius temperature and the values of coefficients \( A_0, A_1, \) and \( A_2 \) are shown in Table 6.8.

The coefficient of thermal expansion above 2173 K (1900°C) (cm/cm – °C) is described by the equation (Petukhov and Chekhovskoi, 1972)

\[
\alpha = [(5.262 + 0.875 \times 10^{-3})T - (0.0997 \times 10^{-6})T^2 + (0.21 \times 10^{-9})T^3] \times 10^{-6} \quad (6.5)
\]

where \( T = T(°C) - 1900 \).

The thermal conductivity of tungsten is presented as a function of temperature in Fig. 6.5. The thermal conductivity as a function of relative density is shown in Fig. 6.6 (Francois \textit{et al.}, 1972).

### 6.2.2.3. Enthalpy, Specific Heat, and Entropy

The specific heat of tungsten from 0 to 3000°C is well represented by the equation (Hoch, 1969)
Table 6.8. Values of Coefficients in Eq. (6.4) for Tungsten Thermal Expansion at Intermediate Temperatures, 298–2773K

<table>
<thead>
<tr>
<th>Material</th>
<th>( A_0 )</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder metallurgy rod</td>
<td>(-8.69 \times 10^{-3})</td>
<td>(3.83 \times 10^{-4})</td>
<td>(7.92 \times 10^{-8})</td>
</tr>
<tr>
<td>Powder metallurgy sheet</td>
<td>(-4.58 \times 10^{-3})</td>
<td>(3.65 \times 10^{-4})</td>
<td>(9.81 \times 10^{-8})</td>
</tr>
<tr>
<td>Arc-cast sheet</td>
<td>(-6.76 \times 10^{-3})</td>
<td>(3.91 \times 10^{-4})</td>
<td>(8.98 \times 10^{-8})</td>
</tr>
</tbody>
</table>

* Conway and Losekamp, 1966.

Fig. 6.5. Thermal conductivity vs. temperature for tungsten: (○) Backlund, 1967; (○) Neimark and Voronin, 1968; (△) (■) R. E. Taylor et al., 1969a; (□) Vertogradskii and Chekhovskoi, 1970.

Fig. 6.6. Relative thermal conductivity \( \lambda/\lambda_0 \) as a function of relative density \( \delta \). \( \lambda_0 \) indicates the thermal conductivity at 100\% theoretical density, and the relative density is shown as a fraction of the theoretical. \( \phi \) indicates the average powder particle size in microns (Francois et al., 1972).
\[ C_p = 3R \left( 1 - \frac{\theta_D^2}{20T^2} \right) + 2bT + 4dT^3 \]  \hspace{1cm} (6.6)

where \( \theta_D \) is the Debye characteristic temperature. For \( C_p \) (cal/g·°C) and \( T \) (K), the equation is

\[ C_p = 0.032426 \left( 1 - \frac{4805}{T^2} \right) + (2.1773 \times 10^{-6})T + (5.52461 \times 10^{-13})T^3 \]  \hspace{1cm} (6.7)

The linear term in \( T \) represents the contribution by the electronic specific heat. This equation compares well with the curves plotted in the works of Rieck (1967), Smithells (1953), and Kirilllin \textit{et al.} (1962), as well as the newer data of Schmidt \textit{et al.} (1970).

Enthalpy is the integral of specific heat. Integrating Eq. (6.6) and setting 298 K as the constant of integration, which is the usual standard state for calculation, we have

\[ H_T - H_{298} = 3R \left( T + \frac{\theta_D^2}{20T} \right) - 3R \left( 298 + \frac{\theta_D^2}{20 \times 298} \right) + bT^2 + dT^4 \]  \hspace{1cm} (6.8)

In units of calories per gram we have

\[ H_T - H_{298} = 0.032426 \left( T + \frac{26.14}{T} \right) - 10.19 + (1.0884 \times 10^{-6})T^2 \]

\[ + (1.38102 \times 10^{-13})T^4 \]  \hspace{1cm} (6.9)

This equation fits the data from 1208 to 3248 K of Hein and Flagella (1968). The equation is also a good fit to data of Kirilllin \textit{et al.} (1962) from 573 to 3073 K, and an adequate fit to data of Hoch and Johnson (1961) in the range of 1373–1773 K as referred to by Rieck (1967).

The entropy at 298 K, which we have taken as the reference state, is measured as (Clusius and Franzosini, 1959)

\[ S_p(298 K) = 4.259 \times 10^{-2} \text{ cal/g·°K} \]  \hspace{1cm} (6.10)

The entropy at other temperatures can be calculated if the relation

\[ dS_p = C_p d\ln(T) \]  \hspace{1cm} (6.11)

is integrated. The previous equation for calculating specific heat yields the analytical integral.
Table 6.9. Comparison of Calculated and Measured Values of Entropy of Tungsten

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( S_p ) calculated from Eq. (6.13)</th>
<th>( S_p ) measured*</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>400</td>
<td>0.0094</td>
<td>0.0089</td>
</tr>
<tr>
<td>1000</td>
<td>0.0402</td>
<td>0.0390</td>
</tr>
<tr>
<td>1900</td>
<td>0.0640</td>
<td>0.0625</td>
</tr>
</tbody>
</table>

* Schmidt et al. (1970).

\[
S_p = \int_{298}^{T} \left[ 0.032426 \left( 1 - \frac{4805}{T^2} \right) + (2.1773 \times 10^5)T + (5.52461 \times 10^{-13})T^3 \right] d(\ln T)
\]

(6.12)

By the method of substitution of variables \( x = \ln T \), Eq. (6.12) yields the following equation from which can be calculated the standard entropy at a given Kelvin temperature \( T \) in calories per gram-degree Kelvin:

\[
\Delta S_p |_{298} = 0.03246(\ln T - 5.6971) + 77.9035 \left[ \exp \left( -2 \ln T \right) - (1.12608 \times 10^{-5}) \right]
\]

\[
+ (2.1773 \times 10^{-6})(T-298) + (5.52461 \times 10^{-13})[\frac{1}{3} \exp (3 \ln T) - (8.8212 \times 10^5)]
\]

(6.13)

For comparison, some calculated and measured values of the entropy of tungsten are shown in Table 6.9.

6.2.3. Optical Properties

Tungsten is used not only as an incandescent lamp filament but also as a comparison temperature standard in specially constructed lamps; therefore, the optical emission properties of tungsten at high temperature have been carefully measured.

Light of a particular wavelength incident on a surface is either transmitted, absorbed, or reflected. Metals are very effective absorbers of light in the visible portion of the spectrum. If the surface is hot, a metal will emit with the same efficiency that it absorbs at a given wavelength (Kirchhoff’s law). Therefore, the fraction of light of reflected \( R_\lambda \) plus the fraction of light emitted \( E_\lambda \) equals 1, i.e., \( R_\lambda + E_\lambda = 1 \). From this we see that a perfectly black body has an emissivity of 1 at the wavelength \( \lambda \) under consideration, because no light is reflected from a black body by definition.

The emissivity of an actual sample depends strongly on its surface condition. Generally, impurities such as oxides raise the emissivity above that of the pure, film-free, flat, grain-boundary-free, perpendicular metal surface.
The total heat power radiated per unit area \( P \) in watts per square centimeter is proportional to the difference of the fourth power of the absolute temperatures of source and surroundings multiplied by the mean emissivity, \( \varepsilon \) of the surface (Stefan–Boltzmann law):

\[
P = \sigma \varepsilon (T_1^4 - T_2^4)
\]

(6.14)

where \( T_1 \) is the temperature of the source, \( T_2 \) is the temperature of surroundings, and the Stefan–Boltzmann constant is \( \sigma = 5.67032 \times 10^{-12} \text{ W/cm}^2 \cdot (\text{°K})^4 \). For tungsten the experimental values of \( \varepsilon \) are well represented by the empirical equation (R. E. Taylor, 1972)

\[
\varepsilon = (-2.6858 \times 10^{-2}) + (1.819696 \times 10^{-4})T_1 - (2.1946163 \times 10^{-8})T_1^2
\]

(6.15)

where \( T_1 \) is in degrees Kelvin. Taylor gives this equation for the temperature range 1600–2800 K, but it fits well the experimental data of the literature over the range 400–3600 K. The power radiated from a clean, outgassed (above 2300 K) arc-cast specimen (in a 10^-7 Torr vacuum or lower) can be calculated. The results compared with the measured emissivity values are shown in Table 6.10.

The determination of the true temperature of a tungsten specimen by radiometry requires that consideration be given to the spectral distribution of emissivity, since as can be seen from Fig. 6.7, the emissivity of tungsten is relatively higher in the blue than the red compared to a uniform gray body. This fact means that the brightness temperature of tungsten measured at 0.65 \( \mu \text{m} \) in a disappearing-filament pyrometer will be higher than the true temperature of a gray surface in thermal equilibrium with the tungsten, and having a constant spectral emissivity.

<table>
<thead>
<tr>
<th>True temperature</th>
<th>Radiated heat(^b)</th>
<th>Emissivity calculated from Taylor (1972)</th>
<th>Measured emissivity(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^°\text{C})</td>
<td>(^°\text{K})</td>
<td>(P) (W/cm(^2))</td>
<td></td>
</tr>
<tr>
<td>3327</td>
<td>3600</td>
<td>327.4</td>
<td>0.344</td>
</tr>
<tr>
<td>2927</td>
<td>3200</td>
<td>197.0</td>
<td>0.331</td>
</tr>
<tr>
<td>2527</td>
<td>2800</td>
<td>108.2</td>
<td>0.311</td>
</tr>
<tr>
<td>2127</td>
<td>2400</td>
<td>53.3</td>
<td>0.283</td>
</tr>
<tr>
<td>1727</td>
<td>2000</td>
<td>22.6</td>
<td>0.249</td>
</tr>
<tr>
<td>1327</td>
<td>1600</td>
<td>7.72</td>
<td>0.208</td>
</tr>
<tr>
<td>927</td>
<td>1200</td>
<td>1.87</td>
<td>0.160</td>
</tr>
<tr>
<td>527</td>
<td>800</td>
<td>0.238</td>
<td>0.105</td>
</tr>
<tr>
<td>127</td>
<td>400</td>
<td>0.0042</td>
<td>0.0424</td>
</tr>
</tbody>
</table>

\(^a\) Surrounded temperature 300 K.
\(^b\) Using total emissivity calculated from R. E. Taylor, 1972.
\(^c\) Gray, 1972.
equal to that of the average emissivity of the tungsten. For example, if a gray body of emissivity $e_r = 0.283$ at $T = 2400$ K, which corresponds to the total emissivity of tungsten at 2400 K, were to radiate in thermal equilibrium (at the same power level) as a tungsten body whose temperature is measured by its brightness at $\lambda = 0.65 \, \mu m$ (the usual optical pyrometer mean comparison wavelength), then we have

$$P_{\text{gray body}} = \sigma e_{(T=2400 \, K)} T_r^4 \quad (6.16)$$

$$P_w = \sigma e_{(\lambda=0.65 \, \mu m)} T_b^4 \quad (6.17)$$

where $T_r$ is the true temperature, $T_b$ is the brightness temperature, $P_w$ is the heat power radiated by tungsten, and the Stefan–Boltzmann constant $\sigma = 5.67032 \times 10^{-12}$ W/cm$^2$-(K)$^4$.

Since, in equilibrium,

$$P_{\text{gray body}} = P_w \quad (6.18)$$

then

$$T_b = T_r \left( \frac{e_{(T=2400 \, K)}}{e_{(\lambda=0.65 \, \mu m)}} \right)^{1/4} \quad (6.19)$$
using the value of $\varepsilon$ calculated previously for tungsten at $T_w = 2400$ K and the value of $\varepsilon_4$ for $\lambda = 0.65 \mu m$ from Table 6.11 (or Fig. 6.8.), we obtain

$$T_b = \left( \frac{0.283}{0.424} \right)^{1/4} (2400) = 2169 \text{ K}$$

(6.20)

The calculation of $T_b$ from $T_w$ is done by iteration procedure, and the results are shown in Table 6.12 and plotted in Fig. 6.9. Also listed in the table is color temperature, which is the value of true temperature that a blackbody would have to achieve to radiate with the same approximate intensity distribution of wavelength (color) as tungsten. The fact that color temperature is higher than true temperature is

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>1200 K</th>
<th>1400 K</th>
<th>1600 K</th>
<th>1800 K</th>
<th>2000 K</th>
<th>2200 K</th>
<th>2400 K</th>
<th>2600 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.300</td>
<td>0.486</td>
<td>0.483</td>
<td>0.480</td>
<td>0.477</td>
<td>0.474</td>
<td>0.471</td>
<td>0.468</td>
<td>0.465</td>
</tr>
<tr>
<td>0.350</td>
<td>0.485</td>
<td>0.482</td>
<td>0.479</td>
<td>0.476</td>
<td>0.473</td>
<td>0.470</td>
<td>0.467</td>
<td>0.464</td>
</tr>
<tr>
<td>0.400</td>
<td>0.482</td>
<td>0.479</td>
<td>0.476</td>
<td>0.473</td>
<td>0.470</td>
<td>0.467</td>
<td>0.464</td>
<td>0.461</td>
</tr>
<tr>
<td>0.450</td>
<td>0.479</td>
<td>0.476</td>
<td>0.472</td>
<td>0.469</td>
<td>0.466</td>
<td>0.462</td>
<td>0.459</td>
<td>0.456</td>
</tr>
<tr>
<td>0.500</td>
<td>0.474</td>
<td>0.470</td>
<td>0.466</td>
<td>0.462</td>
<td>0.459</td>
<td>0.455</td>
<td>0.450</td>
<td>0.447</td>
</tr>
<tr>
<td>0.550</td>
<td>0.468</td>
<td>0.464</td>
<td>0.459</td>
<td>0.454</td>
<td>0.450</td>
<td>0.445</td>
<td>0.441</td>
<td>0.436</td>
</tr>
<tr>
<td>0.600</td>
<td>0.461</td>
<td>0.456</td>
<td>0.451</td>
<td>0.446</td>
<td>0.442</td>
<td>0.439</td>
<td>0.437</td>
<td>0.432</td>
</tr>
<tr>
<td>0.650</td>
<td>0.454</td>
<td>0.449</td>
<td>0.444</td>
<td>0.439</td>
<td>0.435</td>
<td>0.432</td>
<td>0.429</td>
<td>0.424</td>
</tr>
<tr>
<td>0.6563</td>
<td>0.453</td>
<td>0.448</td>
<td>0.443</td>
<td>0.438</td>
<td>0.433</td>
<td>0.430</td>
<td>0.427</td>
<td>0.423</td>
</tr>
<tr>
<td>0.700</td>
<td>0.446</td>
<td>0.441</td>
<td>0.436</td>
<td>0.431</td>
<td>0.428</td>
<td>0.425</td>
<td>0.421</td>
<td>0.416</td>
</tr>
<tr>
<td>0.750</td>
<td>0.438</td>
<td>0.433</td>
<td>0.428</td>
<td>0.422</td>
<td>0.418</td>
<td>0.415</td>
<td>0.412</td>
<td>0.407</td>
</tr>
<tr>
<td>0.800</td>
<td>0.428</td>
<td>0.423</td>
<td>0.419</td>
<td>0.418</td>
<td>0.413</td>
<td>0.410</td>
<td>0.404</td>
<td>0.399</td>
</tr>
<tr>
<td>0.900</td>
<td>0.408</td>
<td>0.403</td>
<td>0.399</td>
<td>0.394</td>
<td>0.390</td>
<td>0.386</td>
<td>0.385</td>
<td>0.381</td>
</tr>
<tr>
<td>1.000</td>
<td>0.386</td>
<td>0.382</td>
<td>0.378</td>
<td>0.375</td>
<td>0.371</td>
<td>0.367</td>
<td>0.364</td>
<td>0.360</td>
</tr>
<tr>
<td>1.2</td>
<td>0.342</td>
<td>0.340</td>
<td>0.339</td>
<td>0.337</td>
<td>0.336</td>
<td>0.334</td>
<td>0.333</td>
<td>0.331</td>
</tr>
<tr>
<td>1.28</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
<td>0.322</td>
</tr>
<tr>
<td>1.4</td>
<td>0.295</td>
<td>0.296</td>
<td>0.298</td>
<td>0.299</td>
<td>0.301</td>
<td>0.302</td>
<td>0.304</td>
<td>0.305</td>
</tr>
<tr>
<td>1.6</td>
<td>0.259</td>
<td>0.262</td>
<td>0.265</td>
<td>0.268</td>
<td>0.271</td>
<td>0.274</td>
<td>0.277</td>
<td>0.280</td>
</tr>
<tr>
<td>1.8</td>
<td>0.222</td>
<td>0.228</td>
<td>0.234</td>
<td>0.239</td>
<td>0.245</td>
<td>0.251</td>
<td>0.256</td>
<td>0.262</td>
</tr>
<tr>
<td>2.0</td>
<td>0.186</td>
<td>0.195</td>
<td>0.204</td>
<td>0.213</td>
<td>0.222</td>
<td>0.231</td>
<td>0.239</td>
<td>0.248</td>
</tr>
<tr>
<td>2.2</td>
<td>0.160</td>
<td>0.171</td>
<td>0.182</td>
<td>0.192</td>
<td>0.203</td>
<td>0.214</td>
<td>0.225</td>
<td>0.236</td>
</tr>
<tr>
<td>2.4</td>
<td>0.142</td>
<td>0.154</td>
<td>0.165</td>
<td>0.177</td>
<td>0.188</td>
<td>0.200</td>
<td>0.212</td>
<td>0.223</td>
</tr>
<tr>
<td>2.6</td>
<td>0.129</td>
<td>0.141</td>
<td>0.152</td>
<td>0.164</td>
<td>0.176</td>
<td>0.187</td>
<td>0.199</td>
<td>0.211</td>
</tr>
<tr>
<td>2.8</td>
<td>0.119</td>
<td>0.131</td>
<td>0.142</td>
<td>0.154</td>
<td>0.165</td>
<td>0.177</td>
<td>0.189</td>
<td>0.200</td>
</tr>
<tr>
<td>3.0</td>
<td>0.112</td>
<td>0.123</td>
<td>0.134</td>
<td>0.146</td>
<td>0.157</td>
<td>0.169</td>
<td>0.180</td>
<td>0.191</td>
</tr>
<tr>
<td>3.4</td>
<td>0.100</td>
<td>0.111</td>
<td>0.122</td>
<td>0.134</td>
<td>0.145</td>
<td>0.156</td>
<td>0.167</td>
<td>0.178</td>
</tr>
<tr>
<td>3.8</td>
<td>0.091</td>
<td>0.102</td>
<td>0.113</td>
<td>0.124</td>
<td>0.135</td>
<td>0.146</td>
<td>0.157</td>
<td>0.168</td>
</tr>
<tr>
<td>4.2</td>
<td>0.082</td>
<td>0.093</td>
<td>0.104</td>
<td>0.115</td>
<td>0.126</td>
<td>0.137</td>
<td>0.148</td>
<td>0.159</td>
</tr>
<tr>
<td>4.6</td>
<td>0.079</td>
<td>0.090</td>
<td>0.100</td>
<td>0.111</td>
<td>0.121</td>
<td>0.131</td>
<td>0.142</td>
<td>0.152</td>
</tr>
<tr>
<td>5.0</td>
<td>0.078</td>
<td>0.088</td>
<td>0.098</td>
<td>0.108</td>
<td>0.117</td>
<td>0.127</td>
<td>0.136</td>
<td>0.146</td>
</tr>
</tbody>
</table>

* Latyev et al., 1972.
Fig. 6.8. Normal monochromatic emissivity of tungsten at a wavelength of 0.65 μm.

Table 6.12. Temperature Scale for Tungsten

<table>
<thead>
<tr>
<th>Brightness temperature (°K)</th>
<th>True temperature* (°K)</th>
<th>Color temperatureb (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>1577</td>
<td>—</td>
</tr>
<tr>
<td>1400</td>
<td>1674</td>
<td>—</td>
</tr>
<tr>
<td>1500</td>
<td>1771</td>
<td>—</td>
</tr>
<tr>
<td>1600</td>
<td>1866</td>
<td>—</td>
</tr>
<tr>
<td>1700</td>
<td>1961</td>
<td>—</td>
</tr>
<tr>
<td>1800</td>
<td>2055</td>
<td>—</td>
</tr>
<tr>
<td>1900</td>
<td>2149</td>
<td>2080</td>
</tr>
<tr>
<td>2000</td>
<td>2242</td>
<td>2200</td>
</tr>
<tr>
<td>2100</td>
<td>2335</td>
<td>2320</td>
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<td>2200</td>
<td>2427</td>
<td>2450</td>
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<td>2520</td>
<td>2580</td>
</tr>
<tr>
<td>2400</td>
<td>2612</td>
<td>2700</td>
</tr>
<tr>
<td>2500</td>
<td>2703</td>
<td>2840</td>
</tr>
<tr>
<td>2600</td>
<td>2793</td>
<td>2960</td>
</tr>
<tr>
<td>2700</td>
<td>2886</td>
<td>3100</td>
</tr>
<tr>
<td>2800</td>
<td>2977</td>
<td>3240</td>
</tr>
</tbody>
</table>

* Computed from Eqs. (6.15)–(6.20).

b Computed from the εₜ of Latyev et al. (1972).
again a consequence of the "blueness" of tungsten light; that is, its relatively higher emissivity in the blue than in the red.

6.2.4. Electrical Properties

6.2.4.1. Electron Emission

Even at low temperatures, when the external electric field approaches $10^6$ V/cm, cold emission or field emission appears. Electrons begin to tunnel through the surface barrier by a quantum mechanical effect when the field gradient is sufficient to lower the voltage at a distance of 10 Å from the surface to that of the electrons at the Fermi level. The probability for tunneling becomes appreciable for such a triangular potential barrier of some 4.52-V-high work function and 10 Å thickness in the case of tungsten.

Fowler and Nordheim's equation for a triangular barrier (Mott and Sneddon, 1948) gives the emission current $I$ as a function of field $E$, where the work function is contained in the constant $\beta$ and $B$. 
\[ I = BE^2 e^{B/E} \]  \hspace{1cm} (6.21)

Swanson and Crouser (1967) measured the work function of tungsten in several crystallographic directions using field emission from sharp points of tungsten. Their results are presented in Table 6.13. The data compares well with data evaluated by Rieck (1967). At elevated temperature, the kinetic energy of some of the electrons in a metal exceeds the work function and these electrons leave the metal surface.

The maximum thermionic current density that can be drawn from a pure tungsten filament in the absence of field emission currents at very high voltage gradients is given by the equation (Rieck, 1967):

\[ i = 60.2T^2 \exp(-52230/T) \]  \hspace{1cm} (6.22)

where \( T \) is in degrees Kelvin, \( i \) is in amperes per square centimeter. The current density for a thoriated tungsten filament can be calculated using the following equation, based on data from Rieck (1967):

\[ i = 2.08T^2 \exp(-29051/T) \]  \hspace{1cm} (6.23)

Secondary emission of electrons begins at an energy of the incident electrons of 372 eV and reaches a peak at 700 eV (Rieck, 1967).

### 6.2.4.2. Band Theory

The free-electron model of metals treats the most weakly bound electrons as being nearly free to move about in the metal subject to wave reflections from the periodic lattice. The Pauli exclusion principle requires that two electrons not occupy identical time–energy or space–momentum coordinates; that is to say, all the

<table>
<thead>
<tr>
<th>Crystal orientation of emitter</th>
<th>Emitting plane</th>
<th>Work function (eV)</th>
<th>Temperature Coefficient ((10^3 \text{ eV }/{}^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[310]</td>
<td>(100)</td>
<td>4.59</td>
<td>—</td>
</tr>
<tr>
<td>[100]</td>
<td>(110)</td>
<td>5.15</td>
<td>-10.9</td>
</tr>
<tr>
<td>[110]</td>
<td>(110)</td>
<td>5.79</td>
<td>-17.0</td>
</tr>
<tr>
<td>[310]</td>
<td>(110)</td>
<td>5.02</td>
<td>—</td>
</tr>
<tr>
<td>[310]</td>
<td>(111)</td>
<td>4.49</td>
<td>+3.5</td>
</tr>
<tr>
<td>[310]</td>
<td>(211)</td>
<td>4.93</td>
<td>-14.3</td>
</tr>
<tr>
<td>[310]</td>
<td>(310)</td>
<td>4.21</td>
<td>-3.2</td>
</tr>
<tr>
<td>[110]</td>
<td>(611)</td>
<td>4.32</td>
<td>+5.0</td>
</tr>
<tr>
<td>Polycrystal</td>
<td></td>
<td>4.52</td>
<td>—</td>
</tr>
</tbody>
</table>

* Swanson and Crouser, 1967.
quantum numbers describing any two electrons can not be identical. This requirement limits the number of electrons per range of momentum in momentum space and therefore the number of electrons per atom in crystal lattice space. For a given metal at absolute zero temperature, the range of possible energy levels will be occupied only up to a certain point, the Fermi energy level, because of the limited number of conduction electrons available. A knowledge of the density of states and Brillouin zones of a particular lattice gives one the information required to be able to predict many of the non-structure-sensitive properties of a material. These will be discussed in the following sections.

A. The Brillouin Zone

The crystal lattice structure of tungsten is body-centered cubic. When one wishes to consider the interaction of a nearly free electron with this lattice, one needs to know the momentum \( p \) of an electron when it has a wavelength equal to the atom spacing in a given direction. This wavelength is inversely proportional to the momentum; therefore, a reciprocal lattice polyhedron can be constructed whose lattice points have a magnitude proportional to the cross-sectional crystal lattice area in a plane perpendicular to the direction of the reciprocal lattice vector \( G \). The reciprocal lattice vectors \( G \) are:

\[
G = hA + kB + lC
\]  

(6.24)

where

\[
A = 2\pi \frac{b \times c}{a \cdot b \times c} \tag{6.25a}
\]

\[
B = 2\pi \frac{c \times a}{a \cdot b \times c} \tag{6.25b}
\]

\[
C = 2\pi \frac{a \times b}{a \cdot b \times c} \tag{6.25c}
\]

where \( A, B, C \) are reciprocal lattice vectors; \( a, b, c \) are crystal lattice vectors; and \( h, k, l \) are constants.

The area of the plane passing through the origin of a reciprocal lattice polyhedron for the primitive unit cell times Planck's constant is therefore equal to the electron momentum that produces Bragg reflection in the direction normal to the plane in a crystal. This polyhedron is called the first Brillouin zone of that crystal. The second and higher-order Brillouin zones are constructed from higher-order Bragg reflection momenta (Dekker, 1957).

The dimension of the side of the cubic unit cell lattice of tungsten is (see Sec. 6.2.1.1)

\[
a_0 = 3.16522 \pm 0.00009 \text{ Å at } 25^\circ C
\]  

(6.26)
Since the equivalent positions in $\alpha$-tungsten lie on the special positions $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the distance of closest approach can be calculated as

$$|a| = |b| = |c| = \frac{3}{2}a_0 = 2.74116 \text{ Å} \quad \text{at } 25^\circ\text{C}$$

(6.27)

This is the length of the primitive translation vector of the crystal lattice.

The length of the reciprocal lattice vector $G$ can then be calculated for tungsten in any direction, say $a$, in waves per centimeter, as

$$G = 2\pi \frac{b \times c}{a \cdot b \times c} + 0 + 0$$

$$= \frac{2\pi}{2.74116 \times 10^{-8}} = 2.29216 \times 10^8$$

(6.28)

B. Density of States

The maximum possible number of electrons per unit energy interval as a function of energy is called the density of states curve. This curve has been determined for tungsten both experimentally (Shimizu, 1971) from low-temperature specific heat coefficients and theoretically (Petroff and Viswanathan, 1971) by a nonrelativistic augmented plane wave (APW) solution of the Schrödinger wave equation $H\psi = E\psi$.

C. The Fermi Surface

Augmented plane wave (APW) bond structure calculations on molybdenum and tungsten were performed by Loucks (1965a) and by Mattheiss (1965) for tungsten. They found the calculated Fermi surface of tungsten to be quite similar to that proposed by Lomer (1962). Because of the importance of spin–orbit coupling in tungsten, a fresh APW calculation of the Fermi surface including relativistic effects was performed by Loucks (1965b, 1966). He found that both the electron "lenses" along $\Gamma H$ in band 5 and the holes at $N$ in band 3 disappeared, and the size of the electron "jack" had been reduced.

Later experimental investigation by means of the de Haas–van Alphen effect (Sparlin and Marcus, 1966) and by the anomalous skin effect (Fawcett and Griffiths, 1962) mentioned no trace of the electron lens pockets in band 5. There is experimental evidence that the pockets of holes at $N$, however, are actually present, although they are much smaller than the model suggested by Loucks. For a complete discussion of the Fermi surface, see Cracknell and Wong (1973).

D. Magnetic Susceptibility

In the cgs–emu system, the magnetic susceptibility per unit volume $\chi$ is defined as

$$\chi = \frac{M}{H}$$

(6.29)
where the magnetization $M$ is the magnetic moment per unit volume in maxwells per square centimeter and $H$ is the magnetic field intensity in oersteds. The resulting magnetic induction $B$ is defined (in gauss) as

$$B = H + 4\pi M = \mu H$$  \hspace{1cm} (6.30)$$

where the permeability $\mu$ is therefore

$$\mu = 1 + 4\pi \chi$$  \hspace{1cm} (6.31)$$

The change in energy per unit volume as the field is varied from zero to $H$ is

$$\Delta E/V = -\frac{1}{2} \chi H^2$$  \hspace{1cm} (6.32)$$

Figure 6.10 from Kittel (1971) shows the temperature dependence of the magnetic susceptibility of tungsten, along with that of some other metals.

### 6.2.4.3. Electromagnetic Transport Properties

#### A. Electrical Resistivity

The high-temperature electrical resistivity of powder metallurgy tungsten of 98% theoretical density was measured by Feith (1967) and reported by Conway and Flagella (1967) in the form of two least-squares curve fits. Their equations are presented here with the third coefficients modified to match the ordinates of both curves at 1240 K and to better fit other worker's data on tungsten as reported by Neimark and Voronin (1968) in Fig. 6.11. The single crystal values of Peletskij et al. (1970) fall on this curve, as does the equation of Rieck (1967), and so do the values of Jones and Langmuir (Heath, 1969).

Our modified equation of Conway and Flagella is, for $300-1240$ K,

$$\rho = (4.33471 \times 10^{-12}) T^2 + (2.19691 \times 10^{-8}) T - (1.64011 \times 10^{-6})$$  \hspace{1cm} (6.33)$$

and for $1240-2570$ K,

$$\rho = (-4.06012 \times 10^{-12}) T^2 + (4.67093 \times 10^{-8}) T - (1.94101 \times 10^{-5})$$  \hspace{1cm} (6.34)$$

where $\rho$ is the electrical resistivity in ohm-centimeters, and $T$ is the Kelvin temperature.

At temperatures from 50 to 300 K, the electrical resistivity is given by the solution of the Grüneisen equation (Clinard and Kempter, 1968):

$$\rho = \frac{C}{M\theta_R} \left( \frac{T}{\theta_R} \right)^5 \int_0^{\theta_R/T} \frac{Z^5 \, dZ}{(e^Z - 1)(1 - e^{-Z})} + \rho'_0$$  \hspace{1cm} (6.35)$$
Fig. 6.10. Temperature dependence of the magnetic susceptibility of metals (Kittel, 1971).

Fig. 6.11. Specific electrical resistivity vs. temperature for tungsten: (1) Neimark and Voronin (1968), (2) Reimann and Grant (1936), (3) Tye (1961), (4) Fieldhouse et al. (1958).
where $T$ is the Kelvin temperature; $\theta_R$ is a characteristic temperature for tungsten, close to but not identical to the Debye temperature (here, $\theta_R = 381$ K); $C$ is a constant and equals $2.06 \times 10^{-6}$; $M$ is the molecular weight; $Z$ is a dummy variable of integration, which disappears upon integration; and $\rho_0$ is resistivity at absolute zero temperature in the absence of superconductivity. For tungsten,

$$\rho_\gamma = (2.9409 \times 10^{-11})\left(\frac{T}{381}\right)^5 \int_0^{381/T} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})} + 0.11$$

(6.36)

Table 6.14 is a tabulation of numerical solutions of the integral for several temperatures.

In the range of temperatures 6–50 K, electrical resistivity can be described by the following equation (Clinard and Kempter, 1968), with coefficients selected to fit available data:

$$\rho = (66.5 \times 10^{-12}) + (0.256 \times 10^{-12})T^{3.36}$$

(6.37)

where $T$ is the Kelvin temperature.

At temperatures near absolute zero (below 6 K), the electrical resistivity depends on crystal perfection both internally and at the surface. Size effects are also noted due to surface scattering. The resistivity is given by the equation (Wagner et al., 1971)

$$\rho = \rho_0 + AT^2 + BT^5$$

(6.38)

which is valid for the temperature range 1.5–6.0 K. The coefficients $\rho_0$, $A$, and $B$ in Eq. (6.38) are given in Table 6.15 for the single crystals measured.

B. Magnetoelastic Effects

The Hall constant has the value 10.55 cm$^3$/A-sec (Rieck, 1967).

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Resistivity (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>5.4</td>
</tr>
<tr>
<td>250</td>
<td>4.5</td>
</tr>
<tr>
<td>200</td>
<td>3.4</td>
</tr>
<tr>
<td>150</td>
<td>2.2</td>
</tr>
<tr>
<td>100</td>
<td>1.1</td>
</tr>
<tr>
<td>50</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Numerical solutions of Eq. (6.36).
Table 6.15. Values of Coefficients of Eq. (6.38) for Resistivity of Tungsten Single Crystals near Absolute Zero

| Crystal orientation on axis | Surface condition | Tungsten rod diameter (mm) | Resistivity ratio ($\rho$ / $\rho_{273\, K} / \rho_{4.2\, K}$) | $A$ [10$^{-15}$ $\Omega$-cm/(°K)$^3$] | $B$ [10$^{-15}$ $\Omega$-cm/(°K)$^3$]
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[111] Mirror</td>
<td>1.5</td>
<td>59,000</td>
<td>0.912 ± 0.002</td>
<td>6.8 ± 0.3</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>[110] Mirror</td>
<td>1.5</td>
<td>43,000</td>
<td>1.231 ± 0.004</td>
<td>7.2 ± 0.5</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>[110] Matte</td>
<td>1.0</td>
<td>30,000</td>
<td>1.780 ± 0.004</td>
<td>7.4 ± 0.4</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>[110] Matte</td>
<td>1.5</td>
<td>6,300</td>
<td>5.724 ± 0.006</td>
<td>6.2 ± 0.6</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
<td>[110] Mirror</td>
<td>3.0</td>
<td>21,000</td>
<td>0.848 ± 0.012</td>
<td>6.7 ± 0.1</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>[110] Mirror</td>
<td>3.0</td>
<td>32,000</td>
<td>0.566 ± 0.004</td>
<td>8.7 ± 0.3</td>
<td>0.8 ± 0.1</td>
</tr>
</tbody>
</table>

* Wagner et al. (1971).
* The confidence limits represent the 2σ statistical level of confidence.

C. Thermoelectric Effects

The flow of current in a metal produces irreversible joule heat. If, however, an electrical current flows along a temperature gradient, an additional heat may be produced that is reversible. Therefore, heat $Q$ is absorbed when the direction of the current $j$ or the direction of the temperature gradient $\partial T/\partial X$ is reversed:

$$\frac{l}{V} \frac{dQ}{dt} = -\mu j \frac{\partial T}{\partial X} \quad (6.39)$$

where $\mu$ is called the Thomson coefficient.

In an electrical circuit consisting of two dissimilar metals with the two junctions at different temperatures, an electromotive force (emf) appears (the Seebeck effect). This emf consists of two sources: (1) the two Thomson emf $\mu_a$ and $\mu_b$ due to the temperature gradient along metals a and b; (2) An emf due to the difference of contact potential $\pi_{ab}$ at the junctions due to the temperature difference $d\pi_{ab}/dt$. The line integral of emf around the circuit is

$$\phi = \int_T \left[ \frac{d\pi_{ab}}{dT} - (\mu_a - \mu_b) \right] dT \quad (6.40)$$

The rate of change of $\phi$ with $T$ is known as the thermoelectric power $\theta$, where $\theta = d\phi/dt$. Therefore, for two metals a and b,

$$\theta = \frac{d\pi_{ab}}{dT} - (\mu_a - \mu_b) \quad (6.41)$$

The contact potential $\pi_{ab}$ when applied to a closed circuit will produce heat $H = n j$. This effect is reversible, so that a current $j$ acting on the contact potential $\pi_{ab}$ will produce heat $H$. When the sign of the current is reversed, the heat effect is reversed. This heat effect on a junction of dissimilar metals is termed the Peltier effect.
Table 6.16. Tungsten and Tungsten–Rhenium Thermocouple Electromotive Forces at Various Temperatures for a Reference Junction at 0°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Electromotive force (mV)</th>
<th>Temperature (°C)</th>
<th>Electromotive force (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W vs. W-26 Re</td>
<td>W-5 Re vs. W-26 Re</td>
<td>W-3 Re vs. W-25 Re</td>
</tr>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.564</td>
<td>1.381</td>
<td>1.146</td>
</tr>
<tr>
<td>200</td>
<td>1.006</td>
<td>2.988</td>
<td>2.604</td>
</tr>
<tr>
<td>300</td>
<td>1.965</td>
<td>4.768</td>
<td>4.389</td>
</tr>
<tr>
<td>500</td>
<td>4.793</td>
<td>8.573</td>
<td>8.098</td>
</tr>
<tr>
<td>700</td>
<td>8.351</td>
<td>12.450</td>
<td>12.129</td>
</tr>
<tr>
<td>800</td>
<td>10.300</td>
<td>14.374</td>
<td>14.184</td>
</tr>
<tr>
<td>900</td>
<td>12.319</td>
<td>16.266</td>
<td>16.226</td>
</tr>
<tr>
<td>1000</td>
<td>14.393</td>
<td>18.120</td>
<td>18.242</td>
</tr>
</tbody>
</table>

* Omega Engineering Inc. (1975).

The electromotive forces produced by tungsten and tungsten–rhenium thermocouples at different temperatures for a reference junction at 0°C are shown in Table 6.16. For a more detailed tabulation, the reader is referred to manufacturer's brochures (e.g., Omega Engineering Inc., 1975).

**D. Superconductivity**

The zero magnetic field critical temperature below which tungsten superconducts is 0.016 K according to Triplett et al. (1973). The critical magnetic field above which tungsten is nonsuperconducting at 0 K is 1.237 Oe. The sample of tungsten upon which test values were measured had a resistivity ratio ρ(0.98K)/ρ(4.2K) of 17,000 on a ½-inch (3.2-mm)-diameter polycrystalline specimen.

**6.3. MECHANICAL PROPERTIES OF THE METAL**

As tungsten and its alloys are often used in high-temperature environments their stress–rupture, creep, and fatigue behaviors at elevated temperatures are of major concern. On the other hand, most tungsten hardware must also function at low temperatures, the low-temperature ductility is therefore also to be considered. In the following, discussions will be centered on these aspects.

To compare these mechanical properties of tungsten without referring to the purity, fabrication history, and other conditions is sometimes misleading. Generally speaking, material with a wrought structure is stronger than that with a recrystallized structure. Under similar recrystallization conditions, powder
metallurgy material has higher tensile strength than arc-cast material. Furthermore, different fabrication processes, such as extrusion, swaging, or rolling, yield different properties for the final products. As a rule, the lower the working temperature, and the higher the amount of work incorporated in the material, the higher will be the strength. Grain size and impurity content are other factors that affect the properties of the material.

Under each subsection below, general comparison data will be presented first with similar testing materials. Then, the factors that affect the particular property will be discussed.

6.3.1. Ductility at Low Temperatures

The comparison of ductile–brittle transition temperature of tungsten sheets, using 4-T bend as the testing criterion, is shown in Table 6.17. The representative data for powder metallurgy, arc-cast, electron-beam-melted, and chemical-vapor-deposited materials are plotted in Fig. 6.12.

In general, the ductile–brittle transition temperature for powder metallurgy and arc-cast materials are lower than for other materials in the wrought condition; whereas in the recrystallized condition, powder metallurgy material has the highest ductile–brittle transition temperature, and chemical-vapor-deposited material is the lowest among all materials.

Bechtold and Shewmon (1954) along with Ioshi and Stein (1970) claimed that the brittle fracture of tungsten is intercrystalline; while Wronski and Fourdeux (1964) stated that the brittle fracture of tungsten is of the mixed grain boundary and
<table>
<thead>
<tr>
<th>1-hr annealing temperature [°C (°F)]</th>
<th>Average grain diameter [mm (in.)*]</th>
<th>Interstitial impurities (ppm)</th>
<th>Thickness [mm (in.)]</th>
<th>DBTT [°C (°F)]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1099 (2010)</td>
<td>N.A.</td>
<td>57</td>
<td>46</td>
<td>1.524 (0.06)</td>
<td>77 (170)</td>
</tr>
<tr>
<td>1199 (2190)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ogden, 1962</td>
</tr>
<tr>
<td>1293 (2360)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ogden, 1962</td>
</tr>
<tr>
<td>1393 (2540)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ogden, 1962</td>
</tr>
<tr>
<td>1800 (3272)</td>
<td>0.046 (0.0018)</td>
<td>38</td>
<td>&lt;0.4</td>
<td>6</td>
<td>0.508 (0.02)</td>
</tr>
<tr>
<td>1800–2800 (4712–5072)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Allen et al., 1959</td>
</tr>
<tr>
<td>2600 (4712)</td>
<td>0.071 (0.0028)</td>
<td>4</td>
<td>7</td>
<td>14</td>
<td>1.524 (0.06)</td>
</tr>
<tr>
<td>1300 (2372)</td>
<td>0.02–0.04 (0.00079–0.0016)</td>
<td>21</td>
<td>&lt;5</td>
<td>10</td>
<td>235–280 (455–536)</td>
</tr>
<tr>
<td>2100 (3812)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Farrell et al., 1967</td>
</tr>
<tr>
<td>2300 (4172)</td>
<td>4</td>
<td></td>
<td>&lt;5</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2500 (4532)</td>
<td>15</td>
<td></td>
<td>&lt;5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1427 (2600)</td>
<td>1.8 × 10⁻² (0.07 × 10⁻²)</td>
<td>4</td>
<td>9</td>
<td>2</td>
<td>1.27 (0.05)</td>
</tr>
<tr>
<td>1649 (3000)</td>
<td>5.02 × 10⁻² (0.20 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>337 (638)</td>
</tr>
<tr>
<td>1871 (3400)</td>
<td>1.08 × 10⁻¹ (0.043 × 10⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td>363 (685)</td>
</tr>
<tr>
<td>2035 (3700)</td>
<td>2.74 × 10⁻¹ (0.11 × 10⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td>323 (613)</td>
</tr>
<tr>
<td>2204 (4000)</td>
<td>7 × 10⁻¹ (0.28 × 10⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td>374 (706)</td>
</tr>
<tr>
<td>1538 (2800)</td>
<td>2.36 × 10⁻² (0.093 × 10⁻²)</td>
<td>6</td>
<td>10</td>
<td>6</td>
<td>1.016 (0.04)</td>
</tr>
<tr>
<td>1649 (3000)</td>
<td>2.68 × 10⁻² (0.11 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>304 (580)</td>
</tr>
<tr>
<td>1927 (3500)</td>
<td>4.55 × 10⁻² (0.18 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>366 (690)</td>
</tr>
<tr>
<td>2039 (3800)</td>
<td>7.64 × 10⁻² (0.3 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>346 (655)</td>
</tr>
<tr>
<td>2204 (4000)</td>
<td>15.7 × 10⁻² (0.62 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>349 (660)</td>
</tr>
<tr>
<td>2316 (4200)</td>
<td>32.7 × 10⁻² (1.3 × 10⁻²)</td>
<td></td>
<td></td>
<td></td>
<td>349 (660)</td>
</tr>
<tr>
<td>1871–1982 (3400–3600)</td>
<td>1.9 × 10⁻² (0.075 × 10⁻²)</td>
<td>14</td>
<td>13</td>
<td>3</td>
<td>1.016 (0.04)</td>
</tr>
<tr>
<td></td>
<td>11 × 10⁻² (0.43 × 10⁻²)</td>
<td>4</td>
<td>9</td>
<td>2</td>
<td>363 (685)</td>
</tr>
<tr>
<td></td>
<td>9 × 10⁻² (0.35 × 10⁻²)</td>
<td>4</td>
<td>—</td>
<td>5</td>
<td>299 (570)</td>
</tr>
</tbody>
</table>

A. Powder metallurgy material

B. Arc-cast material

References:
- Ogden, 1962
- Allen et al., 1959
- Farrell et al., 1967
- Klopp and Raffo, 1964
- Klopp and Raffo, 1966
- Klopp and Witzke, 1966
- Raffo et al., 1965
### C. Electron-beam-melted material

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resistance (Ω)</th>
<th>Temperature Coefficient (°C⁻¹)</th>
<th>Density (g/cm³)</th>
<th>Density Coefficient (g/cm³°C⁻¹)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1204 (2200)</td>
<td>4.24 x 10⁻²</td>
<td>4</td>
<td>1.016 (0.04)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>1649 (3000)</td>
<td>9.91 x 10⁻²</td>
<td>13</td>
<td>346 (655)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>1927 (3500)</td>
<td>33.8 x 10⁻²</td>
<td>2</td>
<td>273 (525)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>2093 (3800)</td>
<td>71.3 x 10⁻²</td>
<td>1</td>
<td>237 (460)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>2204 (4000)</td>
<td>118 x 10⁻²</td>
<td>2</td>
<td>374 (705)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>2316 (4200)</td>
<td>104 x 10⁻²</td>
<td>2</td>
<td>399 (750)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td>1871–1982 (3400–3600)</td>
<td>38 x 10⁻²</td>
<td>5</td>
<td>368 (695)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>332 (630)</td>
<td>Klopp and Witzke, 1966</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>251 (485)</td>
<td>Raoult et al., 1965</td>
<td></td>
</tr>
</tbody>
</table>

### D. Chemical-vapor-deposited material

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resistance (Ω)</th>
<th>Temperature Coefficient (°C⁻¹)</th>
<th>Density (g/cm³)</th>
<th>Density Coefficient (g/cm³°C⁻¹)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 (1832)</td>
<td>N.A.</td>
<td>&lt; 10</td>
<td>180 (356)</td>
<td>Schaffhauser, 1966</td>
<td></td>
</tr>
<tr>
<td>1400 (2552)</td>
<td></td>
<td>&lt; 5</td>
<td>190 (374)</td>
<td>Schaffhauser, 1966</td>
<td></td>
</tr>
<tr>
<td>1800 (3272)</td>
<td></td>
<td>7</td>
<td>200 (392)</td>
<td>Schaffhauser, 1966</td>
<td></td>
</tr>
<tr>
<td>2200 (3992)</td>
<td></td>
<td></td>
<td>210 (410)</td>
<td>Schaffhauser, 1966</td>
<td></td>
</tr>
<tr>
<td>2500 (4532)</td>
<td></td>
<td></td>
<td>260 (500)</td>
<td>Schaffhauser, 1966</td>
<td></td>
</tr>
</tbody>
</table>

* N.A. = not available.
cleavage type. The latter observation has been confirmed by the electron microscope studies of Raffo (1969).

The general effect of a superimposed hydrostatic pressure is to increase the ductility of materials. The effect of such pressure on the ductility of tungsten is shown in Fig. 6.13. According to Das and Radcliffe (1968), the data were based on recrystallized powder metallurgy tungsten, while other data presented in the figure were probably of unrecrystallized materials. The considerable scattering of the data is likely due to the difference in purity of the materials.

The effect of surface roughness on the low-temperature ductility of tungsten was investigated by Sedlatschek and Thomas (1957), and Stephens (1960, 1961, 1963a, b). The results are shown in Fig. 6.14 (Stephens, 1961). The beneficial effects of electropolishing are attributed to removal of surface notches and cracks resulting from processing. Oxidation by heating tungsten wrought products in air will result in the removal of a carbon-contaminated layer (Berghezen, 1961) or removal of surface notches (Stephens, 1974). In either case, the ductility of the material is thereby improved. Specimens with surfaces containing notches or cracks resulting from processing.

Fig. 6.13. Effect of pressure on ductility of tungsten at room temperature (Das and Radcliffe, 1968); (1) Bridgman (1953), (2) Bobrowsky (1965), (3) Livshitz et al. (1965), (4) Pugh (1965), (5) Davidson et al. (1966), (6) Das and Radcliffe (1968).

Fig. 6.14. Effect of surface condition on ductile-brittle transition temperature of tungsten (Stephens, 1961).
from peening, grinding, etching, etc., raise the ductile–brittle transition temperature of tungsten.

The effect of strain rate on the ductile–brittle transition temperature of tungsten is shown in Fig. 6.15 (Chilton and Wronski, 1969). A relation of the form

\[ \exp (-\dot{\varepsilon}^{0.09}) = K(\varepsilon_0 - 0.3T_i) \]  

(6.42)
is obeyed, where \( K \) and \( \varepsilon_0 \) are constants, \( \dot{\varepsilon} \) is the strain rate \( \text{(sec}^{-1}\text{)} \), and \( T_i \) is the transition temperature in degrees Kelvin.

Figure 6.16 summarizes the reported grain size dependence and shows that ductile–brittle transition temperature reaches a maximum at an intermediate grain size. The large scatter in the data from the various investigations can be explained by the variation and distribution of impurities in the various lots of material used in the studies. Variation in grain size is normally achieved by annealing at various temperatures above the recrystallization temperature. Depending upon initial impurity content, fabrication process, heating and cooling rates, and so forth, a wide variation in impurity distribution can result, which, as shown by Koo (1963a), can overshadow the grain size effect.

Interstitial impurities, primarily oxygen and carbon, have been believed by some to be responsible for the high ductile–brittle transition temperature of tungsten. Figure 6.17 (Stephens, 1964) illustrates the increase in the ductile–brittle transition temperature on using varying amounts of oxygen or carbon. Oxygen appears to be more detrimental to the ductile–brittle transition temperature than carbon at equal atomic concentrations. The purification of tungsten by arc melting, electron-beam melting, and zone refining has produced no dramatic decrease in ductile–brittle transition temperature of polycrystalline materials (Allen et al., 1959; Stephens, 1964).

The variation of yield stress \( \sigma_y \), with impurity content is shown in Fig. 6.18, where it is noted that in mono- or polycrystalline tungsten, \( \sigma_y \) is more or less

![Fig. 6.15. Effect of strain rate on ductile–brittle transition temperature of tungsten (Chilton and Wronski, 1969).](image-url)

independent of oxygen content, while carbon produces an increase in $\sigma_p$. These data may suggest that two different mechanisms of embrittlement are operative (Stephens, 1964). Embrittlement by oxygen is probably due to segregation on oxygen at grain boundaries, which facilitates intergranular fracture by lowering the surface energy. Carbon embrittlement is believed to be primarily due to the

Fig. 6.17. Effects of oxygen and carbon on ductile–brittle transition temperature of single crystal and polycrystalline tungsten (Stephens, 1964).
interaction between dislocations and carbide particles, which leads to increases in the stress for unpinning dislocations and the yield stress.

A recent investigation was performed by Ioshi and Stein (1970), who, using Auger spectroscopy, reported that the fracture mode of tungsten is essentially intergranular and that oxygen or carbon is not responsible for the variation in ductile–brittle transition temperature of various material, but that segregation of phosphorus to the grain boundaries is the primary cause of embrittlement in powder metallurgy tungsten.

Crutchley and Reid (1969) suggested that the brittleness of the bcc metals is an inherent property related to the nature of the atomic bonding that is manifested in the elastic constants. They consider low values of the ratio of the bulk modulus $K$ to the shear modulus $\mu$ on an active slip system as indicative of inherent brittleness. Group V metals — vanadium, niobium, and tantalum — have $K/\mu$ values ranging from 3.12 to 4.03, while group VI metals — chromium, molybdenum, and tungsten — have $K/\mu$ values ranging from 1.22 to 2.02. Therefore, group VI metals will be extremely notch-sensitive and will behave in a manner quite different from group V metals. The high ductile–brittle transitional temperature of tungsten can be thought of as being controlled by both intrinsic and extrinsic properties.

The most attractive alloy addition to tungsten for improving the low-temperature ductility is rhenium. It is postulated (Crutchley and Reid, 1969), that such gross alloying may have a favorable effect on the $K/\mu$ ratio that improves the ductility of the metal.

6.3.2. Elastic Properties

The single-crystal elastic constants of tungsten at 24°C (75.2°F) are shown in Table 6.18. Equations for these elastic constants at temperatures from 24 to 1800°C are shown in Table 6.19, and that for the elastic properties of polycrystalline tungsten are shown in Table 6.20 (Lowrie and Gonas, 1967). The constants $C_{11}$ and $C_{44}$ as functions of temperature in temperature range —250 to 1800°C are also
Table 6.18. Single-Crystal Elastic Constants of Tungsten at 24°C

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value (10^{12} \text{ dyn/cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_N )</td>
<td>5.221</td>
</tr>
<tr>
<td>( C' )</td>
<td>1.599</td>
</tr>
<tr>
<td>( C_{44} )</td>
<td>1.604</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td>5.216</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>2.018</td>
</tr>
<tr>
<td>( K_b )</td>
<td>3.084</td>
</tr>
</tbody>
</table>

\( C_N = \frac{1}{4} C_{11} + \frac{1}{2} C_{12} + C_{44} \)
\( K_b \) is the bulk modulus.

Table 6.19. Least-Squares Equations for the Variation of the Elastic Constants of Tungsten with Temperature (°C)

\[
\begin{align*}
C &= (5.2349 \times 10^{12}) - (4.5967 \times 10^8)T - (5.467 \times 10^4)T^2 \\
C_{44} &= (1.6083 \times 10^{12}) - (1.0320 \times 10^8)T - (2.054 \times 10^4)T^2 \\
C_N &= (5.2480 \times 10^{12}) - (3.005 \times 10^8)T - (3.163 \times 10^4)T^2 \\
C_{12} &= (2.0445 \times 10^{12}) - (0.3403 \times 10^8)T + (3.249 \times 10^4)T^2 \\
C' &= (1.5952 \times 10^{12}) - (2.1282 \times 10^8)T - (4.358 \times 10^4)T^2
\end{align*}
\]

\( ^{a} \) Lowrie and Gonas (1967).

Table 6.20. Equations for the Elastic Properties of Polycrystalline Tungsten Calculated from Single-Crystal Elastic Stiffness

\[
\begin{align*}
K &= (3.108 \times 10^{12}) - (1.759 \times 10^8)T + (0.344 \times 10^4)T^2 \\
G &= (1.6028 \times 10^{12}) - (1.456 \times 10^8)T - (3.28 \times 10^4)T^2 \\
E &= (4.1027 \times 10^{12}) - (3.489 \times 10^8)T - (7.55 \times 10^4)T^2 \\
\nu &= 0.28005 + (0.05744 \times 10^{-4})T + (0.540 \times 10^{-8})T^2
\end{align*}
\]

\( ^{a} \) Lowrie and Gonas (1967).
\( ^{b} \) \( K \) is the modulus of volume expansion or bulk modulus, \( G \) is the shear modulus, \( E \) is the Young's modulus; and \( \nu \) is the Poisson's ratio.

plotted in Figs. 6.19 and 6.20, respectively. The shear modulus, bulk modulus, Young's modulus, and Poisson's ratio vs. temperature plots are shown in Figs. 6.21 and 6.22.

6.3.3. Hardness

Hardness testing is a fast and economical means of obtaining a rough measure of the strength of a material. Table 6.21 (Rieck et al., 1968) shows Vickers hardness of
different crystallographic planes of single crystals grown by the zone-melting method and also of Pintsch wire crystals by the van Arkel process. It also shows the hardness of different polycrystalline samples at different conditions.

The hardness anisotropy of tungsten is clearly demonstrated by Figs. 6.23 and 6.24 (Rieck et al., 1968). The range of the angle between the long diagonal of the
Knoop indentation and the (110) direction covers from 0 to 360/2n degrees, where n is the multiplicity of the symmetry axis normal to the plane of indentation.

The relationship between the hardness and grain size is shown in Fig. 6.25 (Vashi et al., 1970). The material used for this investigation was submicron tungsten powder, approximately 0.05-μm diameter, consolidated under high pressure and temperature. The relation is given approximately as

\[ H = H_0 + K_H l^{-1/2} \]  

where \( H_0 \) and \( K_H \) are constants, \( H \) is the hardness number, and \( l \) is the average grain diameter.

Fig. 6.21. Shear modulus and bulk modulus of tungsten vs. temperature as calculated from single-crystal elastic constants \((G_p \text{ and } K_p)\) (Lowrie and Gonas, 1967), and from measurements on polycrystalline tungsten \((G_p \text{ and } K_p)\) (Lowrie and Gonas, 1965).
Fig. 6.22. Young’s modulus and Poisson’s ratio of tungsten vs. temperature, as calculated from single-crystal elastic constants (E and ν) (Lowrie and Gonas, 1967) and from measurements on polycrystalline tungsten (Eₚ and νₚ) (Lowrie and Gonas, 1965).

The hardness data from room temperature to 2700°C are shown in Fig. 6.26. Starting with the equations

\[ H = K_n H_0 \exp(-\alpha_n T) \]  \hspace{1cm} (6.44)

\[ \sigma = M_n \sigma_0 \exp(-\beta_n T) \]  \hspace{1cm} (6.45)

Borisenko (1965) derived a relationship between hardness and ultimate strength of tungsten as follows:
Table 6.21. Microhardness of Polycrystalline and Monocristalline Tungsten Samples

1. Vickers microhardness $H_v$ of different polycrystalline samples and under different loads

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_v$ (kg/mm$^2$) at different applied loads$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 g</td>
</tr>
<tr>
<td>Polycrystalline tungsten “normally” doped with potassium, silicon, and aluminum oxides</td>
<td></td>
</tr>
<tr>
<td>Swaged ingot, annealed</td>
<td>392(10)</td>
</tr>
<tr>
<td>Rolled and recrystallized</td>
<td>401(12)</td>
</tr>
<tr>
<td>Swaged rod, as-worked</td>
<td>498(16)</td>
</tr>
<tr>
<td>Undoped electron-beam-melted tungsten</td>
<td>397(9)</td>
</tr>
</tbody>
</table>

2. Vickers microhardness $H_v$ of tungsten single crystals on different crystallographic planes and under different loads

<table>
<thead>
<tr>
<th>Plane of indentations</th>
<th>Single crystals of tungsten grown on a Pintsch wire at different applied loads</th>
<th>Zone-melted single crystals at different applied loads</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$100$ g</td>
<td>$200$ g</td>
</tr>
<tr>
<td>(100)</td>
<td>360(6)</td>
<td>362(5)</td>
</tr>
<tr>
<td>(110)</td>
<td>395(9)</td>
<td>389(7)</td>
</tr>
<tr>
<td>(111)</td>
<td>408(12)</td>
<td>410(11)</td>
</tr>
</tbody>
</table>

$^a$ Rieck et al. (1968).
$^b$ Values in parentheses are standard deviations corresponding to twenty indentations.

$$
\sigma = \frac{M_n \sigma_0}{K_n H_0} H \exp \left[ (\alpha_n - \beta_n)T \right] 
$$

(6.46)

where $H$, $H_0$, $\sigma$, and $\sigma_0$ are hardness and ultimate strength at testing temperature and 0 K, respectively; $\alpha_n(\alpha_1, \alpha_2, \alpha_3)$ and $\beta_n(\beta_1, \beta_2, \beta_3)$ are temperature coefficients of hardness and ultimate strength, respectively, for particular segments; $K_n(K_1, K_2, K_3)$ and $m_n(m_1, m_2, m_3)$ are constants for the segments; and $T$ is the absolute temperature. The plots of hardness vs. yield limit from Borisenko (1965) are reproduced in Fig. 6.27.

6.3.4. Tensile Properties

Plots of ultimate tensile strength, yield strength, percent elongation, and reduction of area vs. temperature for tungsten are shown in Figs. 6.28 through 6.31, respectively. Electron-beam-melted material is lowest in strength and highest in ductility. Chemical-vapor-deposited tungsten, being the second lowest in strength,
Fig. 6.23. Anisotropy of Knoop hardness on a (001) plane of a single crystal of pure tungsten grown on a Pintsch wire (triangles) and zone-melted tungsten single crystals (circles) (Rieck et al., 1968).

demonstrates the lowest ductility. Powder metallurgy and arc-cast materials are high in strength but low in ductility.

The peak in the temperature–yield stress curve for powder metallurgy or electron-beam-melted material is not fully understood; it may be caused by a dislocation interaction with substitutional impurities, or precipitation hardening, or by strain aging effects (King and Sell, 1965; Bechtold and Shewmon, 1954; Pugh, 1957).

The ultimate tensile strength for commercially available tungsten wires, including doped and thoriated, together with W–3 Re wire, in the as-drawn condition is shown in Fig. 6.32. It is apparent that doped or thoriated wire improves the strength of tungsten, especially at elevated temperatures. It should be pointed out that the strength for tungsten in the as-worked condition (Fig. 6.32) is much higher than that in the annealed condition (Fig. 6.28). For more information about the mechanical properties of thoriated tungsten and tungsten alloys, the reader is referred to Secs. 8.2 and 8.3.

The effects of pressure on the yield stress of tungsten have been investigated by Das and Radcliffe (1968), Wronski and Chilton (1969), and Mellor and Wronski (1970). These studies indicate that the yield stress is unaffected by hydrostatic pressures from 10.2 to 285.6 kg/mm² for the temperature range 77–725 K.

The effect of strain rate on the tensile properties of tungsten is greater than that for some of the more common metals, such as copper, aluminum, or iron. Bechtold (1956) studied the effect of strain rate on the yield stress at 525 K and established the relationship

\[
\ln \sigma_y = \tau \ln \dot{\varepsilon}
\]

(6.47)
where \( \tau \) is the strain rate exponent and \( \dot{\varepsilon} \) is the applied strain rate. The plot of yield stress against strain rate is shown in Fig. 6.33, and the value of \( \tau \) is found to be 0.15.

Raffo (1969) has determined the strain rate sensitivity of tungsten over a range of temperatures. The rate sensitivity is defined as

\[
\lambda = \frac{(\Delta \sigma)_{\tau}}{\Delta \ln \dot{\varepsilon}}
\]

A plot of \( \lambda \) against \( T \) is shown in Fig. 6.34. It is noted that \( \lambda \) passes through a maximum at a temperature near 500 K, near the ductile–brittle transition temperature for the material used in the study. The occurrence of a maximum in the strain rate sensitivity at an intermediate temperature is typical also of other bcc metals (Conrad, 1965).
Fig. 6.25. Vickers hardness (diamond pyramid hardness, DPH) vs. reciprocal square root of average grain diameter for tungsten (Vashi et al., 1970).

Fig. 6.26. Hardness of tungsten as a function of temperature in the range 25–2700°C (Pisarenko et al., 1962).
Fig. 6.27. Hardness vs. yield limit for tungsten (Borisenko, 1965).

Fig. 6.28. Ultimate tensile stress vs. test temperature for tungsten. (1) Rod, 2.36 mm diameter, annealed $\frac{1}{2}$ hr at 2400°C (Sell et al., 1966). (2) Rod, 4.06-mm diameter, annealed 1 hr at 1982°C (Klopp and Raffo, 1964). (3) Rod, 4.06-mm diameter, annealed 1 hr at 1648°C (Klopp and Raffo, 1964). (4) Rod, 4.06 mm diameter, annealed 1 hr at 1371°C (Klopp and Witzke, 1966). (5) Rod, 4.06-mm diameter, annealed 1 hr at 1982°C (Klopp and Witzke, 1966). (6) Rod, 4.06-mm diameter, annealed 1 hr at 2845°C (J. L. Taylor and Boone, 1964).
The effect of grain size on the yield stress of tungsten, although not as well documented as the ductile-brittle transition temperature behavior mentioned in the previous section, is found to obey a Petch relation (Koo, 1961; McLean, 1962)

\[ \sigma_y = \sigma_0 + k_y d^{-1/2} \]  \hspace{1cm} (6.49)

where \( \sigma_y \) is equal to the yield stress of a single crystal, \( d \) is the average grain diameter, and \( k_y \) is a measure of the stress for propagation of yielding through a polycrystalline material. The plot of some available data is shown in Fig. 6.35.

Figure 6.36 shows the plot of yield stress vs. temperature for single crystals of various purities. It reveals that the temperature dependence of the yield stress is about the same for high- and low-purity material. These results suggest that the high temperature dependence of the yield stress is due to an intrinsic property rather than an extrinsic property such as impurity content.

J. L. Taylor (1965) has reviewed the temperature dependence of crystallographic slip in tungsten. At low temperatures, \( \{110\} \langle 111 \rangle \) slip occurs; at room
temperature, an additional $\{112\} <111>$ slip takes place; and at temperatures between 1371 and 2760°C (2500 and 5000°F), $\{123\} <111>$ slip operates in addition to the first two modes.

The effect of orientation on the stress–strain curves is shown in Fig. 6.37. It would be expected that the proportional limit $\sigma_p$ should be the same for $<100>$ or $<110>$ oriented crystals, since the Schmid factors for slip on all above-mentioned slip modes are essentially identical for both orientations. Garfinkle (1966), using sensitive strain measurements, found that the departure from stress–strain linearity was indeed quite similar for the $<100>$ and $<110>$ orientations, as shown in the insert in Fig. 6.37.

The macroscopic stress–strain curves for various orientations are still of interest, since they indicate highly different rates of work hardening for different orientations. The investigation of Argon and Maloof (1966) help clarify the orientation dependence of plastic flow in tungsten. Figure 6.38 shows a plot of dislocation density $N$ against strain for three orientations. The extremely low rate of dislocation multiplication for $<110>$ oriented crystals suggests that dislocations can glide large distances on parallel planes without intersecting other dislocations and
activating sources. The low density of dislocations and the large mean free path over which they can move would be expected to induce little work hardening.

The effect of temperature on the yield stress $\sigma_y$ of tungsten single crystals of different orientations is shown in Fig. 6.39. In addition to the orientation dependence, a sharp temperature dependence of $\sigma_y$ is noted for all three orientations.

It should be pointed out that the ductility of tungsten is greatly increased when tested in single-crystal form. Necking is observed at 20 K if the specimen is not embrittled by scratches resulting from handling (Beardmore and Hull, 1965).

### 6.3.5. Creep Behavior

Since the tensile strength and creep strength of tungsten at elevated temperatures exceed those of any other metal, these properties are of considerable interest. For practical purposes, creep behavior investigations are concentrated on the secondary creep rate and stress–rupture properties. There is a potential use of tungsten wire in composites for elevated-temperature applications (see Sec. 8.5.3),
Fig. 6.32. Ultimate tensile strength vs. test temperature for commercially available, as-drawn tungsten wires. (1) 0.71-mm diameter (Schmidt and Ogden, 1963). (2) 0.2-mm diameter (Petrasek and Signorelli, 1969; Schmidt and Ogden, 1963). (3) 0.2 mm diameter (Petrasek and Signorelli, 1969). (4) 0.38 mm diameter (Petrasek and Signorelli, 1969). (5) 0.2 mm diameter (Petrasek and Signorelli, 1969; Schmidt and Ogden, 1963).

Fig. 6.33. Effect of strain rate on yield stress for tungsten at 525 K (0.14T_m) (Bechtold, 1956).
and for this reason, emphasis has been placed on heavily drawn tungsten wire in the temperature range 649–1371°C (1250–2500°F) in some recent work.

Figure 6.40 shows the 1-hr rupture strength of tungsten for different fabrication history and different sizes. Figure 6.41 is a plot of stress vs. rupture life of tungsten wire. Some stress–rupture data for tungsten tested in vacuum are shown in Fig. 6.42.
Fig. 6.36. Temperature dependence of yield stress for tungsten single crystal of different purities. (1) Crystal grown by one pass of electron-beam zoning (Oku and Galligan, 1970); (2) crystal grown by three passes (Das and Radcliffe, 1968); (3) Stephens (1964).

Fig. 6.37. Stress–strain curves for tungsten single crystals at 300 K (Rose et al., 1962; Garlick and Probst, 1964; Garfinkle, 1966).
The secondary creep rate of tungsten as a function of stress and temperature is shown in Fig. 6.43, and the temperature dependence of the secondary creep rate of tungsten is shown in Fig. 6.44.

In order to compare the creep strength of tungsten consolidated by different methods tested at different temperatures, the temperature-compensated creep rate as a function of applied stress is used and plotted in Fig. 6.45. The compensated
Fig. 6.40. One-hour rupture strength vs. temperature plot for tungsten: (1) McDanels and Signorelli (1966), (2) Hum and Donlevy (1961), (3) Drury et al (1963), (4) Green (1959), (5) Sutherland and Klopp (1963), (6) Pugh (1957).

Fig. 6.41. Stress vs. rupture life for 0.127-mm (0.005-in.)-diameter as-drawn tungsten wire (McDanels and Signorelli, 1966).
Fig. 6.42. Stress vs. rupture life for tungsten tested in vacuum: (1), (2) Klopp and Witzke (1966); (3), (4) McCoy (1966).

Fig. 6.43. Secondary creep rates of tungsten as functions of stress and temperature (Harris and Ellison. 1966, copyright by American Society for Metals).
creep rate is calculated by the equation

\[ K = \dot{\varepsilon} \exp \left( \frac{Q}{RT} \right) \]  

(6.50)

where \( \dot{\varepsilon} \) is the steady-state creep rate and \( Q \) is the activation energy of volume self-diffusion. The value of \( Q \) varies with temperature, while a mean value of 155 cal/mole for the temperature range is used here (Sell, 1968).

6.3.6. Twinning and Dislocation Structures

Deformation behavior depends upon dislocation mobility that produces slip and twinning. The slip systems and the orientation effect on the stress–strain curves have been discussed in Sec. 6.3.3.
Twinning in bcc metals generally occurs at low temperature, at high strain rate, and in high-purity material. Wolff (1962) reported room-temperature twinning in tungsten on {112} planes and associated this with fracture after considerable deformation by slip. Koo (1963b) observed that increased purity promoted twinning at temperatures ranging from 95 to 180 K, but found no twinning at 77 K. Beardmore and Hull (1965) found no evidence for twin-initiated fracture and indicated that twins were caused by cracks.

Stacking faults were produced by heating tungsten above 2775 K and quenching (Nakayama et al., 1962); they were also formed by heating a thin foil of tungsten directly in the electron microscope while the foil was held rigidly (Demny, 1967). Under normal loading conditions, stacking faults have not been observed in tungsten, which indicates a minimal dissociation of dislocations. The high stacking fault energy suggests that stacking faults do not play a direct role in the deformation behavior of tungsten.

Effects of temperature on dislocation distribution and structures are shown in Fig. 6.46 (Stephens, 1970). Specimens deformed at 150 K (0.04T_m) are characterized by long, straight screw dislocations lying parallel to the primary slip direction. By contrast, deformation at 590 K (0.16 T_m) resulted in a structure consisting both edge
Fig. 6.46. Effect of temperature on dislocation substructure in single-crystal tungsten tested in compression to 2% strain (Stephens, 1970): (a) 150 K (0.04T_m), (b) 590 K (0.16T_m).
and screw dislocations and characterized by edge dislocations lying parallel to the $\langle 121 \rangle$ direction.

Based on these observations (Stephens, 1968, 1970), it is concluded that at temperatures less than $0.1T_m$, edge dislocation mobility is much greater than screw dislocation mobility. Consequently, edge dislocations can move through the crystals leaving behind the long screw segments. At temperatures greater than $0.1T_m$, edge and screw mobilities are comparable so that both types of dislocations are observed. The decrease in screw dislocation mobility with decreasing test temperature can be correlated with the temperature dependence of yield stress for tungsten. Higher stresses are required at lower temperatures to produce dislocation movement after edge dislocations have moved out of the crystal.
Chemical Properties of Tungsten and Tungsten Compounds

7.1. GENERAL REMARKS

The chemical properties of tungsten, especially its reactivity with oxygen and chemical reagents, are important because tungsten end products are to be used in various environments. A knowledge of tungsten compounds is also essential because some intermediate products, such as sodium tungstate and ammonium paratungstate, play important roles in the extraction processes of tungsten. Furthermore, tungsten compounds such as tungsten carbides are widely used as machine tools; tungsten bronzes as paints; calcium and magnesium tungstates as phosphors; and ammonium tungstate, tungstic oxide, and tungsten disulfide are used as catalysts in the petroleum industry (see Chapter 10).

Tungsten is a transition element, and belongs to group VI, and has an atomic number of 74. Its electronic configuration is 1s², 2s², 2p⁶, 3s², 3p⁶, 3d¹⁰, 4s², 4p⁶, 4d¹⁰, 4f¹⁴, 5s², 5p⁶, 5d⁴, and 6s². The atomic mass of tungsten's natural isotopic composition is 183.85 (see Sec. 6.1.1 for details).

Its oxidation states range from 2− to 6+. The lower oxidation states (2− to 1+) exist only in organometallic compounds and compounds of π acceptor ligands (Rollinson, 1973). In high oxidation states, it exhibits acidic properties, while in lower oxidation states, it exhibits basic properties. Its maximum coordination number is 8.

Tungsten does not react with water at room temperature, but above 600°C, it readily forms oxides with steam. At room temperature, bulk tungsten metal does not react with hydrochloric, sulfuric, or hydrofluoric acids at any concentration. Warm nitric acid or the mixture of nitric and hydrofluoric acid reacts with tungsten and forms WO₃. Aqua regia attacks tungsten only when an oxidizing agent such as hydrogen peroxide is present.

Aqueous solutions of alkali and ammonia do not corrode tungsten in the absence of oxygen. Tungsten resists the corrosion of molten sodium hydroxide or potassium hydroxide, but is subject to vigorous corrosion when these solutions contain an oxidizing agent such as a nitrate, nitrite, or chlorate. At lower
Table 7.1. Reaction of Tungsten below 300°C with Various Chemicals⁴, ⁵

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>F₄</th>
<th>HF + HNO₃</th>
<th>HCl + HNO₃</th>
<th>H₂SO₄</th>
<th>H₂PO₄</th>
<th>KOH</th>
<th>H₂O₂ (or O)</th>
<th>KOH + H₂O₂ (or O)</th>
<th>NaNO₂ + Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>→WF₄</td>
<td>dis.</td>
<td>ox.</td>
<td>sl. at.</td>
<td>—</td>
<td>—</td>
<td>sl. at.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>250–300</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>


Key: sl. at. = slight attack; ox. = oxidation; dis. = dissolution; → = product formed.

Temperatures tungsten forms nitrides with NH₃ and carbides with CO. Tungsten is attacked by N₂O, NO, and NO₂ at high temperatures, and by CO₂ at 1200°C. Hydrogen does not dissolve in tungsten. No tungsten hydride of any form has been confirmed, although the existence of tungsten hydride under special conditions is still possible (Goldschmidt, 1957).

The reaction of tungsten with various chemicals below 300°C (572°F) is shown in Table 7.1; chemicals that attack tungsten at higher temperatures are shown in Table 7.2 (Rieck, 1967).

The compounds are divided into two major categories, namely, the intermetallic compounds and those of tungsten and nonmetallic elements. The dividing line between metallic and nonmetallic is inserted diagonally from the top to the bottom of the periodic table at the left side of the elements boron, silicon, arsenic, tellurium, and astatine. In each category, the sequence of discussion will generally follow the group numbers of the elements from the lowest to the highest. Under the nonmetallic compounds, tungsten hydrates and their salts will also be discussed because of their importance.

### 7.2. Oxidation Behavior of Tungsten

Tungsten oxidizes according to the parabolic rate law to form adherent blue oxides below 400°C and oxidizes at a linear rate with time at temperatures above 1100°C. Oxidation in the intermediate temperatures between 400°C and 1100°C follows a mixed rate, which tends toward a linear rate as the time of exposure increases and as the amount of cold work increases in the tungsten. Above 500°C,

Table 7.2. Temperature Scale of Attack of Tungsten by Various Compounds⁶

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>500</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1200</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound:</td>
<td>HClO₃</td>
<td>NH₃</td>
<td>CO, Br, I</td>
<td>C₂H₆</td>
<td>C</td>
<td>CO₂</td>
<td>N₂</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>H₂O, H₂O</td>
<td>N₂H₃</td>
<td>CS₂</td>
<td>H₂O</td>
<td>N₂H₃</td>
<td>H₂</td>
<td>C</td>
<td>CO₂</td>
<td>N₂</td>
</tr>
</tbody>
</table>

cracks appear in the oxide film. Above 800°C, evaporation of WO$_3$ oxide becomes substantial, and above 1100°C, the WO$_3$ sublimes as fast as it is formed (Ivanov et al., 1969). The surface of the tungsten becomes saturated with oxygen for a certain depth during oxidation.

The rate of expenditure of tungsten due to oxidation (Ong, 1962; Ong and Fassel, 1962) at temperature from 700°C to 1300°C, and pressure $P$ from 0.0013 to 20.8 atm can be determined as follows:

$$-rac{d(m/A)}{dt} = (5.89 \times 10^5) \exp \left(-\frac{12,170}{T} P^{1/2}\right)$$  \hspace{1cm} (7.1)

in units of mg/cm$^2$-hr, where $m/A$ (mg/cm$^2$) is the weight change per unit area of a specimen, and for depth per unit time in units of cm/hr,

$$-rac{dx}{dt} = (3.05 \times 10^2) \exp \left(-\frac{12,170}{T} P^{1/2}\right)$$  \hspace{1cm} (7.2)

where $P$ is pressure in atmospheres and $T$ is the absolute temperature. At temperatures above 2000°C, the rate of expenditure of tungsten is independent of temperature and directly proportional to oxygen pressure from $10^{-6}$ to $10^{-3}$ atm. The rate of expenditure of tungsten also depends on the rate of motion of the gas boundary film adjacent to the surface. Figure 7.1 gives the rate of recession of a tungsten filament in a pure oxygen atmospheres with natural convection and diffusion (Bartlett, 1964). The behavior of tungsten, along with molybdenum and tantalum, as heating elements toward various furnace atmospheres is shown in Table 7.3 (Barth and Rengstorff, 1961).

7.3. INTERMETALLIC COMPOUNDS AND INTERMETALLIC PHASES

Of the elements in the first three groups of the periodic table, only boron, beryllium, and aluminum are known to form compounds with tungsten; none of the other elements even form substantial solid solutions. The compounds of beryllium and aluminum will be treated in the following, while those of boron, which belong to the nonmetallic category, will be discussed in Sec. 7.4.

The reaction of tungsten with alkali metals has been reviewed by Di Stefano and Hoffman (1964). No reaction has been found between tungsten and pure alkali metals at temperatures up to 1000°C, and the solubility of tungsten in the liquid metals is very low; however, in the presence of oxygen, corrosion will take place. Beryllium forms the following compounds with tungsten: Be$_{23}$W, Be$_{12}$W, and Be$_2$W (Misch, 1936; Batchelder and Raeuchle, 1957; Matynshenko et al., 1963).

The compounds of aluminum and tungsten are: Al$_{12}$W, Al$_3$W, Al$_4$W, and
probably Al₃W, Al₅W₃, and Al₂W (Adam and Rich, 1954, 1955; Clark, 1940; Kubaschewski, 1950). The cerium–tungsten system has been investigated by Obrowski (1957), who found a solid solution at the tungsten end and possibly CeW₂ and other compounds. Little information has been published about the tin–tungsten system; tin has no reaction with tungsten at 1000°C (Reed, 1954). Wurms and Steinitz (1962) stated that the solubility of tungsten in liquid lead was less than 0.1 at %. The phase diagram of the tungsten–titanium system is given by Hansen (1958). There are no intermetallic compounds existing within this system. Tungsten is only slightly soluble in α-titanium, but about 10–20 at % of titanium dissolves in tungsten. The phase diagram of the tungsten–zirconium system has been determined by Hansen et al. (1953). The solid solubility of zirconium in tungsten is about 6 at % and that of tungsten in α-zirconium about 0.5 at % and in β-zirconium about 4 at %.

The tungsten–hafnium system has been investigated by Giessen et al., (1962). β-Hafnium dissolves about 13 at % tungsten at 1930°C, and α-hafnium dissolves only 0.9 at % at 1500°C. The solid solubility of hafnium in tungsten is about 4 at % at
<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Molybdenum</th>
<th>Tungsten</th>
<th>Tantalum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air or gases containing oxygen</td>
<td>Incipient oxidation beyond 400–500°C; strong evaporation above 800°C</td>
<td>Incipient oxidation beyond 500°C; strong evaporation above 1200°C</td>
<td>Oxidation and nitride formation above 500°C</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry (&lt;0.5 g water/m³)</td>
<td>Stable up to melting point</td>
<td>Stable up to melting point</td>
<td>Hydride formation at 400–800°C; beyond that, stable up to melting point, surface oxidation</td>
</tr>
<tr>
<td>Wet (&lt;20 g water/m³)</td>
<td>Stable up to 1400°C; beyond that, growth of metal needles on surface with material wastage</td>
<td>Stable up to 1400°C; beyond that, growth of metal needles at surface with material wastage</td>
<td>Hydride formation and strong oxidation beyond 450°C</td>
</tr>
<tr>
<td>Cracked ammonia (dry)</td>
<td>Stable up to melting point</td>
<td>Stable up to melting point</td>
<td>Nitride and hydride formation above 400°C; at higher temperatures, thorough nitrification</td>
</tr>
<tr>
<td>Partially burnt ammonia (dry)</td>
<td>Stable up to melting point</td>
<td>Stable up to melting point</td>
<td>Nitride and hydride formation above 400°C; at higher temperatures, thorough nitrification</td>
</tr>
<tr>
<td>Partially burnt illumination gas, generator gas, etc.</td>
<td>Stable up to 1300°C; surface carbonization above 1200°C</td>
<td>Stable up to 1400°C; surface carbonization above 1300°C</td>
<td>Nitride, carbide, and hydride formation; becomes brittle</td>
</tr>
<tr>
<td>Inert gas (argon, helium)</td>
<td>Stable up to melting point</td>
<td>Stable up to melting point</td>
<td>Stable up to melting point</td>
</tr>
<tr>
<td>Vacuum</td>
<td>Stable up to 1700°C</td>
<td>Stable up to 2000°C</td>
<td>Becomes brittle through getter action on gas residues</td>
</tr>
<tr>
<td>&lt;10⁻² Torr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;10⁻⁴ Torr</td>
<td>Strong evaporation above 1800°C</td>
<td>Strong evaporation above 2400°C</td>
<td>Strong evaporation above 2200°C</td>
</tr>
</tbody>
</table>

*a* Kieffer and Benesovsky (1958).
800°C, but increases to 15 at % at 2600°C. In the uranium–tungsten system, tungsten dissolves up to about 0.1 at % γ-uranium, and uranium dissolves up to about 0.9 at % tungsten (Sammers-Smith, 1955). No compounds have been found in the thorium–tungsten system. There is a eutectic of 9 at % tungsten at 1474°C (Hansen, 1958).

Arsenic forms compounds with tungsten, which will be discussed in Sec. 7.6.3, and antimony and bismuth do not appear to alloy with tungsten (Reed, 1954). Vanadium dissolves up to 15 at % tungsten (Rostoker and Yamamoto, 1954), while niobium and tantalum form continuous solid solutions with tungsten (Schramm et al., 1950). Chromium forms a continuous solid solution with tungsten at temperatures above 1495°C (Greenaway, 1952). At 800°C only about 5 at % chromium is soluble in tungsten and less than 19 at % tungsten in chromium. Molybdenum and tungsten form continuous solid solutions, although there may be indications that a compound WMo exists (Grun-Grzhimalo and Prokof'ev, 1958). For more details of this system and properties of tungsten–molybdenum alloys, the reader is referred to Sec. 8.2.1. The phase diagram of the tungsten–rhenium system (see Fig. 8.6) shows that a compound exists up to the melting point (~2900°C), and another containing more rhenium exists below about 2000°C. For more details of this system and the properties of W–Re alloys, the reader is referred to Sec. 8.2.2.

The extent of solid solutions of tungsten in group VIII metals is up to 13–60 at %; but the solid solubility of these metals, other than osmium, in tungsten is small or absent. Tungsten forms various compounds with all these elements except palladium and platinum.

In the iron–tungsten system, two compounds exist — Fe₂W and Fe₃W₆ (Hansen, 1958). Above 6 at % tungsten, no γ-iron phase exists, and therefore no α–γ transition occurs. Tungsten steels generally represent multiphase systems in which precipitation of carbides, such as WC and W₂C, or double carbides, such as W₃Fe₄C and (WFe)₆C, may give dispersion hardening. For more information on the properties of steels, the reader is referred to Sec. 8.5.1. The compounds Co₃W and Co₂W₆ are well established, but others, such as Co₃W₂ (Reuth, 1959) and Co₂W₃ (Goldschmidt, 1957; Reuth, 1959) are in controversy. Alloys including cobalt, such as the Stellites, are discussed in Sec. 8.5.2, and cemented tungsten carbides, which use cobalt as a binding material, are discussed in Chapter 9. The nickel–tungsten phase diagram has been determined by Ellinger and Sykes (1940). Nickel addition to tungsten powder usually activates the sintering process, which has been discussed in Sec. 4.2.3.3. The heavy alloys, which contain nickel, copper, and tungsten, are discussed in Sec. 8.4.1.

Equilibrium phase diagrams of the systems of tungsten with ruthenium and osmium have been determined by Rapperport (1962) and by Taylor et al., (1961); system of tungsten with palladium, by Goetz and Brophy (1964). The iridium–tungsten system has been studied by Raub and Walter (1951) and by Tyulkina et al. (1963).

The physical constants and crystal structure data of binary tungsten intermetallic compounds and some nonstoichiometric phases mentioned above are shown in Table 7.4.
### Table 7.4. Physical Constants and Crystal Structure Data of Binary Intermetallic Compounds and Nonstoichiometric Phases

<table>
<thead>
<tr>
<th>Formula</th>
<th>Phase</th>
<th>Density $D_\alpha$ (g/cm$^3$)</th>
<th>$D_\beta$ (g/cm$^3$)</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$, $\alpha$, or $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI$_2$W$^a$</td>
<td>$\gamma$</td>
<td>3.88</td>
<td></td>
<td>Cub</td>
<td>Zn$_2$Zr</td>
<td>11.62</td>
<td>7.532</td>
<td>4.216</td>
<td>0.573</td>
<td></td>
</tr>
<tr>
<td>AI$_2$W$^b$</td>
<td>$\delta$</td>
<td>5.50</td>
<td>5.71</td>
<td>Hex</td>
<td>MoAl$_4$</td>
<td>4.902</td>
<td>8.857</td>
<td>1.807</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AI$_2$W$^c$</td>
<td>$\epsilon$</td>
<td>6.60</td>
<td>6.70</td>
<td>Mono</td>
<td></td>
<td>5.272</td>
<td>17.771</td>
<td>5.218</td>
<td>$\beta$: $100^\circ 12'$</td>
<td></td>
</tr>
<tr>
<td>AI$_3$W$_7$$^f$</td>
<td>$\eta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AI$_4$W$^g$</td>
<td>$\theta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_2$W$_7$</td>
<td></td>
<td>4.25</td>
<td>Tet</td>
<td>Mn$_2$Th</td>
<td>7.632</td>
<td>4.466</td>
<td>7.289</td>
<td>1.639</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_2$W$_3$</td>
<td></td>
<td></td>
<td>Hex</td>
<td>C$_{18}$</td>
<td>MgZn$_2$</td>
<td>5.130</td>
<td>4.128</td>
<td>0.8407</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$_2$W$^h$</td>
<td>$\beta$</td>
<td></td>
<td>Hex</td>
<td>DO$_{19}$</td>
<td>Ni$_3$Sn</td>
<td>8.94</td>
<td>30.42'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$_2$W$_2$$^i$</td>
<td>$\gamma$</td>
<td></td>
<td>Rhom</td>
<td>D$_{8h}$</td>
<td>Fe$_7$W$_6$</td>
<td>4.745</td>
<td>7.722</td>
<td>1.627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_2$W$_4$$^j$</td>
<td>$\delta$</td>
<td>13.0</td>
<td>Hex</td>
<td>C$_{18}$</td>
<td>MgZn$_2$</td>
<td>9.04</td>
<td>$\beta$: $30^\circ 30.5'$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_2$W$_6$$^k$</td>
<td>$\epsilon$</td>
<td></td>
<td>Rhom</td>
<td>D$_{8h}$</td>
<td>Fe$_7$W$_6$</td>
<td>7.591</td>
<td>4.465</td>
<td>1.615</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfW$_2$$^l$</td>
<td>$\gamma$</td>
<td></td>
<td>Cub</td>
<td>C$_{15}$</td>
<td>Cu$_3$Mg</td>
<td>6.67</td>
<td>501</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf$_x$W$_y$</td>
<td>$\epsilon$</td>
<td></td>
<td>HCP</td>
<td>A$_3$</td>
<td>Mg</td>
<td>2.765</td>
<td>4.465</td>
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<tr>
<td>IrW</td>
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<td></td>
<td>Hex</td>
<td>DO$_{19}$</td>
<td>Ni$_3$Sn</td>
<td>9.67</td>
<td>501</td>
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<tr>
<td>Ir$_2$W$^m$</td>
<td>$\sigma$</td>
<td></td>
<td>Ortho</td>
<td>B$_{19}$</td>
<td>$\beta$: AuCd</td>
<td>4.452</td>
<td>2.760</td>
<td>4.811</td>
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<tr>
<td>Ni$_2$W$_2$$^n$</td>
<td>$\beta$</td>
<td></td>
<td>Tetra</td>
<td>D$_{8h}$</td>
<td>CrFe</td>
<td>9.700</td>
<td>4.99</td>
<td>0.516</td>
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</tr>
<tr>
<td>Os$_2$W$^o$</td>
<td>$\sigma$</td>
<td></td>
<td>Tetra</td>
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<td>MoNi$_2$</td>
<td>5.730</td>
<td>3.533</td>
<td>0.620</td>
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<tr>
<td>Re$_2$W$^p$</td>
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<td>CrFe</td>
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<td>5001</td>
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</tr>
<tr>
<td>Ru$_2$W$^q$</td>
<td>$\sigma$</td>
<td></td>
<td>Cub</td>
<td>A$_{12}$</td>
<td>Fe$_3$Mn</td>
<td>9.588</td>
<td>4.37</td>
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<td></td>
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<tr>
<td>Ru$_2$W$_3$$^r$</td>
<td>$\gamma$</td>
<td></td>
<td>Tetra</td>
<td>D$_{8h}$</td>
<td>Fe$_3$Mn</td>
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<td>5015</td>
<td>0.520</td>
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<tr>
<td>Ru$_2$W$_4$$^s$</td>
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<td></td>
<td>HCP</td>
<td>A$_3$</td>
<td>Mg</td>
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<td>4.328</td>
<td>1.598</td>
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<tr>
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<td>$\delta$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Rh$_2$W$_3$$^u$</td>
<td>$\sigma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru$_2$W$_5$$^v$</td>
<td>$\epsilon$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru$_2$W$_6$$^w$</td>
<td>$\sigma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Density indicates the measured density; $D_\alpha$ indicates the calculated density based on x-ray lattice spacings.


$^d$ E.T.: R.T., 1327°C (Clark, 1940).


$^f$ E.T. for Al$_2$W$_4$: 1318–1422°C; for Al$_2$W$_7$: 1336–1652°C (Kubaschewski, 1950).

$^g$ E.T.: for both, R.T. (Batchelder and Baesdke, 1957).

$^h$ Matynienko et al., 1963.


$^j$ E.T. for Co$_2$W, R.T., 1490°C; for Co$_3$W, R.T., 1686°C (Magneli and Westgren, 1938).

$^k$ E.T. for Fe$_2$W, R.T., 1060°C; for Fe$_2$W, R.T., 1641°C (Hansen, 1958).

$^l$ Smith, 1941.

$^m$ Gleson and Wassenber, 1961.

$^n$ E.T.: R.T., 2650°C (Gleson et al., 1962).

$^{10}$ Braun and Rudy, 1960.

$^{11}$ E.T. for α-Ir-W, R.T., 2490°C; for α-Ir-W, 1813–2545°C (Raub and Walter, 1951).

$^{12}$ Knapper, 1958.

$^{13}$ Tykma et al., 1963.

$^{14}$ E.T. for Nb$_2$W, R.T., 971°C; for Ru$_2$W, 1670–2304°C (Obrowski, 1957).

$^{15}$ Ellinger and Sykes, 1940.

$^{16}$ Epermen and Harker, 1949.

$^{17}$ E.T.: R.T., 2951°C (Rappporte, 1962).

$^{18}$ Taylor et al., 1961.

$^{19}$ E.T. for σ phase, R.T., 3006°C (Becker and Moors, 1930).

$^{20}$ Colimeter and Richardson, 1959.

$^{21}$ Savitskii et al., 1959.

$^{22}$ E.T. for Rh–W, R.T., 2254°C; for Rh–W, 1300°C (Greenfield and Beck, 1956).

$^{23}$ Gresen and Grant, 1965.

$^{24}$ E.T.: R.T., 2150°C (Domagala et al., 1953).
7.4. BORIDES OF TUNGSTEN

Tungsten borides exist in four forms — $W_2B$, $WB$, $W_B$, and $WB_4$. The phase $WB_2$ reported by Halla and Thury (1942) has not been confirmed by others (Kiesling, 1947; Post et al., 1954; Brewer et al., 1951). The physical constants and crystal structure data of borides are shown in Table 7.5.

Tungsten borides are usually obtained by direct sintering of elemental tungsten powder and boron. Other methods include reduction of a mixture of the oxides $WO_2$ and $B_2O_3$ by aluminum, electrolysis of the molten salts, and deposition from a vapor phase (Chrétien and Freundlich, 1959). The elements titanium, tantalum, and zirconium reduce $W_2B$ to tungsten metal. $W_2B$ transforms to $WB$ when it is heated with carbon at 1900°C (Brewer et al., 1951).

$WB$ does not react with hydrochloric acid, but reacts with warm sulfuric and nitric acids. It dissolves easily in aqua regia, especially in the presence of hydrofluoric acid (Weiss, 1946). All the borides of tungsten react with dry ammonia and form nitrates at 1100°C (Kiesling and Liu, 1951). All borides are hard (above 9 Moh) and brittle and are electrically conductive.

7.5. TUNGSTEN WITH GROUP IV ELEMENTS

7.5.1. Carbides

Tungsten carbides exist in three forms — $W_2C$, $\gamma$-WC$1-x$, and WC. For more information about the carbides and their applications, the reader is referred to Chapter 9.

### Table 7.5. Physical Constants and Crystal Structure Data of Tungsten Borides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density ($g/cm^3$)</th>
<th>Melting point ($^\circ$C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_2B$</td>
<td>16.00</td>
<td>16.72</td>
<td>Tetra</td>
<td>C-16</td>
<td>Al$_2$Cu</td>
<td>5.564-5.5660</td>
<td>4.745-4.748</td>
</tr>
<tr>
<td>$\delta$-$W_2B$</td>
<td>15.30</td>
<td>16.00</td>
<td>1950</td>
<td>Gray</td>
<td>Bg</td>
<td>MoB</td>
<td>3.110</td>
</tr>
<tr>
<td>$\beta$-$W_2B$</td>
<td>13.6</td>
<td>2920</td>
<td>Ortho</td>
<td>B$_4$</td>
<td>CrB</td>
<td>3.124</td>
<td>8.445</td>
</tr>
<tr>
<td>$WB$</td>
<td>11.0</td>
<td>2000</td>
<td>He</td>
<td>C-32</td>
<td>AlB$_3$</td>
<td>6.35-8.24</td>
<td>16.4-15.6</td>
</tr>
<tr>
<td>$\alpha$-$WB$</td>
<td>8.3</td>
<td>4.34</td>
<td>Tetra</td>
<td>D$_{1}$</td>
<td>W$_2$B$_4$</td>
<td>2.982</td>
<td>13.87-13.89</td>
</tr>
<tr>
<td>$WB_4$</td>
<td>8.40</td>
<td>1600</td>
<td>He</td>
<td>X</td>
<td>ThB$_4$</td>
<td>6.34</td>
<td>4.50</td>
</tr>
</tbody>
</table>

* Kiesling (1947).
* Brewer et al. (1951).
* Kieffer et al. (1952).
* Post et al. (1954).
* Rudy et al. (1963).
* Schwartzkopf and Glaser (1953).
* Post and Glaser (1952).
* Goldschmidt (1967).
* Chrétien and Holgorsky (1961).
7.5.2. Silicides

The forms of tungsten silicides, their physical constants, and crystal structure data are shown in Table 7.6. The silicides can be prepared by direct reaction between tungsten and silicon powder in argon. According to Matynshenko et al. (1959), W$_3$Si is a product of a diffusion couple consisting of silicon and tungsten, but Kieffer et al. (1962) denied the existence of such a compound.

WSi$_2$ is stable in air up to 900°C; it reacts with fluorine above 15°C and reacts with chlorine at around 450°C, yielding the chlorides SiCl$_4$ and WCl$_6$. It is attacked only slowly by concentrated hydrofluoric acid, more rapidly by a mixture of nitric and hydrofluoric acids. It resists the attack of fused potassium sulfate but is corroded by fused alkalies. At 200°C, molten copper reduces WSi$_2$ to elemental tungsten and yields copper silicide (Chrétien and Freundlich, 1959).

7.6. TUNGSTEN WITH GROUP V ELEMENTS

7.6.1. Nitrides

Tungsten dissolves about 0.2–0.5 at % nitrogen at temperatures between 1200 and 2400°C (Hansen, 1958). Various forms of tungsten nitrides, their physical constants and crystal structure data are shown in Table 7.7.

WN$_2$ can be obtained by the direct heating of a tungsten wire in pure nitrogen at 2500°C (Langmuir, 1913). It is stable in vacuum up to 400°C. Oxygen reacts with WN$_2$ and yields an oxide according to the equation

$$2\text{WN}_2 + 3\text{O}_2 = 2\text{WO}_3 + 2\text{N}_2$$

(7.3)

W$_2$N is obtained by passing ammonia over tungsten powder at 825–875°C (Kiesling and Liu, 1951). The intermediate tungsten nitrides, from W$_2$N to W$_3$N$_6$, can be prepared by nitriding a thin film of tungsten with NH$_3$ at various temperatures above 700°C.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm$^3$)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSi$_2$</td>
<td>9.75</td>
<td>9.30</td>
<td>2165</td>
<td>Blue-gray$^*$</td>
<td>Tetra</td>
<td>C-11B</td>
<td>MoSi$_2$</td>
<td>a (Å) 3.211  b (Å) 7.868 c (Å) 2.453</td>
</tr>
<tr>
<td>W$_7$Si$_3$</td>
<td>12.2</td>
<td>2450</td>
<td></td>
<td>Tetra $^*$</td>
<td>D-8$_m$</td>
<td>W$_5$Si$_3$</td>
<td>9.605  4.964</td>
<td></td>
</tr>
<tr>
<td>W$_2$Si$_3$</td>
<td>2370</td>
<td></td>
<td></td>
<td>Tetra $^*$</td>
<td>D-8$_m$</td>
<td>W$_5$Si$_3$</td>
<td>9.56   4.94</td>
<td></td>
</tr>
<tr>
<td>W$_7$Si$_3$</td>
<td>2370</td>
<td></td>
<td></td>
<td>Hex $^*$</td>
<td>D-8$_h$</td>
<td>Mn$_2$Si$_3$</td>
<td>7.19   4.85  0.6750</td>
<td></td>
</tr>
<tr>
<td>W$_2$Si$_3$</td>
<td></td>
<td></td>
<td></td>
<td>Tetra $^*$</td>
<td>D-8$_m$</td>
<td>W$_5$Si$_3$</td>
<td>9.605  4.964 0.5168</td>
<td></td>
</tr>
</tbody>
</table>

* Matynshenko (1964).
$^*$ Dauben et al. (1956).
$^*$ Goldschmidt (1967).
$^*$ Pearson (1967).
Table 7.7. Physical Constants and Crystal Structure Data of Tungsten Nitrides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³), Dₜ</th>
<th>Melting point (°C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>Parameter</th>
<th>Reference</th>
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<tr>
<td>δ₃ W₂N</td>
<td>~12</td>
<td></td>
<td></td>
<td>Hex</td>
<td></td>
<td>NaCl</td>
<td>2.89</td>
<td>7.8</td>
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<tr>
<td>WN₁₋₀.₀₇₋₁.₀₀</td>
<td></td>
<td></td>
<td></td>
<td>FCC</td>
<td>Bl</td>
<td>NaCl</td>
<td>4.12–4.14</td>
<td>2</td>
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<tr>
<td>δ₂ W₁₋₁.₃₅₋₁.₁₅N</td>
<td>15.7</td>
<td></td>
<td></td>
<td>Hex</td>
<td></td>
<td>NaCl</td>
<td>2.885</td>
<td>5.3</td>
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<tr>
<td>δ₂ W₁₋₁.₁₇N</td>
<td>13.6</td>
<td></td>
<td></td>
<td>Rhom</td>
<td></td>
<td>WC</td>
<td>2.89</td>
<td>8.07</td>
</tr>
<tr>
<td>WN</td>
<td></td>
<td></td>
<td></td>
<td>Hex</td>
<td>Bh</td>
<td>WC</td>
<td>2.893</td>
<td>0.977</td>
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<tr>
<td>δ₂ W₂₋₂.₆₅N₄</td>
<td>11.0</td>
<td></td>
<td></td>
<td>Hex</td>
<td></td>
<td>WC</td>
<td>2.89</td>
<td>3.81</td>
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<tr>
<td>δ₂ W₀₋₀.₈N</td>
<td>10.63</td>
<td></td>
<td></td>
<td>Hex</td>
<td></td>
<td>WC</td>
<td>2.89</td>
<td>3.73</td>
</tr>
<tr>
<td>δ₂ W₃N₆ or WN₂</td>
<td>400 (dec)³</td>
<td>Brownish-black</td>
<td></td>
<td>Rhom</td>
<td></td>
<td>WC</td>
<td>2.89</td>
<td>5.67</td>
</tr>
<tr>
<td>W₂N</td>
<td></td>
<td></td>
<td></td>
<td>Cub</td>
<td>Bl</td>
<td>NaCl</td>
<td>4.126</td>
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³ dec = decomposition.
7.6.2. Phosphides

Physical constants and crystal structure data of tungsten phosphides together with arsenides are shown in Table 7.8.

WP₂ is prepared by heating tungsten powder with red phosphorus under vacuum at temperatures between 700 and 950°C (Faller et al., 1941). It can also be prepared by reduction of WO₃ by phosphorus at 550°C (Heinerth and Biltz, 1931). WP₂ is a black crystalline substance, insoluble in water, acids, alcohol, and ether. WP is obtained from the dissociation of WP₂ (Faller et al., 1941) or by the reduction of WP₂ with copper phospheide at 1200°C. It is insoluble in water, hydrochloric acid, and alkalis, but soluble in a mixture of hydrofluoric acid and aqua regia.

7.6.3. Arsenides

Physical constants and crystal structure data of tungsten arsenides with those of phosphides are shown in Table 7.8.

W₆As₂ can be prepared by heating tungsten and arsenic at 620°C (Heinerth and Biltz, 1931) or by the reaction of dry AsH with WCl₆ gas at about 350°C in the absence of air (Defacqz, 1901). W₆As₂ is a black crystalline substance. It is stable in air but oxidizes readily in heated oxygen to yield WO₃ and As₃O₃. It reacts with hydrogen above 400°C; and with chlorine around 500°C. W₆As₂ is insoluble in hydrofluoric and hydrochloric acids but is attacked by a mixture of hydrofluoric acid and aqua regia. It reacts with nitric acid to form WO₃, and reacts with sulfuric acid to yield gaseous sulfur. Aqueous alkali solutions do not react with W₆As₂, but molten alkalis attack W₆As₂ and form arsenates and alkaline tungstates (Defacqz, 1901).

7.7. TUNGSTEN WITH GROUP VI ELEMENTS

7.7.1. Oxides

The phase diagram of the tungsten–oxygen system is shown in Fig. 7.2 (St. Pierre et al., 1962; Phillips and Chang, 1964). The physical constants and crystal structure data of various oxides are shown in Table 7.9.

W₃O has been considered as an oxide and sometimes as a metal phase (β-tungsten). It can be prepared by the electrolysis of fused mixtures of WO₃ and alkali metal phosphates. It decomposes into W and WO₂ at 725°C (MacInnis, 1968).

WO₂ (brown oxide) exists in the range of WO₁.₉₄ to WO₂.₀₂ (Zelikman and Meerson, 1973). It can be obtained by reducing WO₃ with tungsten powder in the stoichiometric ratio 2:1 at 1000°C in nitrogen (Friederich and Sittig, 1925). WO₂ is stable in air and also in an atmosphere of 40–55% H₂ and 45–60% H₂O at 900°C (Rollinson, 1973). N₂O and NO oxidize WO₂ and produces the blue oxide, W₄O₁₁, at 500°C. NO₂ oxidizes WO₂ to tungstic oxide WO₃ below 300°C.
Table 7.8. Physical Constants and Crystal Structure Data of Tungsten Phosphides and Arsenides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³), D,</th>
<th>Melting point (°C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP²⁺</td>
<td>9.17</td>
<td>Black</td>
<td>Ortho</td>
<td>MoP₂</td>
<td>3.166</td>
<td>11.161</td>
<td>4.973</td>
</tr>
<tr>
<td>WP²⁺</td>
<td>12.3</td>
<td>Gray</td>
<td>Ortho</td>
<td>B-31</td>
<td>MnP</td>
<td>5.734</td>
<td>3.249 6.222</td>
</tr>
<tr>
<td>W₂P⁴⁺</td>
<td>14.3 (dec)²</td>
<td>Gray</td>
<td>Hex</td>
<td>NbP₂</td>
<td>6.19</td>
<td>6.79</td>
<td>1.097</td>
</tr>
<tr>
<td>W₂As⁴⁻</td>
<td>6.9</td>
<td>Black</td>
<td>Mono</td>
<td>NbAs₂</td>
<td>9.085</td>
<td>3.318 7.690</td>
<td>β = 119°31'</td>
</tr>
<tr>
<td>W₂As³⁻</td>
<td>13.346</td>
<td>Mono</td>
<td>Mono</td>
<td>9.599</td>
<td>β = 124°48'</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Rundqvist and Lundström, 1963.*  
*Taylor et al., 1965.*  
*Pearson, 1967.*  
*dec = decomposition.*

(Friedrich and Sittig, 1925). Heated in an inert atmosphere, WO₂ disproportionate to tungsten metal and WO₃. WO₂ dissolves in warm concentrated mineral acids. It reacts with boiling concentrated alkali solutions and yields the alkali tungstate and hydrogen (Young, 1932). Direct chlorination of WO₂ produces WCl₄ or WO₂Cl₂, depending on whether oxygen is present.

The composition of the intermediate oxide W₄O₁₁ (mixture of W₁₈O₄⁹ and W₂₀O₅₈) (blue oxide) has been in controversy for many years. The best explanation is probably as follows: W₁₈O₄⁹ exists in the range of WO₂.0₂ to WO₂.66₄, and W₂₀O₅₈ exists in the range of WO₂.6₆₄ to WO₂.₉₄ (St. Pierre et al., 1962). However, these oxides ordinarily mix and assume the general formula W₄O₁₁, which is called

---

Fig. 7.2. Phase diagram for equilibrium of the tungsten–oxygen system for total pressure of 1 atm.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>Symbol</th>
<th>Prototype</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dₘ</td>
<td>Dₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W₂O</td>
<td>15.0</td>
<td>14.8</td>
<td>725 (dec)</td>
<td>Gray</td>
<td>Cub</td>
<td>A15</td>
<td>β-W</td>
<td>5.036</td>
</tr>
<tr>
<td>WO₂</td>
<td>11.05</td>
<td>10.88</td>
<td>1500–1600</td>
<td>Brown</td>
<td>Tetra</td>
<td>C4</td>
<td>TiO₂</td>
<td>4.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td>Cₘ</td>
<td>VO₂</td>
<td>5.560 2.77</td>
</tr>
<tr>
<td>δ-WO₂</td>
<td></td>
<td></td>
<td>2000</td>
<td>Brown</td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-W₁₈O₄₉</td>
<td>7.72</td>
<td>8.01</td>
<td></td>
<td>Reddish-violet</td>
<td>Mono</td>
<td></td>
<td></td>
<td>18.32 3.79</td>
</tr>
<tr>
<td>WO₂₉</td>
<td>7.16</td>
<td></td>
<td></td>
<td>Blue-violet</td>
<td>Mono</td>
<td></td>
<td></td>
<td>3.80 3.81 3.7</td>
</tr>
<tr>
<td>α-WO₂₉</td>
<td>7.29</td>
<td></td>
<td>1473</td>
<td>Yellow</td>
<td>Tetra</td>
<td></td>
<td></td>
<td>5.27 3.920</td>
</tr>
<tr>
<td>&gt; 740°C</td>
<td>7.07</td>
<td></td>
<td>1700</td>
<td></td>
<td>Ortho</td>
<td></td>
<td></td>
<td>7.28 7.45 3.81</td>
</tr>
<tr>
<td>350–735°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td>3.824 7.501 7.274</td>
</tr>
<tr>
<td>&lt; 350°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td>7.30 7.53 7.68</td>
</tr>
<tr>
<td>Room temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tricl</td>
<td></td>
<td></td>
<td>7.30 7.52 7.69</td>
</tr>
<tr>
<td>− 40–17°C</td>
<td>7.29</td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td>5.27 5.16 7.67</td>
</tr>
<tr>
<td>&lt; 40°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* dec = decomposition.
* Sublimation point, 1100°C.
“blue oxide” because of the color of the mixture (Robin and Day, 1967). It has been observed that the compositions of the intermediate oxides formed during the course of reduction are strongly affected by the reducing agent and conditions (Cerulli and Wei, 1963).

The blue oxide may be prepared by heating the anhydride WO₃ for 1 hr at 800°C in a mixture of 1 volume of hydrogen to 2 volumes of water vapor at 1 atm pressure (Wöhler and Kunst, 1932). The blue oxide dissociates completely above 1700°C. When wet, it is easily attacked by aqua regia in the presence of nitric acid. At high temperature, it reacts with hydrogen chloride gas according to the equation

$$3W_4O_{11} + 22HCl = W + 11WO_2Cl_2 + 11H_2O$$

(7.4)

WO₃ has three allotropic forms, as shown in the Table 7.9. WO₃ absorbs hydrogen and carbon oxides up to 450°C. Adsorption isotherms are known for water vapor, alcohol, acetic acid, and ether (Pearce and Rice, 1929). WO₃ is the final product of the oxidation of tungsten or of its compounds. It is insoluble in acids but dissolves easily in the alkalis. Tungsten oxides unite with basic oxides and produce tungstates of different forms. These tungstates will be discussed in Sec. 7.9.2.

Both hydrogen and carbon monoxide reduce tungsten oxides from higher oxidation states to lower ones and eventually to pure metal. Methane also reduces WO₃ to W₄O₁₁ near 670°C and reduces WO₃ to metal at 950°C.

### 7.7.2. Sulfides

Physical constants and crystal structure data of tungsten sulfides, together with those for selenides and telluride are shown in Table 7.10.

WS₂ can be prepared by direct synthesis of sulfur and tungsten at 800–900°C in pure nitrogen atmosphere (Van Arkel, 1926). It can also be prepared by passing sulfur or a sulfide vapor over tungsten or tungstic oxide powder at 1400°C; the reaction takes place as follows:

$$2WO_3 + 4S = 2WS_2 + 3O_2$$

(7.5)

Thermal decomposition of tungsten(VI) sulfide also generates this compound (Glemser et al., 1948). WS₂ is insoluble in water and resists the corrosion of nitric and sulfuric acids. Hydrofluoric–aqua regia mixtures attack WS₂ vigorously. It is soluble in molten alkalis and alkali carbonates and very soluble in the carbonates with the presence of an oxidation agent (Weiss, 1946).

WS₃ is prepared by the reaction between Na₂WS₄ and heated sulfuric acid (Weiss and Martin, 1909) or by the reaction of hydrochloric acid and a solution of (NH₄)₂WS₄ (Glemser et al., 1948). WS₃ is a reddish-brown powder. Its solubility in water depends on the temperature. It is soluble in basic solutions. WS₃ dissociates into WS₂ and sulfur above 170°C. Hydrogen reduces it to metallic tungsten. Heated with lime, WS₃ yields tungsten according to the equation

$$WS_3 + 2CaO = W + 2CaS + SO_2$$

(7.6)
Table 7.10. Physical Constants and Crystal Structure Data of Tungsten Sulfides, Selenides, and Telluride

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Melting point (°C)</th>
<th>Color</th>
<th>Crystal structure data</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_m$</td>
<td>$D_x$</td>
<td></td>
<td>Symmetry</td>
<td>Symbol</td>
</tr>
<tr>
<td>WS₂⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rhom</td>
</tr>
<tr>
<td>WS₂⁺</td>
<td></td>
<td></td>
<td>170 (dec)</td>
<td>reddish-brown</td>
<td></td>
</tr>
<tr>
<td>WSe₂⁺</td>
<td>9.22</td>
<td>9.32</td>
<td>800 (dec)</td>
<td>Black</td>
<td>C7</td>
</tr>
<tr>
<td>WSe₂⁺</td>
<td></td>
<td></td>
<td>220 (dec)</td>
<td></td>
<td>Rhom</td>
</tr>
<tr>
<td>WTe₂⁺</td>
<td>9.44</td>
<td>9.49</td>
<td>972 (dec)</td>
<td>Yellow</td>
<td>C7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rhom</td>
</tr>
</tbody>
</table>

* Wildervanch and Jellineh, 1964.
* Glemser et al., 1948.
* Knop and Haraldsen, 1956.
* Zelikman, 1970.
* Brixner, 1962.
* Opalovskii and Fedorov, 1971.
7.7.3. Selenides

Physical constants and crystal structure data of tungsten selenides together with those of sulfides and telluride are shown in Table 7.10. WSe₂ is prepared by combining the elements, tungsten and selenium at 950°C in nitrogen (Glemser et al., 1948) or by the thermal dissociation of WSe₃. WSe₃ is prepared by saturating a solution of Na₂WO₄ with SeH₂ and then precipitating with dilute sulfuric acid. The precipitates are further purified by CS₂ (Moser and Atynski, 1925). WSe₃ is black in color and soluble in concentrated hydrochloric acid. It decomposes at 220°C to WSe₂.

7.7.4. Telluride

Only one compound, WTe₂, has been established in the tungsten–tellurium system. The physical constants and crystal structure data of this compound together with those of sulfides and selenides are shown in Table 7.10. WTe₂ is prepared by direct combination of the elements in vacuum below 750°C (Goldschmidt, 1929), and it crystallizes into yellow needles. It is inert in water, ammonia, hydrochloric acid, and sulfuric acid (Obolonchik et al., 1972). It decomposes in nitric acid (Morette, 1944), reacts with oxygen at around 650–700°C, and dissociates in vacuum at about 972°C.

7.8. TUNGSTEN WITH GROUP VII ELEMENTS

Under this group, simple halides and oxyhalides will be discussed. Hexahalides of fluorine, chlorine, and bromine are well known. Some of the pentahalides, all the tetrahalides, and all the dihalides except that of fluorine have been prepared.

Except for fluorides, the tungsten halides are solid compounds at room temperature. When heated, they often decompose before starting to melt. If heated in the presence of air or moisture, oxyhalides are formed. Physical constants and crystal structure data of tungsten halides are shown in Table 7.11. For thermodynamic properties of tungsten halides, the reader is referred to Rieck (1967).

7.8.1. Fluorides and Oxyfluorides

Tungsten tetrafluoride, WF₄, is prepared by the reduction of the hexafluoride WF₆ with benzene at 110°C for 3–9 days (Priest and Schumb, 1948). It can be prepared in low yields by the reduction of WF₆ with PF₃ in the presence of liquid HF at room temperature (O'Donnell and Steward, 1966). WF₄ is hygroscopic and hydrolyzes in a heated alkali solution. It oxidizes in an acidic medium and forms WO₃. It decomposes to tungsten and fluorine at 800°C in vacuum.

Tungsten hexafluoride WF₆ can be prepared by one of the following methods:
a. Direct synthesis: Powdered tungsten reacts with fluorine gas directly. This reaction occurs at a temperature of 350–400°C and is very exothermic (Barber and Cady, 1956).

b. Reaction between tungsten hexachloride and hydrofluoric acid: This reaction takes place at temperatures between 0°C and 20°C according to the equation

\[
WC\text{Cl}_6 + 6HF = W\text{F}_6 + 6HCl
\]  

(7.7)

c. Reaction of fluorides such as AsF$_3$ or SbF$_5$ with tungsten hexachloride:

\[
W\text{Cl}_6 + 2\text{AsF}_3 = W\text{F}_6 + 2\text{AsCl}_3
\]

(7.8a)

\[
W\text{Cl}_6 + 3\text{SbF}_5 = W\text{F}_6 + 3\text{SbF}_3\text{Cl}_2
\]

(7.8b)

The latter reaction is often explosive (Chrétien and Freundlich, 1959).

WF$_6$ is a colorless gas at room temperature. It solidifies into white substance at 2.5°C under a pressure of 375 Torr. WF$_6$ is very reactive, attacking all metals with the exception of gold and platinum. Dry WF$_6$ gas slowly erodes glass. The erosion increases rapidly in the presence of moisture. It is very hygroscopic (Ruff et al., 1907), and hydrolizes with the formation of tungsten hydrate (Sidgwick, 1924). It is soluble in alkalis and in alkaline fluorides (Ruff et al., 1907). When dissolving in organic solutions, it changes their colors: in benzene and cyclohexane, red; in dioxane, pale red; and in ether, violet-brown.

WOF$_2$ is prepared by the reaction between WO$_2$ and hydrofluoric acid at 600°C (Priest and Schumb, 1948) as follows:

\[
WO_2 + 2HF = \text{WOF}_2 + H_2O
\]

(7.9)

WOF$_2$ is gray in color, is very inert, and resists concentrated acids and boiling alkalis (Chrétien and Freundlich, 1959).

WOF$_4$ is prepared through a double decomposition between the oxychloride WOC$_4$ and hydrofluoric acid. It can also be prepared through the reaction of lead fluoride PbF$_2$ on the trioxide WO$_3$ at 700°C. The following reaction produces WOF$_4$ as well as WF$_6$ (Wiechert, 1950):

\[
5W + 26HF + 6\text{HNO}_3 = 3\text{WF}_6 + 2\text{WOF}_4 + 16H_2O + 3\text{N}_2
\]

(7.10)

WOF$_4$ is a crystalline white substance. It is soluble in water, readily soluble in chloroform, slightly soluble in CS$_2$, and insoluble in CCl$_4$. It combines with NH$_3$ to form an orange solid, WOF$_4$·$\frac{1}{2}$NH$_3$ (Ruff et al., 1907).

7.8.2. Chlorides and Oxychlorides

Tungsten bichloride, WCl$_2$, is prepared by disproportionation of the tetrachloride at 450–500°C (McCarley and Brown, 1964):
<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³), $D_m$</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Color</th>
<th>Crystal structure data</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
</tr>
<tr>
<td>WF₆</td>
<td>$149^b$</td>
<td>2.5</td>
<td>17.5</td>
<td>White</td>
<td>Cub (0°C)</td>
<td>6.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(at 375 mm)</td>
<td></td>
<td></td>
<td></td>
<td>Ortho (~30°C)</td>
<td>2.68</td>
<td>18.81</td>
</tr>
<tr>
<td>WF₄</td>
<td></td>
<td></td>
<td></td>
<td>Reddish-brown</td>
<td>Ortho</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOF₄</td>
<td>119</td>
<td>190</td>
<td></td>
<td>White</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOF₂</td>
<td></td>
<td></td>
<td></td>
<td>Gray</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO₂F₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCl₆</td>
<td>3.52</td>
<td>275</td>
<td>346.4</td>
<td>Steel blue</td>
<td>Hex</td>
<td>6.100</td>
<td>16.70</td>
</tr>
<tr>
<td>WCl₅</td>
<td>3.875</td>
<td>248</td>
<td>276</td>
<td>Dark green</td>
<td>Ortho</td>
<td>8.07</td>
<td>8.89</td>
</tr>
<tr>
<td>WCl₄</td>
<td>4.624</td>
<td></td>
<td></td>
<td>Sublimes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCl₂</td>
<td>5.436</td>
<td></td>
<td></td>
<td>Black</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>WOCl₄</td>
<td>11.92d</td>
<td>209</td>
<td></td>
<td>Red needles</td>
<td>Ortho</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO₂Cl₂</td>
<td></td>
<td></td>
<td></td>
<td>Sublimes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOC₁₇</td>
<td></td>
<td></td>
<td></td>
<td>Yellow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOC₁₇</td>
<td></td>
<td></td>
<td></td>
<td>Green</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOC₁₂</td>
<td>5.92</td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td>12.87</td>
<td>3.76</td>
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### Compounds with Bromine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Color</th>
<th>Melting Point</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBr$_2$</td>
<td></td>
<td></td>
<td>400 (dec)</td>
<td>Black</td>
</tr>
<tr>
<td>WBr$_3$</td>
<td></td>
<td></td>
<td>50 (dec)</td>
<td>Black</td>
</tr>
<tr>
<td>WBr$_4$</td>
<td></td>
<td></td>
<td>400 (dec)</td>
<td>Black</td>
</tr>
<tr>
<td>WBr$_5$</td>
<td></td>
<td></td>
<td>276 333 (dec)</td>
<td>Brown-black</td>
</tr>
<tr>
<td>WBe$_6$</td>
<td></td>
<td></td>
<td></td>
<td>Bluish-black</td>
</tr>
<tr>
<td>WBBr$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WBBr$_3$</td>
<td></td>
<td></td>
<td></td>
<td>Brown</td>
</tr>
<tr>
<td>WBBr$_4$</td>
<td></td>
<td></td>
<td>277 327 (dec)</td>
<td>Brown, black, red</td>
</tr>
</tbody>
</table>

### Compounds with Iodine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Color</th>
<th>Melting Point</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>WI$_2$</td>
<td></td>
<td>Brown</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>WI$_{4.5}$</td>
<td></td>
<td>Brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WI$_4$</td>
<td></td>
<td></td>
<td>5.2</td>
<td>Gray needles</td>
</tr>
<tr>
<td>WI$_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOI$_2$</td>
<td></td>
<td></td>
<td></td>
<td>Black</td>
</tr>
<tr>
<td>WO$_2$I$_2$</td>
<td></td>
<td>Tetra</td>
<td>6.39 6.40 200</td>
<td>18.01 7.58</td>
</tr>
<tr>
<td>WO$_2$I$_3$</td>
<td></td>
<td>Mono</td>
<td></td>
<td>17.095 3.899 7.492 $\beta = 102.66^\circ$</td>
</tr>
<tr>
<td>WO$_3$I$_4$</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>WOI$_4$</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>


* Using density of hydrogen as unit.

* Ketelaar et al., 1943.

* Using density of air as unit.
\[ 3\text{WCl}_4 = \text{WCl}_2 + 2\text{WCl}_5 \] (7.11)

The reduction of WCl₆ by sodium amalgam also produces WCl₂ (Hill, 1916). It is a gray solid, nonvolatile, and infusible, and it is a strong reducer.

Tungsten tetrachloride, WCl₄, is prepared by reduction of WCl₆ with hydrogen, aluminum, or white phosphorus (McCarley and Brown, 1964). The reaction between the chlorides WCl₅ and WCl₂, also produces WCl₄:

\[ 2\text{WCl}_5 + \text{WCl}_2 = 3\text{WCl}_4 \] (7.12)

WCl₄ is a nonvolatile crystalline solid, very hygroscopic, and easily hydrolyzed. Hydrogen reduces WCl₄ to WCl₂ and then to tungsten.

Tungsten pentachloride, WCl₅, is prepared by reducing the hexachloride with hydrogen at 400°C (Hein and Herzog, 1965) or with phosphorus at 280°C (Brown and Ruble, 1967). It can also be prepared by the following reaction at 100°C (Brown and McCann, 1968):

\[ 2\text{WCl}_6 + \text{C}_2\text{Cl}_4 = 2\text{WCl}_5 + \text{C}_2\text{Cl}_6 \] (7.13)

WCl₅ is very hygroscopic and sensitive to hydrolysis. It is slightly soluble in dry carbon disulfide. By combustion in air it oxidizes and forms WOCl₄. It disproportionates thermally into WCl₄ and WCl₆.

Tungsten hexachloride, WCl₆, is easily prepared by direct combination of the metal with extremely dry and oxygen-free chlorine:

\[ \text{W} + 3\text{Cl}_2 = \text{WCl}_6 \] (7.14)

The pure WCl₆ is obtained by several consecutive sublimations (Hönigschmid and Menn, 1936). It can also be prepared by the reaction of S₂Cl₂, PCl₅, HCl, COCl₂, or CCl₄ with tungsten and by the reaction of HCl with WS₃ (Hein and Herzog, 1965). A solid-state transformation occurs between 168 and 270°C that causes WCl₆ to expand drastically (MacInnis, 1968). Pure WCl₆ is relatively stable in dry air. In the presence of moisture, it transforms into WOCl₄, then into the hydrate WO₃·2H₂O (Bergstrom, 1925). The hydrides BrH, IH, H₂S, H₃P, and H₃As may displace the chlorine in WCl₆ completely to form WBr₅, WI₂, WS₂, WP₂, and WAs₂, respectively. Sometimes they partially displace chlorine and form mixed chlorine compounds, such as chlorosulfide, chlorobromide, or chloroarsenide. The formation of one or the other of these compounds depends upon the temperature and the experimental procedure (Defacqz, 1901). Most of the metallic elements reduce the hexachloride WCl₆ to lower chlorides; the reduction can be continued down to the metallic tungsten.

WCl₆ is soluble only slightly in water at 15°C and does not become hydrolyzed until the temperature reaches 60°C. It is very soluble in alcohol, chloroform, carbon tetrachloride, carbon disulfide, ether, benzene, acetone, ammonia, and many other organic solvents. These solutions decompose slowly in air, but decompose rapidly when heated or with the addition of water. WCl₆ reacts with
phenol at the boiling point, yielding a dark red residue of tungsten hexaphenolate
(Funk and Baumann, 1937):

\[ \text{WCl}_6 + 6\text{HOC}_6\text{H}_5 = \text{W} (\text{OC}_6\text{H}_5)_6 + 6\text{HCl} \]  
(7.15)

Gaseous \( \text{WCl}_6 \) can be thermally reduced by hydrogen to lower oxidation states according to the following chain (Saeki and Matsuzaki, 1973):

\[ \text{WCl}_6 \rightarrow \text{WCl}_5 \rightarrow \text{WCl}_4 \rightarrow \text{WCl}_{2.6} \rightarrow \text{WCl}_2 \rightarrow \text{W} \]

Tungsten(IV) oxychloride is prepared by heating the mixture of the powders of tungsten, tungstic oxide, and hexachloride under vacuum in a capsule at a temperature range of 250–450°C (Tillack et al., 1970):

\[ \text{W} + \text{WO}_3 + \text{WCl}_6 = 3\text{WOCl}_2 \]  
(7.16)

It crystallizes into needles with the luster of copper. When the compound is heated in air, it forms \( \text{WO}_2\text{Cl}_2 \) and finally decomposes to \( \text{WO}_3 \). It does not react with \( \text{HCl}, \text{H}_2\text{SO}_4, \text{HNO}_3, \text{or CH}_3\text{COOH} \) at room temperature, but it is soluble in hot \( \text{HNO}_3 \) and \( \text{H}_2\text{O}_2 \). Neither cold nor hot \( \text{NH}_3 \) attacks the \( \text{WOCl}_2 \) crystals. \( \text{WOCl}_2 \) reacts with \( \text{NaOH} \) solution and produces a black deposit.

Tungsten(V) oxychloride is prepared by heating the mixture of tungsten pentachloride and antimony oxide under vacuum at 100°C, followed by gradually raising the temperature to 170°C. The reaction that takes place is:

\[ 3\text{WCl}_5 + \text{Sb}_2\text{O}_3 = 3\text{WOCl}_3 + 2\text{SbCl}_3 \]  
(7.17)

The product is a gray crystalline substance (Crouch et al., 1968). It can also be prepared by the reduction of \( \text{WOCl}_4 \) with tetrachloroethylene (Brown and McCann, 1968) or by the aluminum reduction of the oxytetrachloride (Crouch et al., 1968). Upon heating, \( \text{WOCl}_3 \) disproportionates according to the equation

\[ 2\text{WOCl}_3 = \text{WOCl}_4 + \text{WOCl}_2 \]  
(7.18)

Tungsten(VI) oxychlorides appear in two forms — \( \text{WO}_2\text{Cl}_2 \) and \( \text{WOCl}_4 \). The former is prepared by chlorination of the oxide \( \text{WO}_3 \) at 900°C according to the equation (Galmiche, 1948)

\[ 2\text{WO}_3 + 2\text{Cl}_2 = 2\text{WO}_2\text{Cl}_2 + \text{O}_2 \]  
(7.19)

Also, hydrogen chloride gas reacts with \( \text{WO}_3 \) and forms \( \text{WO}_2\text{Cl}_2 \) at or above 300°C (Spitsyn and Kaschtaffoff, 1926). \( \text{WO}_2\text{Cl}_2 \) crystallizes into a light yellow substance and is insoluble in common organic solvents. Upon heating, \( \text{WO}_2\text{Cl}_2 \) dissociates into \( \text{WOCl}_4 \) and \( \text{WO}_3 \). It does not react with liquid hydrofluoric acid but reacts slightly with HF gas at about 180°C. \( \text{WO}_2\text{Cl}_2 \) is soluble in the alkalis and forms tungstates (Ruff et al., 1907).
WOCl₄ is prepared by any of the following methods (Chrétien and Freundlich, 1959):

a. Direct reaction of chlorine on tungsten powder or tungsten sulfide in the presence of oxygen or water vapor.

b. Reaction of WCl₆ vapor and WO₃:

\[ \text{WO}_3 + 2\text{WCl}_6 = 3\text{WOCl}_4 \]  
(7.20)

c. Reaction of a mixture of CCl₂F₂ and WO₂ in a nickel container:

\[ 2\text{WO}_2 + 2\text{CCl}_2\text{F} = \text{WOCl}_4 + \text{WO}_4\text{F}_4 + 2\text{CO} \]  
(7.21)

WOCl₄ crystallizes into scarlet needles. It is soluble in carbon disulfide and sulfur chloride. It hydrolyzes quite readily in slightly acidic warm water, reacting in the following manner:

\[ \text{WOCl}_4 + 2\text{H}_2\text{O} = \text{WO}_3 + 4\text{HCl} \]  
(7.22)

WOCl₄ reacts with carbon to form WCl₆, with oxygen to form WO₂Cl₂ and then WO₃, with dry ammonia to form tungsten nitrates, with PCl₅ to form WCl₆, and with HF to form WOF₄. At high temperatures, WOCl₄ reacts with silica according to the equation

\[ \text{SiO}_2 + 2\text{WOCl}_4 = \text{SiCl}_4 + 2\text{WO}_2\text{Cl}_2 \]  
(7.23)

7.8.3. Bromides and Oxybromides

Tungsten dibromide, WBr₂, is prepared by reduction of the pentabromide with hydrogen in the presence of zinc chloride at about 400°C. It can also be prepared by the disproportion of tetrabromide at 450°C (McCarley and Brown, 1964):

\[ 3\text{WBr}_4 = \text{WBr}_2 + 2\text{WBr}_5 \]  
(7.24)

WBr₂ is a black solid, with properties similar to those of WCl₂. Reaction between WBr₂ and KNH₂ yields W(KN)₂NH₂ (Bergstrom, 1925).

Tungsten tribromide, WBr₃, is prepared by soaking WBr₂ in liquid bromine at 50°C for a period of time. It is black compound and decomposes at about 80°C (Siepmann and Schaffer, 1965). At 450–500°C, WBr₃ disproportionates to WBr₅ and WBr₂ (McCarley and Brown, 1964).

Tungsten tetrabromide, WBr₄, is prepared by the reduction of WBr₅ with aluminum or tungsten. It can also be obtained by the decomposition of WBr₅ at 180°C in vacuum.

Tungsten pentabromide, WBr₅, is prepared by the direct vapor bromination of tungsten powder. It can also be prepared by reducing WCl₆ with HBr (Rollinson,
1973). WBr$_5$ crystallizes into brownish-black needles. It melts at 276°C and boils at 333°C. It is hygroscopic, unstable in air, and soluble in ether, carbon tetrachloride, chloroform, bromoform, and benzene. Upon heating, WBr$_5$ decomposes (Rollinson, 1973) according to the reaction

$$2\text{WBr}_5 = 2\text{WBr}_4 + \text{Br}_2$$  \hspace{1cm} (7.25)

Tungsten hexabromide, WBr$_6$, is prepared by direct synthesis with bromine vapor and slightly heated tungsten powder (Schaffer and Smith, 1896). It crystallizes in the form of bluish-black needles. WBr$_6$ decomposes on heating and hydrolyzes readily. It reacts with water to form W$_4$O$_{11}$, and dissolves in ammonia.

Tungsten(V) oxybromide, WOBr$_3$, is prepared by heating the mixture of tungsten pentabromide and antimony oxide powders under vacuum at 100°C for 1 hr; and then the temperature is raised to and held at 150°C for 24 hr. The reaction that takes place is (Crouch et al., 1969)

$$3\text{WBr}_5 + \text{Sb}_2\text{O}_3 = 3\text{WOBr}_3 + 2\text{SbBr}_3$$  \hspace{1cm} (7.26)

WOBr$_3$ crystallizes into a brown fibrous structure. The decomposition of WOBr$_3$ begins at 250°C according to the reaction

$$3\text{WOBr}_3 = \text{WOBr}_4 + \text{WO}_2\text{Br}_2 + \text{WBr}_3$$  \hspace{1cm} (7.27)

Tungsten(VI) oxybromides exist in two different forms: WOBr$_4$ and WO$_2$Br$_2$ (Chrétien and Freundlich, 1959). WOBr$_4$ is prepared by the reaction of bromine vapor on a heated mixture of WO$_3$, carbon, and tungsten powder. It is a brownish-black crystal, very hygroscopic, and decomposes rapidly in air. WO$_2$Br$_2$ is formed by passing a mixture of air and bromine vapor over tungsten powder at 700–800°C. It is an infusible red or brown substance that is less volatile than WOBr$_4$. With rapid heating, it decomposes as follows:

$$2\text{WO}_2\text{Br}_2 = \text{WO}_3 + \text{WOBr}_4$$  \hspace{1cm} (7.28)

7.8.4. Iodides and Oxyiodides

Tungsten diiodide, W$_6$I$_{12}$ (Schäfer et al., 1967), is prepared by passing iodine vapor over tungsten powder at 800°C (Defacqz, 1901). It can also be prepared by the reaction between iodine and W(CO)$_6$ in nitrogen atmosphere. In this reaction, W(CO)$_6$ and iodine gas first form WI$_x$, where $x$ equals approximately 3.2 at about 250°C. At 600°C, WI$_x$ and iodine gas form W$_6$I$_{12}$ (Schulz et al., 1970). It is a brownish crystalline substance with a hexagonal crystal structure in the form of [W$_6$I$_8$] I$_3$I$_{12}$ (Schäfer et al., 1967). W$_6$I$_{12}$ reacts with 6 N HCl solution and forms [W$_6$I$_8$]Cl$_4$·2H$_2$O.

W$_6$I$_{15}$ is prepared by the reaction between W$_6$I$_{12}$ and iodine gas at 350°C in vacuum for 3 days (Schulz et al., 1970). The product W$_6$I$_{15}$ coexists with WI$_3$. 
W₆I₁₅ is a brown substance and exists probably in the form of [W₆I₈]₄[I₃]₂/₁₂. Its crystal structure has not been determined; however, it does present a unique x-ray powder diffraction pattern. It is stable in air and decomposes in a solution of KOH or concentrated H₂SO₄.

Tungsten triiodide, WI₃, is prepared by the reaction between W₆(CO)₆ and iodine gas at 247–267°C (Virmani et al., 1974). WI₃ is also one of the products of the reaction between W₆I₁₂ and iodine gas. WI₃ crystallizes in the form of gray needles.

Tungsten tetraiodide, WI₄, is prepared by heating WCl₆ with HI gas at 110°C. It can also be prepared from the reaction of WO₂ with AI₃. WI₄ is a black, crystalline substance that changes slowly in air and volatilizes, decomposing to WI₂ and I₂. It is insoluble in water but will hydrolyze. It is insoluble in ether and chloroform but is slowly soluble in cold alcohol (Defacqz, 1901). Chlorine replaces iodine in WI₄ at 18°C, bromine in WI₄ at 100°C. KOH solutions, liquid potassium, molten alkali carbonates, and molten potassium bisulfide dissolve WI₄ and release iodine.

Tungsten(IV) oxyiodide, WO₁₂, is prepared by heating a mixture of tungsten, tungstic oxide, and iodine powders under vacuum in a two-zone furnace, which is held at 500°C and 700°C, respectively, for 36 hr. The reaction that occurs is (Bartecki et al., 1972)

\[ 2W + WO_3 + 3I_2 \rightarrow 3WOI_2 \]  

(7.29)

The resulting WOI₂ is then purified by benzene extraction. The pure WOI₂ crystallizes in the form of glittering black plates. It is diamagnetic, slightly soluble in water and organic solvents, and very soluble in NaOH or KOH solutions.

Tungsten(VI) oxyiodide, WO₂I₂, is prepared by the direct reaction of WO₂ and iodine gas (Dettingmeijer and Meinders, 1968). It can also be prepared by using the chemical transport technique (Tillack et al., 1970). WO₂I₂ decomposes to WO₂I and iodine gas at 277°C. During this decomposition process, WOI₃ can also be observed in a gaseous state (Gupta, 1969).

7.9. TUNGSTEN HYDRATES (TUNGSTEN ACIDS) AND THEIR SALTS

7.9.1. Tungsten Hydrates — Tungsten Acids

The hydrates of tungsten are also considered to be acids. They are the products of the reaction of a strong acid, preferably hydrochloric acid, and a solution of alkali tungstate, such as sodium tungstate (Chrétiens and Freundlich, 1959). Different forms of hydrates may occur depending on the concentration of the acid and temperature. Table 7.12 lists the formation conditions of the different hydrates (Freedman, 1959) and their properties.

The monohydrate WO₃·H₂O is very stable up to 150°C and is soluble in hydrofluoric acid, ammonia, and in basic solutions. The dihydrate WO₃·2H₂O is
Table 7.12. Formation Conditions and Properties of Tungsten Hydrates — Tungsten Acids

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Density</th>
<th>Color</th>
<th>Temperature</th>
<th>HCl concentration (N)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monohydrate</td>
<td>WO₃·H₂O</td>
<td>5.5</td>
<td>Orange-yellow</td>
<td>100°C</td>
<td>2-9</td>
<td>WO₃(H₂O)·1.0H₂O</td>
</tr>
<tr>
<td>Dihydrate</td>
<td>WO₃·2H₂O</td>
<td>4.613</td>
<td>Yellow gel</td>
<td>25°C</td>
<td>0.5-9.0</td>
<td>WO₃(H₂O)·2.2H₂O</td>
</tr>
<tr>
<td>Tungsten gel</td>
<td>WO₃·2H₂O</td>
<td></td>
<td>White colloidal</td>
<td>25°C</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>WO₃·H₂O</td>
<td></td>
<td>White</td>
<td>100°C, gel + water</td>
<td>1</td>
<td>(Heating WO₃·H₂O with saturated Na₂WO₄ solution)</td>
</tr>
<tr>
<td>Acid derivative</td>
<td>Na₂O(WO₃·H₂O)₄·10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Freedman, 1959.

stable up to 55°C, loses water in the temperature range of 55–75°C, and transforms to the monohydrate. The term "tungstic acid" usually refers to the mixture of these two hydrated forms of tungsten oxide (Schwarzmann and Glemser, 1961).

Tungsten gel, or amorphous hydrates, or metatungstic acid anhydride, WO₃·2H₂O, appears glassy when completely dried.

The hemihydrate of tungsten WO₃·½H₂O is prepared by dissolving tungsten gel in warm water. It is soluble in ammonia. It often contains some alkali and therefore is also written as Na₂O·(WO₃·½H₂O)₈·40 (sodium octatungstate) (Freedman, 1959).

Tungstic acid derivative exists in the form Na₂O·(WO₃·H₂O)₄·10 (sodium tetratungstate) (Freedman, 1959). It is formed when WO₃·½H₂O is boiled with 0.1 N NaOH.

7.9.2. Tungstates

The tungstate compounds can be classified in the following categories:

A. Normal tungstates or monotungstate. Normal tungstates are derived from the acids H₃WO₄ or H₃WO₅. The standard formula of normal tungstates is M₂O·WO₃ or MO·WO₃, i.e., one molecule of WO₃ for each radical. It may also have more than one molecule of WO₃ for each radical.

B. Polytungstates

1. Isopolytungstates. These tungstates are so called because the anion contains only one metallic element, tungsten, e.g., [H₈W₄O₁₇]²⁻ in Na₂[H₈W₄O₁₇].
   a. Metatungstate. The standard formula for metatungstate is 3M₂O·12WO₃·aq, with the ratio M₂O:WO₃ = 1:4.
   b. Paratungstate. The standard formula for paratungstate is 5M₂O·12WO₃·aq, with the ratio M₂O:WO₃ = 5:12.

2. Heteropolytungstates and other tungstic complexes. When some of the hydrogen atoms in the anion of an isopolytungstate are replaced by an element such as phosphorus, arsenic, boron, silicon, or germanium, the tungstate is called a heteropolytungstate. Other tungstic complexes include those in which oxygen
atoms are replaced by such elements as sulfur (thiotungstate), fluorine (fluorotungstate), or organic radicals.

### 7.9.2.1. The Normal Tungstates of Monovalent Metals

The physical constants and crystal structure data of these tungstates are listed in Table 7.13. Sodium tungstate, Na₂WO₄, is prepared by dissolving anhydrous WO₃ in molten Na₂CO₃. Hydrogen reduces Na₂WO₄ to tungsten at 100°C. Na₂WO₄ forms oxychlorides when heated with chlorine and thiotungstate when heated with sulfur. Hydrogen chloride gas reacts with Na₂WO₄ and forms NaCl, WO₃, and H₂O at 350°C (Spitsyn and Kaschtanoff, 1926). Commercial sodium tungstate exists in the form of Na₂WO₄·2H₂O, which loses its water of hydration near 100°C. The hydrate salt is soluble in water, but not in common organic solvents such as alcohol or nitrobenzene.

Potassium tungstate, K₂WO₄ is prepared by melting a stoichiometric equivalent mixture of WO₃ and K₂CO₃. The anhydrous form is obtained by cooling a warm saturated solution. Below 10°C, the bihydrate crystallizes (K₂WO₄·2H₂O). The salt K₂WO₄ is very soluble in water. In warm aqueous solution, it transforms into paratungstate:

$$12K₂WO₄ + 7H₂O = 5K₂O·12WO₃ + 14KOH \quad (7.30)$$

At 570°C, zirconium reduces K₂WO₄ and releases potassium vapor (Boer et al., 1930).

Ammonium tungstate, (NH₄)₂WO₄ is prepared by the reaction of liquid

#### Table 7.13. Physical Constants and Crystal Structure Data of Normal Tungstates — General

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Color</th>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂WO₄</td>
<td>3.17</td>
<td>738°</td>
<td>660°</td>
<td>White</td>
<td>Rhom</td>
<td>8.888°</td>
<td></td>
<td></td>
<td>107.76°</td>
<td></td>
</tr>
<tr>
<td>Na₂WO₄</td>
<td>695°</td>
<td>578°</td>
<td></td>
<td></td>
<td></td>
<td>8.99°</td>
<td></td>
<td></td>
<td>n = 2</td>
<td></td>
</tr>
<tr>
<td>K₂WO₄</td>
<td>3.12</td>
<td>928°</td>
<td>362°</td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
<td>4 or 5°</td>
<td></td>
</tr>
<tr>
<td>Rb₂O·nWO₃</td>
<td>959</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n = 2, 3</td>
<td></td>
</tr>
<tr>
<td>Cs₂O·nWO₃</td>
<td>948</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n = 3 and 4</td>
<td></td>
</tr>
<tr>
<td>3Bi₂O₃·WO₃/</td>
<td>1011</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>or 5°</td>
</tr>
<tr>
<td>Bi₂O₃·WO₃</td>
<td>1064</td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi₄(WO₄)₂</td>
<td>842</td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu₄(WO₄)₂</td>
<td>1130</td>
<td></td>
<td></td>
<td></td>
<td>White</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceu₄(WO₄)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mono</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Belyaev, 1961.
* Spier, 1962.
* Spitsyn et al., 1938.
* Lindqvist, 1950.
* Smolyaninov and Belyaev, 1962.
* Nelson and McKee, 1946.
Tungsten and Tungsten Compounds: Chemical Properties

ammonia on the hydrate \( \text{WO}_3 \cdot \text{H}_2\text{O} \). It is a white salt and readily soluble in water (Rosenheim and Jacobsohn, 1906). When reacted with ammonia, ammonium tungstate forms compounds of the type \( \text{W}_{0.75}\text{N}_2\text{O}_1 - z \), which are cubic with the lattice parameter \( a = 1.22 \pm 1.130 \text{ Å} \) (Neugebauer et al., 1959).

Rubidium and cesium tungstates, \( \text{Rb}_2\text{WO}_4 \) and \( \text{Cs}_2\text{WO}_4 \), are prepared by double decomposition between the respective alkali chloride and silver tungstate \( \text{Ag}_2\text{WO}_4 \). They are colorless, strongly hygroscopic, and very soluble in water (Spitsyn, 1947). These two salts form hydrates readily. At 100°C, about 99.5% of the combined water is lost.

7.9.2.2. The Normal Tungstates of Divalent Metals

The crystal structures of the normal tungstates of divalent metals vary depending on the size of the cations; they are tetragonal for large cations (scheelite) and monoclinic for small ones ( wolframites). Accordingly, the tungstates of bivalent metals can be divided into two groups: scheelite (\( \text{CaWO}_4 \)) group: \( \text{SrWO}_4, \text{CdWO}_4, \text{BaWO}_4, \text{PbWO}_4 \); wolframite (\( \text{FeWO}_4 \)) group: \( \text{MnWO}_4, \text{ZnWO}_4, \text{CoWO}_4, \text{MgWO}_4, \text{NiWO}_4 \). The physical constants and crystal structure data of these tungstates are shown in Table 7.14.

Calcium tungstate, \( \text{CaWO}_4 \), constitutes the main portion of the natural mineral scheelite. It can be prepared by melting the sodium salt \( \text{Na}_2\text{WO}_4 \) with an

<table>
<thead>
<tr>
<th>Table 7.14. Physical Constants and Crystal Structure Data of Normal Tungstates of Divalent Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density (g/cm(^3)), Melting point (°C), Color, Symmetry, Prototype, a (Å), b (Å), c (Å), c/a or β</strong></td>
</tr>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>( \text{CaWO}_4 )</td>
</tr>
<tr>
<td>( \text{SrWO}_4 )</td>
</tr>
<tr>
<td>( \text{BaWO}_4 )</td>
</tr>
<tr>
<td>( \text{PbWO}_4 )</td>
</tr>
<tr>
<td>( \text{FeWO}_4 )</td>
</tr>
<tr>
<td>( \text{MnWO}_4 )</td>
</tr>
<tr>
<td>( \text{ZnWO}_4 )</td>
</tr>
<tr>
<td>( \text{CoWO}_4 )</td>
</tr>
<tr>
<td>( \text{NiWO}_4 )</td>
</tr>
</tbody>
</table>

\( ^{a} \) Swanson et al., 1956.
\( ^{b} \) Nassau and Mills, 1962.
\( ^{c} \) Sillen and Nylander, 1943.
\( ^{d} \) Rooksby and Steward, 1946.
\( ^{e} \) Shapovalova et al., 1960.
\( ^{f} \) Komandin et al., 1960.
excess of calcium chloride. CaWO$_4$ is slightly soluble in water; the solubility decreases as the temperature increases. Aluminum reduces calcium tungstate by liberating tungsten (Weiss and Martin, 1909):

$$\text{CaWO}_4 + 2\text{Al} = \text{W} + \text{CaO} \cdot \text{Al}_2\text{O}_3$$  (7.31)

Strontium tungstate, SrWO$_4$, is prepared by double decomposition in an aqueous solution of an alkali monotungstate and a soluble strontium salt, e.g., strontium acetate. SrWO$_4$ usually precipitates as a white amorphous substance. The crystalline SrWO$_4$ is prepared by melting a mixture of Na$_2$WO$_4$, SrCl$_2$, and NaCl. The salt is only slightly soluble in water but readily soluble in a boiling solution of oxalic acid (Chrétien and Freundlich, 1959).

The preparation of barium tungstate BaWO$_4$ is similar to that of SrWO$_4$. It is also formed by direct reaction of BaO and WO$_3$ at 300–500°C. It is slightly soluble in water and forms hydrates of the following compositions: BaWO$_4$·4H$_2$O, BaWO$_4$·2.5H$_2$O, BaWO$_4$·2H$_2$O, and BaWO$_4$·0.5H$_2$O. BaWO$_4$·4H$_2$O is formed by the reaction of Ba(OH)$_2$ on metatungstic acid (Chrétien and Freundlich, 1959).

Lead tungstate, PbWO$_4$, is prepared by the direct reaction of PbO and WO$_3$. It is a white powder but becomes gray and then yellow when heated in the air. Its crystal is transparent and colorless. In its natural state, lead tungstate is found in two forms — tetragonal and monoclinic. It is insoluble in water and in cold nitric acid but soluble in molten potassium (Chrétien and Freundlich, 1959).

Magnesium tungstate, MgWO$_4$, is prepared by sintering a pressed mixture of MgO and WO$_3$ powders at a temperature between 300 and 600°C. Large crystals of MgWO$_4$ are obtained upon slow cooling of the melted mixture of Na$_2$WO$_4$, MgCl$_2$, and NaCl. There are two hydrated forms — MgWO$_4$·3H$_2$O and MgWO$_4$·7H$_2$O (Chrétien and Freundlich, 1959).

Zinc tungstate, ZnWO$_4$, is prepared by the reaction of a solution of WO$_3$ in aqueous ammonia and zinc chloride or nitrate by carefully adjusting the pH value of the solution with acetic acid (Jander, 1930). Zinc acetate reacts with sodium tungstate in aqueous solution and forms the hydrate, a white precipitate, ZnWO$_4$·H$_2$O.

Ferrrous tungstate, FeWO$_4$, can be prepared by sintering FeO and WO$_3$ powders at a temperature between 300 and 380°C. The natural mineral wolframite consists mainly of (Fe,Mn)WO$_4$ with varying proportions of Fe(II) and Mn(II).

7.9.2.3. Isopolytungstates — The Metatungstates

When a normal tungstate solution is acidified with a strong acid, the tungstate ions polymerize to form the more complicated isopoly ions. The transformations are still not completely understood, mainly because of the inability to obtain well-defined solid derivatives and the extremely slow reaction rate (Craig and Tyree, 1965; LeMeur and Chauveal, 1970). These tungstic complexes are generally categorized as metatungstate (M$_2$O:WO$_3$ = 1:4) and paratungstate (M$_2$O:WO$_3$ = 5:12).
Two different species of metatungstate are generally known — the (true) metatungstate and the pseudometatungstate (or \( \psi \)-metatungstate). Their condensation behavior can be explained as follows (Kerpert, 1962):

\[
(WO_4)^{2-}_{\text{pH=4}} \rightleftharpoons (H_3W_6O_{21})^{3-} \rightleftharpoons [H_2(W_3O_{10})_4]^{6-} \tag{7.32}
\]

The metatungstates are very soluble in water, while the pseudometatungstates, except sodium pseudometatungstate, are only slightly soluble. The pseudometatungstates cannot be obtained directly from the metatungstate, but the reverse transformation is possible. By direct cooling of a supersaturated hot pseudometatungstate solution, one can obtain the vitreous metatungstate salt (Souchay, 1943).

The pseudometatungstate of potassium, \( K_3(H_3W_6O_{21}) \cdot 9H_2O \), is a white salt that can be obtained by the addition of a potassium chloride solution to a sodium tungstate solution at \( \text{pH}=4 \). Potassium metatungstate is obtained by precipitation from a supersaturated potassium pseudometatungstate solution. With addition of \( K_2H_2W_{12}O_{40} \) in a solution containing \( Ba^{2+} \) ions, the pseudometatungstate \( Ba_3(H_3W_6O_{21})_2 \cdot 21H_2O \), a white salt, will precipitate (Souchay, 1943). The hydrate form of potassium metatungstate is \( K_6(H_2W_{12}O_{40}) \cdot 18H_2O \).

The sodium pseudometatungstate will precipitate when alcohol is added to a monotungstate, while hydrochloric acid is used for adjusting the pH value. The sodium metatungstate \( Na_2O \cdot 4WO_3 \cdot 10H_2O \) precipitates upon cooling of a saturated solution from the boiling point to 0°C. Other variations of sodium metatungstate include \( Na_6(H_2W_{12}O_{40}) \cdot 5H_2O \), \( Na_2O \cdot 8WO_3 \cdot 4H_2O \), and those with large numbers (10–40) of \( WO_3 \) radicals (Rieck, 1967).

7.9.2.4. Isopolytungstates — The Paratungstates

The paratungstates usually maintain the ratio \( M_2O:WO_3 = 5:12 \). The condensation behavior from \( WO_4^{2-} \) to paratungstates generally pursue the following course (Kerpert, 1962):

\[
WO_4^{2-}_{\text{pH=6}} \rightleftharpoons HW_6O_{21}^{2-} \rightleftharpoons \text{paratungstate B} \rightleftharpoons H_{10}W_{12}O_{46}^{10-} \tag{7.33}
\]

Paratungstates are prepared by the reaction between the alkali salts and normal tungstate solutions; hydrochloric acid is used to adjust the pH value. Some other paratungstates are formed by double decomposition in aqueous solutions (Souchay, 1944). The paratungstates decompose before complete dehydration. With the exception of the alkali salts and magnesium salt, they are insoluble in water (Chrétien and Freundich, 1959). Physical constants and crystal structure data of some paratungstates are listed in Table 7.15.

Sodium paratungstate, \( 5Na_2O \cdot 12WO_3 \), has three hydrate forms, with 28, 25, and 21 molecules of \( H_2O \), respectively. They are prepared by crystallization from the solution at temperatures of 68, 80, and 100°C, respectively. Sodium
Table 7.15. Physical Constants and Crystal Structure Data of Some Paratungstates

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density</th>
<th>Structure</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Na₂O·12WO₃·28H₂O⁴⁺</td>
<td>3.987</td>
<td>Trid</td>
<td>0.5341</td>
<td>1</td>
<td>1.1482</td>
<td>93°56'</td>
<td>113°36'</td>
<td>85°55'</td>
</tr>
<tr>
<td>5K₂O·12WO₃·11H₂O⁶⁻</td>
<td>0.9317</td>
<td>Trid</td>
<td>1.0315</td>
<td>1</td>
<td>1.3626</td>
<td>65°36'</td>
<td>117°22'</td>
<td>115°39'</td>
</tr>
<tr>
<td>5(NH₄)₂O·12WO₃·11H₂O⁴⁺</td>
<td>Orth</td>
<td>19.29</td>
<td>24.46</td>
<td>11.02</td>
<td>113°6'</td>
<td>117°8'</td>
<td>63°2'</td>
<td></td>
</tr>
<tr>
<td>5(NH₄)₂O·12WO₃·7H₂O⁸⁻</td>
<td>Mono</td>
<td>21.44</td>
<td>23.58</td>
<td>13.4</td>
<td>113°6'</td>
<td>117°8'</td>
<td>63°2'</td>
<td></td>
</tr>
</tbody>
</table>

* Chéttien and Freundlich, 1959.

Paratungstate is stable at 20°C and starts to lose hydrated water on heating. The dehydrated salt contains at least five WO₃ molecules per Na₂O molecule. It is insoluble in water, alcohol, nitrobenzene, pyridine, and aniline. It melts with decomposition around 760°C and transforms into a yellow liquid. When cooled, this liquid forms a white crystalline mass that is partially soluble in water (Spitsyn and Kashtanoff, 1928). From 700 to 900°C, hydrogen reduces the paratungstate into a mixture of tungsten and normal tungstate Na₂WO₄ (Spitsyn 1925).

Potassium paratungstate, 5K₂O·12WO₃·11H₂O, is prepared by cooling the heated aqueous solution of potassium salt, potassium carbonates, or saturated normal potassium tungstate with the anhydride WO₃. It can also be prepared by the reaction of potassium chloride with a solution of sodium paratungstate (Vallance, 1931). The salt is stable in air but loses hydrated water gradually on heating. The anhydrous salt when exposed to air absorbs water very rapidly. Potassium paratungstate becomes yellow when heated and melts while pyrolyzing. The salt is barely soluble in water at 20°C; the solubility increases with increase of temperature (Vallance, 1931).

Ammonium paratungstate, 5(NH₄)₂·12WO₃, is prepared by dissolving tungstate gel in ammonia. It is of technical importance in the purification of tungstic acid as a step in producing the pure metal. For this purpose, the salt as prepared in the above manner is dispersed in water. By adding the same volume of boiling concentrated hydrochloric acid, one can obtain a very pure WO₃·nH₂O precipitate (see Sec. 2.3). Paratungstate can be reduced by hydrogen directly to tungsten (see Sec. 3.2). Two hydrated forms of paratungstates are known that contain 11 and 7 molecules of H₂O, respectively. The transition point is 50°C (Hähnert, 1961). During heating, these two salts tend to lose the hydrated water and finally lose ammonia.

7.10. PEROXYTUNGSTIC ACID AND PEROXYTUNGSTIC COMPOUNDS

When tungsten trioxide or a tungstate reacts with hydrogen peroxide, it forms peroxytungstic acid or peroxytungstate. Peroxytungstic acid H₂WO₃H₂O₂ can also be obtained by dissolving tungsten powder in H₂O₂·H₂O. The solubility is
proportional to the concentration of $\text{H}_2\text{O}_3$ and can reach more than 100 g/liter (Ganiev et al., 1973). The peroxytungstic compounds exist in a series of compositions. They can be generally be classified according to the ratio of oxygen to tungsten — 4:1, 3:1, 2:1, and 1:1. Compounds with less defined ratio or less than 1:1 also exist. The formation of each category depends on the pH value of the solution (Connor and Ebsworth, 1964). All peroxytungstic compounds are unstable. The degree of instability increases with the increase of the ratio of oxygen to tungsten. Hence the compound with a 4:1 ratio is sometimes explosive (Chrétien and Freundlich, 1959).

General classification and examples of peroxytungstic compounds are shown in Table 7.16. The class 1 compounds degenerate to class 4 through the two intermediate compounds. In an aqueous solution, the following reaction also occurs (Chrétien and Freundlich, 1959):

$$2\text{[W(O}_2\text{)]}_4^2^- + 2\text{H}^+ + 3\text{H}_2\text{O} \rightleftharpoons [(\text{O}_2\text{)}_2\text{OW}\text{OWO(O}_2\text{)]}_2^2^- + 4\text{H}_2\text{O}_2 \quad (7.34)$$

Peroxytungstic acids, $\text{H}_2\text{WO}_6$ and $\text{H}_2\text{W}_2\text{O}_{11}$, can be extracted from nitrate media with trialkyl (C$_7$-9) benzyl ammonium nitrate solutions in trichloroethylene (Zolotareva et al., 1973).

In addition to the peroxytungstic compounds shown in Table 7.16, two rare earth compounds are also known. Sc$_2$(WO$_6$)$_3$·4H$_2$O is prepared by the reaction of 35–40 vol % H$_2$O$_2$ with Na$_2$WO$_4$ and Sc(NO$_3$)$_3$ at 0–2°C followed by the addition of acetone or ether (Tereshkina et al., 1971). Yttrium peroxytungstates occur in the following forms: $\text{Y}_2$(WO$_5$)$_3$·H$_2$O; $\text{Y}_2$(WO$_5$)$_3$·3H$_2$O; $\text{Y}_2$(WO$_7$)$_3$·2H$_2$O; $\text{Y}_2$(WO$_8$)$_3$·H$_2$O; and $\text{Y}_2$(WO$_9$)$_3$·2H$_2$O (Garkushenko and Karpenko, 1971). The complex peroxytungstates that have been prepared are fluorides, oxalates, tartrates, phosphates, and sulfates (Connor and Ebsworth, 1964).

**Table 7.16. General Classification of Peroxytungstic Compounds**

<table>
<thead>
<tr>
<th>Class</th>
<th>Ratio</th>
<th>Formula</th>
<th>Example of M</th>
<th>Methods of formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4:1</td>
<td>$\text{M}^\text{I}_{\text{I}}\text{WO}<em>6$ or $\text{M}^\text{II}</em>{\text{I}}\text{WO}_6$</td>
<td>Ca, Sr, Ba, Na, K, Co</td>
<td>Excess H$_2$O$_2$ with tungstate in basic solutions</td>
</tr>
<tr>
<td>2</td>
<td>3:1*</td>
<td>$\text{M}^\text{II}_{\text{I}}\text{WO}_7$</td>
<td>Ca, Sr</td>
<td>Thermal Decomposition of 4:1 compound</td>
</tr>
<tr>
<td>3</td>
<td>2:1</td>
<td>$\text{M}^\text{I}<em>{\text{I}}\text{WO}<em>4$ or $\text{M}^\text{II}</em>{\text{I}}\text{WO}</em>{11}$</td>
<td>K</td>
<td>Reaction of high-concentration H$_2$O$_2$ solution with alkali tungstate in acid solution</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>$\text{M}^\text{I}_{\text{I}}\text{WO}<em>3$ or $\text{M}^\text{III}</em>{\text{I}}\text{WO}_3$</td>
<td>—</td>
<td>Neutralizing H$_2$O$_2$–tungstic acid solutions</td>
</tr>
</tbody>
</table>

* Connor and Ebsworth, 1964.
* 3:1 compounds may be a mixture of 4:1 and 2:1 compounds.
7.11. TUNGSTEN BRONZES

Tungsten bronzes are a series of well-defined nonstoichiometric compounds of the general formula $\text{M}_x\text{WO}_3$, where $x$ is a number ranging from 0 to 1. The cation M is generally an alkali, although alkaline earth, ammonium, rare earth metal ions, etc., are also known. They are called bronzes because they have the characteristics of metallic luster with intense colors (from golden yellow to bluish-black). They are electrical conductors or semiconductors because of their oxygen deficiency. Most of the tungsten bronzes crystallize into cubic structures, although by varying the value $x$, they may be tetragonal, hexagonal, or orthorhombic.

The tungsten–sodium bronzes have been the most thoroughly studied. The polytungstate loses an atom of oxygen to form a tungsten bronze at about 500°C (Spitsyn, 1925):

$$\text{Na}_2\text{O} \cdot 5\text{WO}_3 + \text{H}_2 \rightarrow 5\text{Na}_{0.4}\text{WO}_3 + \text{H}_2\text{O}$$ (7.35)

$$\text{NA}_2\text{O} \cdot 4\text{WO}_3 + \text{H}_2 \rightarrow 4\text{Na}_{0.5}\text{WO}_3 + \text{H}_2\text{O}$$ (7.36)

It follows from this that the first bronze to be formed contains the same number of metal atoms as the original tungstane. Under prolonged heating, the primary bronze is transformed into bronzes poorer in tungsten until the monotungstate, $\text{Na}_2\text{WO}_4$ is formed. At each step, an atom of tungsten is liberated.

An overlapping sequence of reactions takes place as follows:

$$5\text{Na}_{0.4}\text{WO}_3 \text{ (blue)} + 3\text{H}_2 \rightarrow 4\text{Na}_{0.5}\text{WO}_3 + \text{W} + 3\text{H}_2\text{O}$$ (7.37)

$$4\text{Na}_{0.5}\text{WO}_3 \text{ (violet)} + 3\text{H}_2 \rightarrow 3\text{Na}_{2/3}\text{WO}_3 + \text{W} + 3\text{H}_2\text{O}$$ (7.38)

$$3\text{Na}_{2/3}\text{WO}_3 \text{ (red)} + 3\text{H}_2 \rightarrow 2\text{NaWO}_3 + \text{W} + 3\text{H}_2\text{O}$$ (7.39)

$$2\text{NaWO}_3 \text{ (yellow)} + 2\text{H}_2 \rightarrow \text{Na}_2\text{WO}_4 + \text{W} + 2\text{H}_2\text{O}$$ (7.40)

The color and the density vary progressively with the composition of the bronzes, and the stages of the reduction are not discernible. A more detailed study (Hägg, 1935) shows that the lattice parameter as well as the color vary with the sodium content (Table 7.17). The bronze $\text{Na}_{0.32}\text{WO}_3$ is the least rich in sodium within the cubic lattice series.

Sodium bronzes can also be obtained by reducing mixtures of $\text{Na}_2\text{WO}_4$ and $y\text{WO}_3$ (Rabes and Schenck, 1949). The bronze is formed when $y$ is in the range between 1.4 and 4. For example, the bronze $\text{Na}_{0.67}\text{WO}_3$ results from the initial mixture $\text{Na}_2\text{WO}_4 + 2\text{WO}_3$. By the reaction of sodium on a higher bronze, the above limit can be exceeded, but the ideal composition of NaWO$_3$ cannot be obtained.

The cubic structure of tungsten bronzes belongs to the $\text{E}_2_1$ type (CaTiO$_3$) with a deficiency of sodium ions in the lattice. The valences of tungsten atoms in the crystal vary from V to VI (Straumanis, 1949) so as to preserve the neutrality of
Table 7.17. Lattice Parameters and Colors of Tungsten Sodium Bronzes (Cubic) Varying with the Number of Sodium Atoms in the Formula Na$_x$WO$_3$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.93</td>
<td>3.850</td>
<td>Golden-yellow</td>
</tr>
<tr>
<td>0.64</td>
<td>3.834</td>
<td>Red-yellow</td>
</tr>
<tr>
<td>0.46</td>
<td>3.825</td>
<td>Red-violet</td>
</tr>
<tr>
<td>0.32</td>
<td>3.813</td>
<td>Blue-violet</td>
</tr>
</tbody>
</table>

* Hågg, 1935.

the crystal. The lattice is made up of WO$_6$ octahedra joined at the vertices, thus forming a framework of composition WO$_3$ and possessing an anionic charge; the cations Na$^+$ are placed in the interstices of these lattices. On losing sodium, the cubic lattice shrinks, but it remains stable up to a total loss of 70 out of 100 Na$^+$ ions. Beyond this, the distortion is so great that the cubic symmetry degenerates into a structure of lower symmetry. The string of octahedra may form five- and six-membered rings (Magneli, 1953). The five-membered rings form tetragonal bronzes. In this structure, there are triangular, rectangular, and pentagonal channels along the $c$-axis. The hexagonal bronzes have triangular and hexagonal channels resulting from the six-membered rings (Bouchard and Gillson, 1969).

Potassium, rubidium, and cesium form a series of tungsten bronzes. They have the same formula, M$_x$WO$_3$, where $x$ equals approximately 0.3, and they crystallize in the hexagonal system. Their typical parameters are: K$_{0.27}$WO$_3$, $a$ = 7.40 Å, $c$ = 7.54 Å; Rb$_{0.27}$WO$_3$, $a$ = 7.39 Å; $c$ = 7.54 Å, and Cs$_{0.32}$WO$_3$, $a$ = 7.42 Å, $c$ = 7.63 Å (Magneli and Blomberg, 1951; Wells, 1950).

The bronzes of such metallic elements as lithium, magnesium, calcium, strontium, barium, thallium, lead, and neodymium may be prepared from their chlorides by reacting with WO$_2$ or WO$_3$ (Conroy and Pidolsky, 1968). The mixed bronze group, Na$_x$Ba$_y$WO$_3$ ($y$ is greater than 0 but less than 0.16; and $x+y$ is greater than 0 but less than 0.46) may also be prepared by this method. In this group, each crystallizes in the cubic system. Another mixed bronze group, K$_x$Li$_y$WO$_3$ ($x$ can be as low as 0.13 and $x+y$ as high as 0.51) usually have hexagonal symmetry (Banks and Goldstein, 1968). The bronzes of lithium, ammonium, and tin can also be synthesized hydrothermally.

The bronzes of rare earth metals assume the form of M$_{0.1}$WO$_3$ and crystallize with cubic symmetry and with lattice parameter $a$ varying from 3.828 Å (cerium) to 3.788 Å (lutecium) (Ostertag, 1966). The lattice parameter $a$ for the bronze La$_x$WO$_3$ group varies from 3.829 to 3.485 Å when $x$ increases from 0.08 to 0.19. The yttrium bronze Y$_x$WO$_3$ crystallizes in the cubic system when $x$ is greater than 0.09; otherwise, it crystallizes tetragonal.
Tungsten Alloys, Composites, and Tungsten Used as an Alloying Element

8.1. GENERAL BACKGROUND

With a very high density and the highest melting point among metals, tungsten possesses a unique combination of properties desired for applications in electrical, electronic, nuclear, and space vehicle equipment. On the other hand, the metal's relatively poor fabricability and high ductile-brittle transition temperature cause major concerns of engineers and designers. In order to improve the properties and, hence, the utilization of the metal, much effort has been directed toward the development of tungsten alloys, especially in recent years. The work is essentially centered on the following goals: to improve fabricability, tensile strength, and creep strength, particularly at elevated temperatures, and to lower the ductile-brittle transition temperature of the metal.

Tungsten alloys, just like other metal alloys, can be classified as follows: (1) solid-solution alloys, (2) dispersion-strengthened alloys, (3) precipitation-hardening alloys. These will be discussed in the following sections with emphasis on some well-developed alloys. In addition, there is a well-known class of liquid-phase or pseudoalloys (namely, heavy alloys) and tungsten composites that consist of metals or alloys formed by special processes. Also discussed in this chapter will be steels and other base-metal alloys using tungsten as an alloying element.

In the preparation of alloys, tungsten and alloying elemental powders are used as starting materials; they are required to be of high purity and fine particle size. This is especially so when powder metallurgy processes are employed, because the homogeneity of the alloy is dependent on solid-state diffusion. Minimizing the diffusion distance by reducing the particle size and the intimate mixing is therefore desired. To achieve this aim, comminution by ball milling and repeated sieving may be employed. During milling, a grinding aid, such as an aluminum salt can be used (Morcom and Cerulli, 1966). An alternative method is coreduction or coprecipitation by chemical means for elemental powders (Smiley et al., 1965).

Consolidation methods for tungsten alloys are the same as those for pure (unalloyed) tungsten, ranging from pressing and sintering, arc or electron-beam melting, hot compaction, and powder extrusion to chemical vapor deposition, as
mentioned in Chapter 4. The fabrication processes for tungsten alloys are similar to those of unalloyed tungsten, except that the working temperature required is generally higher. This is due to the fact that most developed alloys have higher elevated-temperature strength and higher recrystallization temperatures than the unalloyed tungsten.

In primary fabrication, extrusion has become the preferred technique, especially in the case of arc or electron-beam-melted materials with coarse grain structures. Billets are usually canned in molybdenum sheaths, which are coated with glass for lubrication. Alternatively, bare tungsten or molybdenum-sheathed tungsten billets can be extruded without coating, depending upon the naturally formed oxides WO₃ or MoO₃ for lubrication. For the purpose of producing tubing, multiple-layer sheaths are used as described in Sec. 5.8. After extrusion, tungsten alloys can be swaged, rolled, and tube-reduced, depending upon the final products desired. However, among all alloys produced, only rhenium- or molybdenum-containing alloys have been successfully fabricated on a production scale.

8.2. SOLID-SOLUTION ALLOYS

It is generally accepted that addition of solute elements increases the strength of the base metal and increases the rate of strain hardening. One factor affecting the strengthening of the alloy is lattice strain, which is proportional to the difference in the size of solute and solvent atoms. A second factor is the difference in valence between the solute and the solvent, which affects the electronic binding of the metal.

Based on dislocation theory for single crystals of dilute alloys in which local lattice strains inhibit the migration of a dislocation, Mott and Nabarro (1948) derived an equation for the yield stress of solid solutions as follows:

$$\sigma_y = G\delta^2 N^{5/3}(\ln N)^2$$

(8.1)

where $G$ is the shear modulus of elasticity, $\delta = (1/a)(\Delta a/\Delta N)$, $a$ is the lattice constant, and $\Delta a/\Delta N$ is the change in lattice constant per mole of the alloying element. This theory does not take into account the valence factor.

Dorn et al. (1950) suggested that solid-solution hardening depends on both the mean lattice strain and the change in the average number of electrons per atom upon the addition of solute elements and formulated the following equation for the hardness:

$$F = |\Delta a| + k|\Delta \nu|$$

(8.2)

where $\Delta a$ is the change in lattice constant during alloying and $\Delta \nu = (\text{at } \% \text{ solute})/100 \times (\text{valence of solute} - \text{valence of solvent})$. They also claimed that the effect of alloying elements was more pronounced at lower concentrations and became less effective at higher levels.

For solid-solution hardening of tungsten, the solute elements should be of relatively high melting point. Generally speaking, the elements considered here are
in group IV, V, VI, VII, and VIII, especially those belonging to the long periods of the periodical table. Molybdenum, tantalum, and niobium are logically the first alloying elements to be considered for tungsten, because of their bcc crystal structure, complete solubility with tungsten, and high melting points. Rhenium additions at certain compositions, due to a unique mechanism, bestow ductility to the metal. These and other alloys will be discussed in separate sections below.

8.2.1. Molybdenum, Niobium, and Tantalum as Alloying Elements

The art of solid-solution strengthening depends upon the compromise condition of lattice straining and difference in electronic binding as mentioned above. There is no valence difference between molybdenum and tungsten, and the lattice difference between the former (3.1468 Å) and the latter (3.1585 Å) is rather small. The straining effect of molybdenum additions is small, and molybdenum–tungsten alloys can be produced essentially at any composition. The lattice parameters of tantalum (3.3026 Å) and niobium (3.3004 Å) are rather large compared to that of tungsten. Furthermore, there is a valence difference between the group V metals and tungsten (group VI). Due to these differences, the straining effect is high, and the additions of tantalum or niobium to tungsten are generally limited to low percentages.

Binary, ternary, and quaternary alloys of molybdenum, niobium, and tantalum with tungsten have been explored (Crucible Steel Company of America, 1961; Semchyshen et al., 1966; Olcott and Batchelor, 1965), and the findings are generally as follows: (1) Additions of these elements to tungsten produce a grain-refining effect in the as cast condition. (2) Additions of these elements confer on tungsten higher strength especially at elevated temperatures. Niobium and tantalum are more effective than molybdenum as strengtheners for tungsten. However, high-percentage tantalum or niobium alloys are difficult to machine and fabricate. Cracking of these alloy ingots has also been encountered during the process of melting and cooling. (3) The preferred consolidation process to be used for solid solution hardening alloys is arc melting with or without centrifugal casting. (4) Alloy additions, with the exception of molybdenum, generally raise the recrystallization temperature of tungsten but also raise the ductile–brittle transition temperature of the material. This latter effect is probably caused by ingredient segregation, especially at grain boundaries, which is observed in most investigations. In order to avoid the segregation, a master alloy with high alloy content should be used as the electrode for the final ingot.

Some ternary alloys, such as W–6 Mo–2 Nb (Reimann, 1962), W–5.7 Mo–5.7 Nb (Crucible Steel Company of America, 1961); and W–20 Ta–12 Mo (Cook, 1965), were reported to have high elevated-temperature strengths. It is a general practice to add small amounts of other elements, such as zirconium, titanium, hafnium, and carbon, to the basic solid solution alloys, in which case these elements are used as scavengers in order to improve the ductility and refine the grain structure of the material. Alloys such as W–3 Mo–0.02 Zr (Norton, 1965), W–3.1 Mo–0.04 Zr–0.001 C (Barr and Semchyshen, 1964), and 0.001–0.002 C additions to various compositions of W–Ta, W–Nb, W–Ta–Nb, and W–Ta–Nb–Mo alloys
(Semchynshen et al., 1966) have been reported. It should be pointed out that these scavenger elements are limited to very low levels; otherwise, a precipitation hardening alloy will result.

The comparison of physical and mechanical properties of tungsten alloys is somewhat confusing and misleading. Although an effort toward standardization of test procedures for alloy sheet has been made (National Materials Advisory Board, 1963), not all the investigators have adhered strictly to the specified procedures. In addition, the alloys, as well as unalloyed tungsten, vary in properties according to their process and fabrication history. Generally speaking, electron-beam-melted material is more ductile than that of arc cast, which is, in turn, more ductile than that produced by powder metallurgy processes. The ductility of the alloys generally decreases with increasing strength. Grain size and alloy content, both interstitial and substitutional, are other factors that affect these properties. Furthermore, the differences in the fabrication processes such as extrusion, swaging, or rolling yield different properties of the final products; and heat treating, such as stress-relieving or recrystallization, also affects the strength and ductility to a great extent.

The main interests are the ductile–brittle transition temperatures and the tensile and creep properties, especially at elevated temperatures. The ductile–brittle transition temperature of some tungsten alloys are shown with other solid-solution alloys in Table 8.1. The test most commonly encountered in ductile–brittle transition temperature data available is the 4T bend, which is therefore chosen whenever possible. However, it should be noted that factors such as recrystallization temperature, grain size, strain rate, and surface roughness of the specimen affect the results of the test. In this table, the fabrication history, test method, and sheet thickness are also indicated for reference. Tensile properties of these and other solid-solution alloys are shown in Figs. 8.1 through 8.4. The alloys are essentially in the recrystallized condition, and the alloy fabrication histories have been chosen to be as similar as possible in order to ensure comparability.

The creep properties of solid-solution alloys are shown in Fig. 8.5, where the temperature-compensated creep rate as a function of applied stress is used. The compensated creep rate is calculated by the equation

$$K = \dot{\epsilon} \exp \left( \frac{Q}{RT} \right)$$ (8.3)

where $\dot{\epsilon}$ is the steady-state creep rate and $Q$ is the activation energy of volume self diffusion. The value of $Q$ varies with temperature and alloy composition, ranging from 90 to 200 kcal/mole; a value of $Q = 155$ kcal/mole is used for all alloys here (Sell, 1968). Due to lack of data, only a few alloys are shown in this figure.

8.2.2. Tungsten–Rhenium Alloys

Rhenium has a higher density (21.0 g/cm$^3$) than tungsten and a melting point (3180°C) and an atomic radius (1.37 Å) close to that of tungsten. With a solubility of approximately 27% (Fig. 8.6), rhenium is likely to be an interesting solute for tungsten in alloying. The fact that rhenium additions increase the ductility of
<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fabrication history</th>
<th>Test method</th>
<th>Sheet thickness [mm (in.)]</th>
<th>Ductile-brittle transition temperature [°C (°F)]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–1 Hf</td>
<td>Electron-beam melted, annealed 1 hr at 1927°C (3500°F)</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>232 (450)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W–2 Hf</td>
<td>Electron-beam melted, annealed 1 hr at 1927°C (3500°F)</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>246 (475)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W–5 Hf</td>
<td>Electron-beam melted, annealed 1 hr at 1927°C (3500°F)</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>260 (500)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W–0.503 Cb</td>
<td>Arc-melted, annealed 1 hr at 1982°C (3600°F)</td>
<td>4T bend</td>
<td>1.01 (0.040)</td>
<td>355 (670)</td>
<td>Raffo et al., 1965</td>
</tr>
<tr>
<td>(W–0.99 at % Cb)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–1.65 Cb</td>
<td>Arc-melted, annealed 1 hr at 1982°C (3600°F)</td>
<td>4T bend</td>
<td>1.01 (0.040)</td>
<td>318 (605)</td>
<td>Raffo et al., 1965</td>
</tr>
<tr>
<td>(W–3.22 at % Cb)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–2.42 Ta</td>
<td>Arc-melted, annealed 1 hr at 1982°C (3600°F)</td>
<td>4T bend</td>
<td>1.01 (0.040)</td>
<td>343 (650)</td>
<td>Raffo et al., 1965</td>
</tr>
<tr>
<td>(W–2.46 at % Ta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–0.15 Ru</td>
<td>Electron-beam melted, annealed 1 hr at 1927°C (2500°F)</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>246 (475)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W–15 Mo</td>
<td>As-extruded</td>
<td>Tensile</td>
<td>4.06 (0.16) (rod)</td>
<td>255 (590)</td>
<td>Schmidt and Ogden, 1963a</td>
</tr>
</tbody>
</table>
Fig. 8.1. Ultimate tensile stress vs. test temperature for solid-solution arc-melted tungsten alloys (other than W-Re). (1) Annealed 1 hr at 1982°C (Raffo and Klopp, 1966a); (2) annealed 1 hr at 1815°C (Cook, 1965); (3) annealed at test temperature (Flagella, 1967); (4) extruded at 1954°C (Schmidt and Ogden, 1963a); (5) annealed 15 min at 1704°C (Barr and Semchyshen, 1964); (6) Sell (1968).

Fig. 8.2. 0.2% Offset yield stress vs. test temperature for solid-solution arc-melted tungsten alloys (other than W-Re). Numbers in parentheses refer to same conditions and sources as in Fig. 8.1.
Fig. 8.3. Reduction in area vs. test temperature for solid-solution arc-melted tungsten alloys. (1) Annealed 1 hr at 1982°C (Raffo and Klopp, 1966a); (2) extruded at 1954°C (Schmidt and Ogden, 1963a); (3) annealed 1 hr at 1815°C (Cook, 1965); (4) Sell (1968).

Fig. 8.4. Elongation vs. test temperature for solid-solution arc-melted tungsten alloys (other than W-Re). Numbers in parentheses refer to same conditions and sources as in Fig. 8.1.
tungsten and molybdenum was reported by Geach and Hughes (1956) and confirmed by Jaffee et al. (1959). Early theories to explain the ductilizing effect have been as follows:

1. Rhenium additions produce a complex oxide with appreciable surface tension in group VI metals. Instead of wetting grain boundaries, the oxide agglomerates into round globules, giving the alloy high intergranular strength and ductility (Jaffee et al., 1959, 1961; Sims and Jaffee, 1959).

2. Interstitial solubility, essentially that of oxygen, is lowered by rhenium additions. The contribution of valence electrons from rhenium to the VI lattice is believed responsible for the reduced solubility (Robins, 1959, 1960).

3. Additions of rhenium to tungsten or molybdenum promote twinning...
during deformation, which is due to the fact that stacking fault energy is reduced by rhenium (Mil'man et al., 1964; Davidson and Brotzen, 1970; Aqua and Wagner, 1966; Klopp et al., 1960a).

4. Grain boundaries in some chromium–rhenium alloys are found to contain a eutectic-type structure surrounded by a rhenium-rich region (Booth, 1963), which is considered to contribute to the alloy's strength by resisting the propagation of small cracks that may develop during the process of deformation.

The rhenium ductilizing effect has been recently reviewed by Simpson (1973).

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**Fig. 8.6.** Tungsten–rhenium phase diagram (Elliott, 1965).
Hypothesis 1, above, is now considered unimportant, since cracks in group VI metals are frequently initiated in what appears to be clean regions of grain boundaries, and these cracks propagate by intergranular cleavage (Gilbert and Allen, 1965; Gilbert, 1966). The decreased interstitial solubility due to rhenium addition has been claimed to be incorrect, and in some cases, the reverse is true (Novick and Machlin 1968; Gilbert et al., 1966). The occurrence of a grain-boundary eutectic-like phase and accompanying local rhenium segregation has received little attention (Allen, 1966a,b).

It is well established that rhenium promotes twinning in group VI alloys (Klopp et al., 1960a). However, twinning only accounts for a minor fraction of the plastic deformation, usually at the onset of macroscopic strain, with slip contributing to the remainder. The exact effect of twinning is not well understood, and its relation to the rhenium ductilizing effect is questionable.

More recently it was suggested that increased dislocation mobility would result from rhenium lowering the lattice resistance to dislocation motion (Peierls–Nabarro stress) (Raffo, 1969; Klopp, 1968; Mitchell and Raffo, 1967; Stephens, 1968, 1970; Stephens and Witzke, 1971, 1972). This is consistent with the well-known solid-solution softening in bcc metals and is attributed to the same cause (Tanaka and Watanabe, 1971; Spitzig and Leslie, 1971; Leslie, 1972; Statham and Christian, 1971; Das and Arsenault, 1968).

There are two components in the flow stress— a thermal component \( \sigma^* \), called effective stress and an athermal component \( \sigma_i \), called internal stress. The latter increases with solute additions, dominating above the temperature of 0.2 \( T_m \) (where \( T_m \) is the melting point of the metal), but does not vary significantly with temperature. Solute additions may either raise or lower the thermal component, which increases rapidly with decreasing temperature below 0.2 \( T_m \). Solid-solution softening results when solute atoms produce a decrease in \( \sigma^* \) that more than offsets the increase in \( \sigma_i \) due to the presence of solute atoms (Arsenault, 1969; Christian, 1970). It is generally accepted that the Peierls–Nabarro stress is responsible for the high temperature dependence of \( \sigma^* \) in bcc metals at low temperatures. The natural extension of this is, therefore, that the alloy-softening effect is caused by solute reductions in the Peierls barriers due to the alloy electronic configuration.

Although rhenium produces alloy softening in tungsten at low concentrations, this phenomenon does not occur at high rhenium concentrations. This could be the result of a different mechanism at high solute contents (Klopp, 1968) or due to the fact that the increased solute contribution to \( \sigma_i \) becomes greater than the reduction of \( \sigma^* \).

Generally speaking, tungsten–rhenium alloys show lower ductile–brittle transition temperatures, better fabricability, higher recrystallization temperatures, and higher tensile strength at elevated temperatures. A hardness minimum exists at a composition of about 5% rhenium, which also shows the highest creep strength of all tungsten–rhenium alloys (Klopp et al., 1966). Alloy compositions close to the solubility limit of rhenium demonstrate the greatest ductility at room temperature but exhibit not much different elevated-temperature creep strength than tungsten (Kieffer et al., 1965; Pugh et al., 1962). The composition for good workability ranges from 18 to 32% rhenium (Maykuth et al., 1962); a minimum forging temperature of
1500°C (2732°F) and a process annealing temperature of 1600–1800°C (2912–3272°F) are recommended. Although there is a limit to the amount of sigma phase that can be tolerated, the precipitation of this second phase tends to strengthen the material, and it still exhibits good workability. Alloys with less than 18% rhenium can be fabricated successfully but require higher initial working temperature (Pugh et al., 1962).

In addition to high-temperature applications in space vehicles and tubing in reactors, tungsten–rhenium alloys are also used in the following categories: (1) Thermocouples in vacuum or hydrogen furnaces, combustion chambers of turbine engines or reactors up to a temperature of 2600°C. The commonly used thermocouples are of the compositions W/W–25 Re and W–3 Re/W–25 Re, which yield a high and stable thermoelectromotive force (Driesner et al., 1962). (2) Electrical contacts, especially under high humidity and corrosive environments. It was reported (Tishkevich, 1964) that erosion resistance increases with increasing content of rhenium in the alloy. (3) Lamp and electronic tube wires. In this case, doped tungsten should be used as a base material. The alloys containing 1–5% rhenium demonstrate high sag resistance similar to commercial nonsag wire but are remarkably ductile even after recrystallization (Pugh et al., 1962).

In order to maintain the room-temperature ductility and further strengthen the elevated temperature strength of the alloy, a small amount of carbon and group IV elements (i.e., hafnium, zirconium, or titanium) may be added to low- or high-rhenium-containing tungsten alloys (Klopp and Witzke, 1971; Friedman, 1968).

Tungsten–rhenium alloy tubing or other forms of mill products can be produced by the chemical vapor deposition process, which yields deposits with mechanical properties approaching those of wrought material (Holman and Huegel, 1967). For details of the process, the reader is referred to Sec. 4.4.6.

Because of high elevated temperature strength, the tungsten–rhenium alloys are difficult to fabricate. In some instances, the fabrication contribution to the production cost of some mill products, such as small-diameter tubing, outweighs even the high cost of the rhenium material. Consequently, W–Mo–Re ternary alloys were developed in the hope of obtaining a compromise in properties between the refractoriness of tungsten alloy and the ductility of the molybdenum alloy. The most common ternary alloys are, in atomic percentage, W–30% Re–30% Mo and W–25 Re–30% Mo (Milner et al., 1967; Flagella, 1967). The ternary alloys can also be produced by the chemical vapor deposition process (Fairchild, 1967).

It was reported (Lessmann and Gold, 1970) that unalloyed tungsten is very sensitive to thermal shock; W–25% Re has improved thermal shock resistance but is basically hot-tear-sensitive in gas tungsten arc welding. High preheat temperatures up to 760°C (1400°F) are beneficial in both cases. The W–25 at % Re–30 at % Mo alloy generally displays excellent weldability except for an extreme sensitivity to oxygen contamination, which causes hot tearing. A post weld anneal at 2560°F (1404°C) is generally beneficial in relieving the residual stress built up during welding, with consequent improvement in the ductility of the material. Most of the welds in powder metallurgy products contain porosity, whereas arc-cast materials produce porosity-free welds.

The ductile–brittle transition temperature for tungsten–rhenium alloys as a
function of composition is shown in Fig. 8.7. The tensile properties of W–Re and W–Re–Mo alloys are shown in Figs. 8.8 through 8.11, and their creep properties, with some other solid solution tungsten alloys, have been shown in Fig. 8.5.

8.2.3. Other Solid-Solution Alloys

Alloys from the tungsten–hafnium and tungsten–ruthenium systems have been investigated by Clark (1963), who produced these alloys by electron-beam melting and found the retention of hafnium in the final ingot to be rather low. The addition of carbon to such alloys promotes retention of a larger hafnium concentration. Both the strength and ductility of W–0.4 Hf–0.01 C are quite attractive in the wrought condition. However, the precipitate in this alloy is HfC, which places the alloy in the precipitation hardening category. A small percentage of the group VIII element, ruthenium, similar to rhodium, has some softening effect on tungsten.

Studies on the effects of other group VIII elements on the properties of group VI metals, including tungsten (Klopp et al., 1960b), found that effects similar to those found for the rhodium addition to tungsten, such as softening, promotion of twinning, and improvement of fabricability, are produced, but the improvement in
Fig. 8.8. Ultimate tensile stress vs. test temperature for tungsten–rhenium solid-solution alloys. (1) Annealed 1 hr at 2298°C (Garfinkle et al., 1968); (2) annealed at test temperature (Flagella, 1967); (3) Sell (1968).

Fig. 8.9. Proportional limit stress vs. test temperature for tungsten–rhenium solid-solution alloys. Numbers in parentheses refer to same conditions and sources as in Fig. 8.8.
Fig. 8.10. Reduction in area vs. test temperature for tungsten–rhenium solid-solution alloys. (1) Annealed 1 hr at 2298°C (Garfinkle et al., 1968); (2) Sell (1968).

Fig. 8.11. Total elongation vs. test temperature for tungsten–rhenium solid-solution alloys. Numbers in parentheses refer to same conditions and sources as in Fig. 8.8.
low-temperature ductility has not been demonstrated. Also, the low solubilities of these elements in tungsten were further substantiated.

Vanadium and chromium are among the elements with high solubility in tungsten, but they give no improvement to its properties (Braun and Sedlatschek, 1960). Aluminum, beryllium, and thorium, just like zirconium or hafnium, form refractory oxides when they are added in small amounts as deoxidizers. \( \text{ThO}_2 \), which is most stable at the sintering temperature, shows the most pronounced influence on the strength and ductility of tungsten. This will be discussed further in the following sections.

8.3. DISPERSION-STRENGTHENED AND PRECIPITATION-HARDENING ALLOYS

The strengthening effect of solid solution alloys generally becomes negligible at a temperature above half the absolute temperature of the melting point of the metal, \( T > \frac{1}{2} T_m \), in which case dispersion-strengthened or precipitation-hardening alloys are superior. Although the precipitates will redissolve at high temperatures and lose their strengthening effects in the precipitation-hardening alloys, they are considered to be a form of dispersion-strengthened alloys.

Theories of dispersion strengthening have been developed by Mott (1952), Orowan (1948), Fisher et al. (1953), and Williams (1957) and reviewed by Ansell (1970). In general, the dispersed second phase should meet the following conditions:

1. The particle size of the second phase should be of submicron range with an interparticle spacing of less than 0.5 \( \mu \text{m} \) (Guard, 1962).
2. The second phase should be chemically stable and resistant to agglomeration during processing and at the service temperature. The degree of resistance to agglomeration is related to the rate of diffusion. Usually, different particle sizes are present, and hence, the chemical potential for diffusion will exist. The result is the solution of smaller particles and the agglomeration of larger particles of the second phase.

The dispersed second phases used in tungsten are metal oxides, carbides, nitrides, and borides. Metal oxides are most promising because of their stability at high temperatures. Carbides follow in second place, although their occurrence is generally caused by heat treating and precipitation.

Since most additives used in dispersion-strengthened alloys are unstable at the melting point of tungsten, 3410°C, and the response to solution-aging treatment is rather sluggish (Semchyshen et al., 1965), melting processes are rarely employed in the consolidation of these alloys. The more common methods here are conventional pressing and sintering, isostatic pressing followed by extrusion, or hot pressing. The last method, as recommended by Sell et al. (1965), has less tendency for the second phase to become agglomerated and yields end products of better quality.

To prepare a fine and well-dispersed powder mixture, comminution by ball milling is generally applied (Sell et al., 1965). The mill is ordinarily built with a tungsten lining and filled with tungsten rods or balls. A grinding aid, such as
aluminum nitrate or chloride may be used (Quatinetz et al., 1965). Alternatively, a coprecipitation or coreduction process may be employed, which will be discussed in more detail when the specific alloys are treated.

8.3.1. Alloys with Oxide Dispersoids

Thoriated tungsten wire has been well known in the lamp industry. For its fabrication, strengthening effects, and high electron emissivity properties, the reader is referred to Sec. 5.6.4. Recent investigations claimed that W–ThO₂ alloys demonstrate the highest tensile and creep strengths at temperatures above 2000°C among all tungsten alloys (Sell et al., 1966). The best composition of the thoria addition is in the neighborhood of 2% by weight, or, as Sell (1968) claimed, 3.8% by volume.

To prepare the powder mixture, the commercial slurry method may be employed, which consists of blending WO₃ with Th(NO₃)₄ solution, followed by air drying, pyrolysis (at 800°C) to convert the nitrate into an oxide, and then reduction with hydrogen. In the last step, tungsten oxide is reduced to metallic tungsten, but thoria remains as oxide.

Alternatively, a coprecipitation method may be applied, consisting of the simultaneous addition of a potassium tungstate solution and a thorium solution to a mixture of oxalic acid and a small amount of hydrochloric acid. The tungstic acid and thorium oxalate thus precipitated are washed by decantation with dilute HCl, filtered, and dried, followed by calcination and reduction as mentioned above (Atkinson et al., 1960).

A freeze-drying technique was used by Ferrante et al. (1971), who claimed that a submicron powder mixture of tungsten and thoria was obtained, but contamination with oxygen was encountered. No advantage in strength properties was realized by this technique as compared with conventional methods.

The addition of ThO₂ to W–25 Re alloy has no further benefit on strength properties and causes a loss of ductility (Sell et al., 1964). Atkinson et al. (1960) reported that the addition of SiO₂ to tungsten makes it difficult to obtain a high sintering density of the material. It is also difficult to remove the SiO₂ during sintering. They also discovered that the addition of ZrO₂ to tungsten causes excessive cracking during fabrication. The only fabricable composition, W–1 ZrO₂, shows no improvement in properties. Alloy W–0.5 HfO₂ was examined by Sell et al. (1962), who stated that only minimal strength gain over unalloyed tungsten was realized. Additions of Ta₂O₅ to tungsten up to 0.2% showed no evidence of precipitation but raised the recrystallization temperature to 2000°C. The strengthening effect is manifested in the stress-relieved condition, which is explained by the fact that the oxide stabilizes the worked structure and, hence, endows a strengthening effect at relatively high temperatures (Sell et al., 1963). Though the stability of Al₂O₃ is high, the comparatively low melting point of this oxide will lead to its reduction and evaporation in the form of AlO or some aluminate (Braun and Sedlatschek, 1960).

The ductile–brittle transition temperatures of alloys of this group, together with other dispersion-strengthened alloys, are shown in Table 8.2. The tensile
Table 8.2. Ductile-Brittle Transition Temperatures for Tungsten Precipitation-Hardening and Dispersion-Strengthened Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fabrication history</th>
<th>Test method</th>
<th>Sheet thickness [mm (in.)]</th>
<th>Ductile-brittle transition temperature [°C (°F)]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-0.04 B(W-0.67 at % B)</td>
<td>Arc melted, annealed</td>
<td>4T bend</td>
<td>1.01 (0.04)</td>
<td>243 (470)</td>
<td>Raffo et al., 1965</td>
</tr>
<tr>
<td>W-0.09 B</td>
<td>Electron-beam melted, annealed</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>316 (600)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W-1 Hf-0.03 C</td>
<td>Electron-beam melted, annealed</td>
<td>4T bend</td>
<td>1.14 (0.045)</td>
<td>260 (500)</td>
<td>Clark, 1963</td>
</tr>
<tr>
<td>W-2 ThO₂</td>
<td>Powder metallurgy, annealed</td>
<td>4T bend</td>
<td>0.889 (0.035)</td>
<td>349 (660)</td>
<td>Schmidt and Ogden, 1963b</td>
</tr>
<tr>
<td>W-1 ThO₂</td>
<td>Powder metallurgy, annealed</td>
<td>4T bend</td>
<td>0.889 (0.035)</td>
<td>365 (690)</td>
<td>Schmidt and Ogden, 1963b</td>
</tr>
<tr>
<td>(W-4 at % Re)-Hf-C*</td>
<td>Arc melted, annealed</td>
<td>4T bend</td>
<td>0.76 (0.03)</td>
<td>191 (375)</td>
<td>Klopp and Witzke, 1971</td>
</tr>
<tr>
<td>W-23.4 at % Re-0.27 at</td>
<td>Arc melted, annealed</td>
<td>4T bend</td>
<td>0.76 (0.03)</td>
<td>-1 (30)</td>
<td>Klopp and Witzke, 1971</td>
</tr>
<tr>
<td>% Hf-1.14 at % C</td>
<td>Powder metallurgy, annealed</td>
<td>4T bend</td>
<td>1.01 (0.04)</td>
<td>125 (257)</td>
<td>Battelle Memorial Institute, 1965</td>
</tr>
<tr>
<td>W-5 Re-2.2 ThO₂</td>
<td>Powder metallurgy annealed</td>
<td>4T bend</td>
<td>1.01 (0.04)</td>
<td>80 (176)</td>
<td>Battelle Memorial Institute, 1965</td>
</tr>
</tbody>
</table>

* Median value for 12 alloys.
properties are shown in Figs. 8.12 through 8.15, and creep information is given in Fig. 8.16.

### 8.3.2. Alloys with Carbide Dispersoids

Dispersion of carbides are produced by heat treatment that results in precipitation from supersaturated solid solutions. The basic requirement for a precipitation-hardenable system is an appreciable solubility at elevated temperatures and a sharp decrease in solubility at lower temperatures. Binary W-C alloys show some strengthening effect over unalloyed tungsten in the temperature range from 204 to 427°C (400 to 800°F) but have little or no effect at higher temperatures. This is probably due to the fact that tungsten carbide particles are coarsened rapidly at those temperatures. Further alloying with an element from group IV or V results in carbides with higher thermodynamic stability than that of W₂C.

Among all carbides of elements from groups IV, V, and VI, hafnium carbide has the highest melting point and the highest thermodynamic stability (Table 8.3). Klopp *et al.* (1971) reported that the response of worked W–Hf–C and W–Re–Hf–C alloys to annealing treatment is rather sluggish. For carbon contents up to 0.51 at %,
recrystallization is incomplete until the carbide particles dissolve and unpin the grain boundaries. The particle-coarsening reaction is essentially controlled by the diffusivity of hafnium, which is slower than that of the commonly used carbide-forming elements. Assuming the strengthening effect is associated with particle size less than 500 Å, the carbide-strengthened tungsten alloys should be stable for thousands of hours at 1650°C (0.52T_m) but only a few hours at 2200°C (0.67T_m). Alloying of tungsten with HfC increases the ductile–brittle transition temperature by 80–110°C in the as-rolled and solution-treated conditions but decreases this temperature slightly in the recrystallized condition. In the temperature range 1650–2200°C, strength improvements up to ninefold can be achieved with an optimum composition of 0.35 mole % of HfC. The high-temperature strengthening effects of HfC and the low-temperature ductility properties associated with 4 at % Re can be incorporated in a single alloy without detrimental interaction. The optimum composition is W–4 at % Re–0.35 at % Hf–0.35 at % C, which shows, in the worked condition, a ninefold strength advantage over unalloyed tungsten in tensile and creep properties at 1927°C (3500°F) (Klopp and Witzke, 1969).

Other carbides, such as TaC, NbC, and ZrC, have been used for precipitation hardening in tungsten or tungsten–rhenium systems (Raffo and Klopp, 1966a; Semchysen et al., 1965; Sell et al., 1963, 1965). The general findings are that these carbides are equally effective as strengtheners as HfC at temperatures up to 1649°C.
Fig. 8.14. Reduction in area vs. test temperature for dispersion-strengthened tungsten alloys. Numbers in parentheses refer to same conditions and sources as in Fig. 8.12.

Fig. 8.15. Total elongation vs. test temperature for dispersion-strengthened tungsten alloys. (1) Sell (1968); (2) annealed 1 hr at 1871°C (Semchyshen et al., 1965); (3) annealed 1/2 hr at 2400°C (Sell et al., 1966); (4) annealed 1/2 hr at 2400°C (Sell et al., 1964); (5) hot worked at 1700°C (Sell et al., 1962).
Fig. 8.16. Temperature-compensated creep of various dispersion-strengthened and precipitation-hardening tungsten alloys. (1) Annealed 1 hr at 1982°C (Raffo and Klopp, 1966a); (2) annealed 1 hr at 2093°C (Klopp and Witzke, 1969); (3) annealed 1 hr at 2426°C (Rubinstein, 1968); (4) annealed 1 hr at 2593°C (Semchyschen et al., 1965); (5) annealed 1 hr at 1982°C (Klopp and Witzke, 1971); (6) hot worked at 2200°C (McCoy, 1966); (7) Sill (1968).

Table 8.3. Melting Points and Thermodynamic Stabilities of Carbides

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Melting point (°C)</th>
<th>Free energy of formation at 1500°C (kcal/g-atom-°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>3150</td>
<td>-38</td>
</tr>
<tr>
<td>ZrC</td>
<td>3420</td>
<td>-39</td>
</tr>
<tr>
<td>HfC</td>
<td>3830</td>
<td>-43</td>
</tr>
<tr>
<td>VC</td>
<td>2780</td>
<td>—</td>
</tr>
<tr>
<td>CbC</td>
<td>3480</td>
<td>-36</td>
</tr>
<tr>
<td>TaC</td>
<td>3825</td>
<td>-38</td>
</tr>
<tr>
<td>Cr3C2</td>
<td>1850</td>
<td>—</td>
</tr>
<tr>
<td>Mo2C</td>
<td>2486</td>
<td>-15</td>
</tr>
<tr>
<td>W2C</td>
<td>2795</td>
<td>-12</td>
</tr>
</tbody>
</table>

* Klopp et al. (1971).

(3000°F) but become weaker at a temperature of 1927°C (3500°F). This is probably attributed to the relative coarsening of the precipitates at high temperatures.

The tensile properties for some alloys of this group, together with other dispersion-strengthened alloys are shown in Figs. 8.17 through 8.20.
Fig. 8.17. Ultimate tensile stress vs. test temperature for precipitation-hardening tungsten alloys. (1) Extruded at 2287°C (Cook, 1965); (2) annealed 1 hr at 2593°C (Semchysken et al., 1965); (3) annealed 1 hr at 1982°C (Raffo and Klopp, 1966a); (4) annealed 1 hr at 2093°C (Klopp and Witzke, 1969); (5) annealed at test temperature (Sell et al., 1963); (6) Sell (1968).

Fig. 8.18. 0.2% Offset yield stress vs. test temperature for precipitation-hardening tungsten alloys. (1) Extruded at 2287°C (Cook, 1965); (2) annealed 1 hr at 1982°C (Raffo and Klopp, 1966a); (3) annealed 1 hr at 2093°C (Klopp and Witzke, 1969); (4) annealed at test temperature (Sell et al., 1963); (5) Sell (1968).
Fig. 8.19. Reduction in area vs. test temperature for precipitation-hardening tungsten alloys. Numbers in parentheses refer to same conditions and sources as in Fig. 8.17.

Fig. 8.20. Total elongation vs. test temperature for precipitation-hardening tungsten alloys. Numbers in parentheses refer to same conditions and sources as in Fig. 8.17.
8.3.3. Other Dispersion-Strengthened Alloys

It has been proposed that boron may exist simultaneously as a substitutional and interstitial impurity in tungsten at dilute concentrations. This concept is consistent with strengthening effects found in tungsten–boron systems, which show that small additions, less than 0.1 at %, of boron produce a rapid initial increase in strength followed by a levelling off at higher boron concentrations (Raffo and Klopp, 1966b). However, the strengthening effect of borides such as HfB or ZrB in tungsten is less effective than that of carbides (Semchyshen et al., 1965).

Addition of nitrides, e.g., HfN, ZrN, or TaN, to tungsten causes embrittlement of the metal and results in cracking during fabrication (Sell et al., 1965). The addition of nitrides, e.g., 1% HfN, to W–25 Re alloy has no further benefit on strength properties and causes a loss of ductility (Sell et al., 1964). The tensile properties of some alloys of this group have been shown in Figs. 8.17 through 8.20.

8.4. Tungsten Composites

Due to the brittle behavior of tungsten metal and most of its alloys at room temperature, intense efforts have been made to search for other means to better utilize the high-temperature properties of the metal. The result is the emergence of tungsten composites, which may be classified as: (1) heavy alloys, (2) infiltrated tungsten, and (3) other composites. They will be discussed in the following sections.

8.4.1. Heavy Alloys

Major applications for heavy alloys, also called heavy metals, are as follows:

1. Rotating inertial members, e.g., gyroscope rotors in inertial guidance systems and navigation equipment. Heavy alloys also serve as flywheels, the rim components of flywheels, or rotating members in governors.

2. Counterweights in static and dynamic balancing applications in airplanes. In these cases, a large mass in a small space is required to balance and stabilize control surfaces that must operate reliably at high air speeds. For the same reason, heavy alloys are also used as actuators of the winding mechanism in self-winding watches, counterbalancing aerial cameras, helicopter blades, radar antennas in aircraft, and flywheels.

3. Heavy alloys are useful in shielding against gamma rays and hard x rays and are used in source-capsule construction for radioactive materials.

4. Because of high densities, rigidity, and heat conductivity, these alloys are used as tool shanks, holders, and boring bars. When they are used as reusable shanks, no grain growth occurs when new carbide tips are brazed on. Their strength properties permit the use of thin sections to cut small precision slots and holes.

5. Some Gyromet grade alloys are employed as electrodes in the resistance welding of fine copper wire and rods because of the properties of high hardness, resistance to indentation, and resistance to sticking of these alloys. Some newly developed heavy alloys containing 95–99% tungsten are being used as backup disks
for semiconductors because of their low coefficient of thermal expansion and good thermal and electrical conductivities.

6. Some Gyromet grade and some newly developed alloys, such as that containing 90% tungsten with 4% Ni–2% Fe–4% Mo, are especially suitable for tooling in brass and aluminum die casting (Clayton, 1972).

The heavy alloys were first produced by McLennan and Smithells (1935). They are essentially three-component pseudoalloys consisting of large amounts of tungsten combined with either a nickel–copper or a nickel–iron matrix. In some recently developed alloys, other elements, such as manganese, cobalt, and molybdenum, are added for strengthening. The alloy development has been reviewed by Larsen and Murphy (1965), and the theories and mechanism of liquid sintering have been summarized by Eremenko et al. (1970).

The high density, ranging from 17 to 19 g/cm³, is a prime requisite of heavy alloys. The only metals with comparable densities are osmium, iridium, platinum, rhenium, gold, uranium, and tantalum, which, however, are generally costly, have limited mechanical properties, or have limited availability.

Preparation of heavy alloys is generally started with the blending of metal powders or coreduction of metal oxides. The choice of the two methods is largely a question of economics and availability of material supplies. After the alloy powder is well blended, pressing and sintering techniques are employed, which include mechanical or hydrostatic pressing, powder rolling or extrusion, hot pressing, etc., as mentioned in Sec. 4.2.

For conventional automatic mechanical pressing, low-residue organic resin-type binders, such as Glyptal, Amberol, or Polycryl, are used to improve the flow characteristics of the powder. To improve compactibility, a solution of paraffin wax in benzol may be used. The benzol is evaporated while the mixture is being stirred. After pressing, the compact is given a two-stage sintering under hydrogen or cracked ammonia. In the first stage, the temperature is increased slowly to 950°C until the wax is evaporated. The second stage is to sinter the compact in the range of 1400–1480°C for periods up to a few hours.

In conventional mechanical or hydrostatic compacting, the pressure employed is in the range of 21.1–42.2 kg/mm² (30,000–60,000 psi) and the green density obtained is about 70% of the theoretical. After sintering, the density is close to the theoretical value of the material, and the as-sintered surface, which is generally smooth, may be further improved by machining or mechanical finishing techniques such as tumbling. Machinability is usually good as compared to tungsten metal or other alloys. Some general machining recommendations are given in Table 5.14.

The presence of a liquid phase during sintering is essential for the process, as it accelerates diffusion and alloying and promotes densification of the material to its theoretical value. To achieve the desired properties, these alloys depend on the solubility of tungsten in nickel, which is about 40% by weight. However, as nickel–tungsten alloys are extremely brittle, they are of little use. Elements such as copper or iron are added to limit the solubility of tungsten and to provide a more ductile and tough matrix.

The volume fraction of the yield phase during sintering may range from less
than 1% to over 50%. The minimum percentage is limited only by the powder preparation technique, which must yield a uniform and complete reaction; and the maximum percentage is limited by the loss of shape, rounding of corners, or degree of collapse that occurs during sintering. The prerequisites for liquid-phase sintering to achieve complete densification are (1) an appreciable amount of liquid, (2) complete wetting of the solid particles by the liquid, and (3) an appreciable solubility of solid in the liquid phase. During sintering between 1000°C (1832°F) and 1100°C (2012°F), the matrix becomes alloyed by diffusion, and some cohesion with tungsten grains takes place. After the melting point of the matrix is reached, the densification process is effected, which may be divided into the following three stages (Kingery, 1959):

1. **Rearrangement stage:** On initial formation of the liquid phase, capillary pressure will tend to rearrange the solid particles in such a way as to give maximum packing and a minimum of total pore surface. This can be started by particles sliding over one another. Subsequently, bridges that are built up will collapse by the solution of small amounts of material at the contact points.

2. **Solution–precipitation stage:** True liquid-phase sintering occurs, and then the smaller particles and high-energy regions, such as edges and corners of larger particles, dissolve preferentially and reprecipitate on the smooth surfaces of larger particles. This results in a dispersion of typically rounded particles in a lower-melting matrix (Dickinson et al., 1972).

3. **Coalescence stage:** When the sintering is continued to its final stage, the dispersoid particles grow together to form an interconnecting network, and solid-state sintering becomes important (Dickinson et al., 1972).

In general, the rate of linear shrinkage for the first stage is greater than that of the second stage, which, in turn, is greater than that for the third stage (Prill et al., 1965).

Brophy and Prill (1966) studied the solution–precipitation shrinkage and found that the mechanism is similar to that of solid-phase sintering with nickel added as the activator. They also claimed that the slope of the log linear shrinkage vs. log time plots goes from ½ to ¾, which indicates a transition from solution control to diffusion control during the solution–precipitation stage.

All heavy alloys, such as the W–Ni–Fe and W–Ni–Cu systems discussed below, can be heat treated or age hardened to improve the strength of the matrix. Heavy alloys can be joined to themselves or with other materials by mechanical joining, brazing, shrink fitting, press fitting, sinter welding, and heliarc welding. Brazing with silver or copper is done in a reducing atmosphere, and surface etching with potassium ferricyanide or fused sodium nitrite will improve braze quality. For heliarc welding, a filler rod similar to the matrix material should be used.

When heating heavy alloys in air to a temperature above 450°C (824°F), a yellow film of tungsten oxide develops and a weight gain results. Protection can be provided to 1000°C (1832°F) or higher in air, if necessary, by various electroplating methods, e.g., by nickel–chromium layer plating. For lower temperatures, a protective layer of lanolin or an electroplate of cadmium or nickel may be used. Surfaces can also be painted after applying a suitable primer such as zinc chromate or an epoxy.
Heavy alloys can be classified according to their compositions as follows:

1. **W–Ni–Cu system:** The standard products of this group consist of 90–95% tungsten, with the balance being 3 parts nickel to 2 parts copper. This composition range tends to give as-sintered densities close to their theoretical values, although nickel and copper form a solid solution at all compositions (Price et al., 1938). The addition of copper reduces the solubility of tungsten in the matrix and avoids the formation of the brittle intermetallic W–Ni compound. In the meantime, the addition of copper lowers the melting point of the nickel matrix and ensures the presence of a liquid phase surrounding the tungsten grains. However, the liquidus of this system stretches almost horizontally for a wide range of compositions, and the sintering temperature is more critical than the system W–Ni–Fe discussed below. Furthermore, the volume change during the solidification of the liquid phase for the W–Ni–Cu is larger than that of W–Ni–Fe. These W–Ni–Cu alloys are essentially nonmagnetic. Their densities range from 17 to 18 g/cm³, and their room-temperature tensile strength reaches the level of 77.3 kg/mm² (110 ksi).

2. **W–Ni–Fe system:** The standard alloys of this group consist of 90–95% tungsten, with the balance being 7 parts nickel to 3 parts iron. The reason for this nickel-to-iron ratio is due to the fact that a minimum of the freezing point appears approximately at this ratio in the binary nickel–iron phase diagram (Hansen, 1958). Assuming this feature is maintained in the presence of tungsten, a liquid of this composition would solidify without primary separation, and thus no occurrence of a cored structure in the matrix will result. These alloys have densities ranging from 17 to 18 g/cm³, with a room-temperature tensile strength at the level of 84.4 kg/mm² (120 ksi). The tensile elongation of these alloys is about 15%, as compared to 5 or 6% for the W–Ni–Cu alloys (Larsen and Murphy, 1965). These W–Ni–Fe alloys can be cold worked to a reduction of up to 60% without intermediate annealing (Wehr, 1962). W–Ni–Fe alloys are therefore selected when secondary forming is required.

3. **Gyromet grades:** These alloys derive their name from their main area of application, gyroscope rotors. They contain 90% tungsten with an iron-to-nickel ratio greater than that for group 2 and, in addition, contain small amounts of molybdenum. The higher iron content with additions of molybdenum have a strengthening effect on the matrix and the strength of this group of alloys is generally greater than that of nickel- or iron-base high-temperature alloys at temperatures above 871°C (1600°F), as shown in Fig. 8.21 (Larsen and Murphy, 1965). This group of heavy alloys is therefore used where high elevated-temperature strength is required.

4. **Others:** With increasing tungsten content, densities of heavy alloys approaching that of tungsten can be obtained. These alloys, possessing still lower coefficients of expansion, reasonable combinations of strength and ductility, and satisfactory machinability, lead to new areas of application, such as heavy counterweights, resistance-welding electrodes, and backup disks for semiconductors. Where desirable, alloys having specific densities or other properties can be obtained by adjusting the powder mix composition and controlling the pressing and sintering cycles.

Attempts were made by Dickenson et al. (1972) to strengthen the matrix by
replacing the nickel–iron mixture with alloy steel and to ductilize the dispersoid tungsten by adding rhenium, platinum, or rhenium–platinum. They conclude that rhenium has a strong strengthening effect, but, due to the sigma phase present in the matrix for high-rhenium-content alloys, a high hardness and brittleness of the alloys results. They also encountered difficulties in obtaining alloy steel powders with proper particle size and good particle size distribution for matrix-strengthening purpose.

8.4.2. Metal-Infiltrated Tungsten

The metal-infiltrated tungsten here refers to a composite essentially produced by powder metallurgy techniques; tungsten-fiber-reinforced metal composites, sometimes also acquiring infiltration, will be treated in Sec. 8.5.3. The metals used as infiltrant are generally of comparatively low melting point, mutually insoluble with tungsten, and possess a high thermal or electrical conductivity, depending upon their application. These composites have been used as electrical contacts and semiconductor supports and more recently have been developed as a major constructional material for rocket nozzles. These will be detailed in the following.

8.4.2.1. Electrical Contacts

Electrical contacts made of silver-infiltrated tungsten have the best arc resistance, high resistance to welding, high conductivity and current carrying capacity, and are less subject to atmospheric oxidation than silver–molybdenum. The general compositions are 35% Ag–65% W, 50% Ag–50% W, 80% Ag–20% W, 65% W–35% Silphos (88% Ag–10% Cu–2% P), 65% W–35% sterling silver (90% Ag–10% Cu), all stated in weight percentage (Westinghouse Corporation, 1971). Copper-infiltrated tungsten has good resistance to wear and arc erosion and
slightly higher contact resistance and lower current-carrying capacity than silver-tungsten and it is used in place of silver-tungsten where service is not so critical and cost is of major concern. The composition range of this type of contact contains from 20 to 50% of copper by weight (Pfizer Inc., 1972).

Composite contacts are made either by first mixing the constituent powders followed by pressing and sintering, or by first preparing the sintered refractory matrix followed by infiltration of the lower-melting-point metal. The infiltration process can be carried out either in vacuum, or under a reducing or inert atmosphere (Meyer, 1965).

The porosity-to-volume ratio of the refractory skeleton, which in turn determines the percentage of the infiltrant, is controlled by the grain size distribution of the tungsten powder, the compacting pressure, sintering temperature, and time. It is of considerable importance in heavy-duty applications that tungsten form a rigid integral skeleton.

Tungsten powder with an average particle size of 5 μm and silver or copper powder of −325 mesh are dry blended and compacted in a mold. The compact is then brought into contact with the infiltrant and heated to 1150–1250°C (2102–2282°F) for 1 hr in a hydrogen atmosphere (Kabayama et al., 1973). In case of vacuum infiltration, hydrogen treatment prior to infiltration is required (Muramatsu, 1965).

The drawback of silver-tungsten is that at the surface of the contact, not only simple tungsten oxides but also other compounds of oxides are formed during arcing, and this results in an acceleration of the oxidation process (Keil, 1956). To overcome this problem, a small percentage of cobalt or iron may be added during blending (Kabayama et al., 1973).

8.4.2.2. Semiconductor Supports

Semiconductors, such as silicon disks, are made into very thin wafers, usually 0.127–0.508 mm (0.005–0.020 in.) thick. The support for this thin disk must have high electrical and thermal conductivity and a thermal expansion coefficient close to that of silicon, $2\times10^{-6}^\circ\text{C}$. In general, stamped molybdenum sheets are used for this purpose. However, higher-quality or higher-power semiconductor devices require a superior support material, such as pure tungsten or silver-infiltrated tungsten. Since the improved thermal and electrical characteristics obtained by silver addition are achieved only at the sacrifice of a higher coefficient of expansion, the silver content is usually limited to 15% by weight (Kosco, 1967). A similar approach has been employed in the manufacture of copper-tungsten materials. The substitution of copper for silver results in slightly lower coefficients of thermal expansion and slightly lower electrical conductivity. The major disadvantage to the use of copper is its lack of corrosion resistance compared with silver.

8.4.2.3. Rocket Nozzles

Early in 1958, rocket nozzles were fabricated of unalloyed tungsten (Sec. 5.3.3). But with the development of solid propellants, theoretical temperatures climb to
3593°C (6500°F) and pressures approach 0.703 kg/mm² (1000 psi). Unalloyed tungsten nozzles have shown erosion, thermal shock, oxidation, and other types of failure due to the severe temperature gradients produced as well as to the high temperature and pressure encountered during firing (Sturiale et al., 1966). This problem led to the application of transpiration cooling concepts as a means to utilize the refractory material more efficiently.

The infiltrant, metal or nonmetal, melts and vaporizes through the open porosity of the refractory matrix and thus absorbs sufficient quantities of heat to maintain the operating temperature of the refractory matrix at or below a safe limit necessary to maintain dimensional stability of the nozzle. Thermal shock problems are also reduced with the inclusion of the infiltrant. Silver or copper is the preferred choice of infiltrant because of high thermal conductivity and relatively large latent heat of transformation.

The tungsten powder used for the matrix must be of high purity with an average particle size of 3–7 μm and nearly normal Gaussian distribution (Matt and Warga, 1965):

\[ f(x) = \frac{1}{(2\pi)^{1/2}} \exp \left( -\frac{x^2}{2} \right) \]  

(8.4)

where \( x \) is the particle size in micrometers. An example of this is the C-20 powder distribution curve shown in Fig. 4.1. When uniformly packed, this kind of particle size distribution will enable the smaller particles to fit into the interstices of the larger particles. An increase in the proportion of any one particle’s size disrupts the uniformity of the packing and results in structural irregularities in porosity or forming particle bridging during sintering. The concentration of fines of less than 2 μm is set between 2 and 3%, since larger quantities than this tend to segregate. Such segregation can cause flash sintering, localized areas of pore closure, and catastrophic grain growth. Powder particles with an average size greater than 7 μm are slowly densified during sintering and will yield material with a pore diameter of such size that capillary forces are inadequate to retain the infiltrant.

Prior to processing, the tungsten powder is screened to remove foreign material and blended to ensure the desired particle distribution, if necessary. After blending, the powder is loaded into rubber bags and is molded to the desired shape and density by jogging or vibration. Care must be exercised during this operation so as not to segregate the coarse and fines. For example, intermittent jogging during loading will cause segregated layers of fines and coarse particles to form. The bagged powder is hydrostatically compacted to a green density of 55–65% of the theoretical at a pressure of 17.6–24.6 kg/mm² (25–35 ksi). However, when the capacity of high-pressure presses is limited, lower pressures may be applied for billets up to 457 mm (18 in.) O.D. × 264 mm (10.4 in.) I.D. × 135 mm (5.3 in.) in size. Pressing pressures as low as 9.84 kg/mm² (14 ksi) are satisfactory both for providing adequate green strength for handling and for obtaining a desired sintered density (Matt and Davis, 1966).

The sintering furnace is preferably of the resistance heating type as shown in
Tungsten Alloys, Composites, and Tungsten

Fig. 4.20, with tungsten heating elements and a combination of tungsten and molybdenum heat shields. The induction furnace with graphite susceptor and shims usually causes carbon contamination of the billet. For details of operation, the reader is referred to Sec. 4.2.3.

Hydrogen used in sintering furnaces is usually purified by passing through a palladium cell, which reduces the oxygen content to less than 1.5 ppm, and then through a dryer, which reduces the dew point to less than $-29^\circ\text{C} (-20^\circ\text{F})$. Vacuum or cracked ammonia may be used in place of hydrogen, but the reduction effect is inferior to the latter. Even with hydrogen, the efficiency of cleanup is limited. The reduction of oxides by hydrogen establishes a gradient of water vapor from the interior of the preform to the furnace chamber. If the time allowed for water vapor transport is too short or if the dew point of hydrogen is too high, the water vapor is not completely removed from the preform, and reoxidation of the tungsten results. Incomplete removal of oxides during sintering frequently results in incomplete infiltration. In general, green compacts should be sintered within 48 hr after compacting to avoid excessive oxidation. If the billet is to be stored for a longer period of time, an atmospherically controlled room with a relative humidity less than 20% should be used.

Before sintering, the green billet is placed on a green tungsten plate of the same powder characteristics as the billet, so that the plate undergoes shrinkage at the same rate as does the billet and the distortion of the billet is minimized. The green tungsten plate is in turn placed on a revolving turntable, which is to be rotated one quarter of a turn every 15–20 min during the run. This ensures even heating of the billet and a uniform density after sintering.

The hydrogen cleanup is normally scheduled prior to the actual sintering phase by holding at temperatures between 800 and 1250$^\circ\text{C}$ (1472 and 2282$^\circ\text{F}$). The actual time required can be judged by the height and color of the hydrogen exhaust flame, because the decomposition of oxides results in a higher and more visible flame. After the cleanup period, the furnace is brought to the sintering temperature. The rate of heating up and the time and temperature for sintering are dictated by the average particle size, the particle size distribution, the impurities of the powder, the billet size, and the desired density of the billet. Generally, the sintering time and temperature increase with the average particle size and the billet size. Impurities such as nickel, iron, or chromium in the amount of 0.25–0.50% behave as activators, shorten the sintering time, and lower the temperature required for sintering (see Sec. 4.2.3.3). However, they also foster grain-boundary melting and lower elevated temperature strength of the material; hence, they are not desirable for this specific application.

Larger billets require slower heating rates than smaller ones, and the particle size distribution is a more important factor for heating rate adjustment. The finer particles sinter at a lower temperature than the coarser particles because of the greater number of points of contact and the higher overall surface energy. If the heating rate is so slow that the fine particles become completely sintered before the final sintering temperature is reached, they will not be bound to the coarser particles. On the other hand, the heating rate must be slow enough to avoid cracking of the billet from thermal stress. Figure 8.22 shows the correlation of average particle size
Fig. 8.22. Sintering temperature vs. average particle size of tungsten powder (Matt and Warga, 1965).

with the sintering temperature, and Fig. 8.23 shows the relationship of time at sintering temperature with sintered density. The dependency of density on time decreases with sintering times greater than 1 hr or so, while the strength of the material still increases with time. This is probably due to the rounding of pores and the subsequent reduction of the notch effects at the points of contact of individual powder particles. Increasing the sintering times to the order of 10–12 hr causes grain growth and excessive loss of strength. The desired density of the sintered tungsten billet for infiltration is within the range of 75–83% of theoretical.

For a billet size of 146 mm diameter × 114 mm (5.75-in. diameter × 4.5 in.), the maximum sintering temperature ranges from 1850 to 2150°C (3362 to 3902°F), and the time at the maximum temperature ranges from ½ to 4 hr, depending upon the powder size used. A detailed list of such schedules together with results obtained are shown in Tables 8.4a–c. The size distribution of different powder lots is essentially of the normal Gaussian distribution, as mentioned before.

Fig. 8.23. Time at sintering temperature vs. density of tungsten matrix (Matt and Warga, 1965).
### Table 8.4a. Sintering Data of Tungsten Billets for Silver Infiltration

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Pressed density (%) theoretical</th>
<th>Sintering schedule</th>
<th>Sintered density (%) theoretical</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>61.8</td>
<td>A-1</td>
<td>76.6</td>
</tr>
<tr>
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<td>61.2</td>
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<td>B-2</td>
<td>79.4</td>
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<tr>
<td>5</td>
<td>61.4</td>
<td>D-3</td>
<td>78.0</td>
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</table>

* Billet size: 146-mm diameter × 114 mm (5.75-in. diameter × 4.5 in.).
* See Table 8.4b for powder type characterization.
* All billets are hydrostatically pressed at 24.6 kg/mm² (35,000 psi).
* See Table 8.4c for sintering schedule.

For a billet size 203 mm O.D. × 102 mm I.D. + 179 mm (8 in. O.D. × 4 in. I.D. × 7 in.), from a powder lot of an average particle size of 5.2–6.1 μm, a sintering schedule may be as follows: (a) 4–900°C–4, (b) 2–1650°C–2, (c) 2–2150°C–2. (The explanation of the notations used here is the same as in footnote c in Table 8.4.)

Alternatively, tungsten billets may be prepared by other powder metallurgy processes described in Sec. 4.4, such as hot pressing (Sturiale et al., 1966).

After the billet is prepared, it should be checked by ultrasonic means for any gross defects. Then the billet is ready for infiltration, which may be carried out in an induction or a resistance heating furnace. Since a long heating zone to maintain a uniform temperature for the billet is important, an induction furnace with this characteristic is preferred. The billet should be prevented from contacting the vessel wall during infiltration and should be placed on graphite or alumina shims that are not wetted by silver. The minor surface contamination at the point of contact is very shallow and can be removed easily after infiltration.

The billet is brought to the infiltration temperature at a rate dictated by the mass so as to prevent thermal cracking of the material. Once at temperature, the billet is soaked for at least 30 min to allow the hydrogen to penetrate the matrix and

### Table 8.4b. Powder Type Characterization

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Table 8.4c. Sintering Schedules

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<td>1st–800°C–1</td>
</tr>
<tr>
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<td>1½–1400°C–1</td>
<td>1½–1400°C–1</td>
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<tr>
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<td>7½–2150°C–4</td>
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<table>
<thead>
<tr>
<th>B-1</th>
<th>B-2</th>
<th>B-3</th>
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* In the first line of each schedule, the number before the temperature indicates time in hours for raising the furnace temperature from room temperature to the indicated one. In consecutive lines, this number indicates time in hours for raising the temperature from the previous line to the indicated temperature.

† The number after the temperature indicates time in hours for holding at this temperature.

To reduce oxides that may be present. The soaking step is also necessary to ensure a uniform temperature throughout the billet so that the infiltrant flow is uniform and controllable.

The proper infiltration temperature for a tungsten billet may be described as that temperature at which the infiltrant enters the billet easily but does not show as droplets on its sides. The larger the pore spaces, the easier it is to infiltrate. If the pore size is small for a billet produced from a powder with an average particle size of less than 3 μm, the pore wall friction exceeds the capillary attraction at a normal infiltration temperature. The temperature, hence, should be raised well above the melting point of silver in order to effect complete pore fill.

Infiltration is accomplished by either top or bottom feeding; however, directional control and the rate of feeding are critical. If the infiltrant is added from different directions or the rate is too high, it will cover the entire outside surface of the billet and trap gases within. The entrapped gases will then develop sufficient back pressure to prevent complete pore filling.

For gravitational infiltration, the infiltrant material, in chunk form, with a maximum dimension of approximately 19 mm (0.750 in.) is fed from the top of the billet. A concave surface may be made on top of the billet in order to exercise the directional control of the infiltrant flow and facilitate the process. For silver infiltration, a standard schedule is as follows: (a) heat from room temperature to 1250°C (2282°F) in 2 hr, and hold at this temperature for 4 hr; (b) add the calculated
amount of silver at such a rate that there is a constant pool of molten silver filling the concave surface at the top of the billet; (c) hold at 1250°C (2282°F) for 3 hr; (d) cool to 1000°C (1832°F) and hold at this temperature for 2 hr; (e) turn power off and cool slowly to room temperature. A hydrogen atmosphere is maintained during the whole process.

After visual, eddy current, dye penetrant, and ultrasonic inspection, some undesired gross porosity may be detected. In such case, reinfiltation is necessary. A typical schedule for this reinfiltation is as follows: (a) heat the billet from room temperature to 900°C (1652°F) in 2 hr, hold at this temperature for 1 hr; (b) heat from 900 to 1275°C (2327°F) in 1 hr and hold at this temperature for 1 hr; (c) add the additional silver required and hold at 1275°C for 1 hr; (d) cool to 1000°C (1832°F) and hold for 1 hr; (e) turn power off and cool slowly to room temperature.

In practice, silver with a minimum of 99.7% purity alloyed with 0.05–0.10% by weight of copper and 0.125–0.250% of silicon is used instead of pure silver. The silicon reduces the oxides that may be present after sintering to a glassy slag, which is dissipated uniformly throughout the billet. Too low a temperature should be avoided during infiltration, since this causes a white, fluffy dross of silicon oxide to form. The dross rapidly plugs the pore passages and forms a watermark pattern. The addition of copper increases the fluidity of the silver and lessens the dross problem.

A detailed analytical heat transfer model for rocket nozzles has been developed by Gessner et al. (1964), who predict composite matrix requirements involving variations in porous microstructure within a nozzle. This type of nozzle may be fabricated by multiple pressing of different tungsten powder sizes before sintering (Schwarzkopf and Seader, 1964).

When copper is used as the infiltrant, it should be of a purity of 99.9% or higher, although it is claimed that an addition of 1% of nickel, iron, or chromium will create a chemical bond between the copper and the tungsten (Maloof, 1964). A standard schedule for sintering of a copper–tungsten composite is as follows: (a) heat from room temperature to 1000°C (1832°F) in 2 hr, and hold at this temperature for 1 hr; (b) heat to 1300°C (2372°F) in 1½ hr, and hold at this temperature for 2 hr; (c) add the calculated amount of copper at the same rate as mentioned for silver infiltration; (d) hold at 1300°C (2372°F) for 1 hr; (e) cool to 1000°C (1832°F) in 1½ hr; (f) turn the power off and slow cool to room temperature. A hydrogen atmosphere is maintained during the whole process.

The silver or copper infiltrant occupies 90% of the pore space in a properly infiltrated structure. Of the remaining 10%, 6% is accounted for by the difference between the combined solidification and cooling shrinkage of the infiltrant and the shrinkage of tungsten. The remaining 4% is the unfilled pore space. By the combined effects of hydrogen degassing of the infiltrant on cooling and the slow cooling rate of the composite, the shrinkage can appear as randomly distributed, spherical, submicron porosity. This porosity pattern substantially reduces the possible expansion stresses that will be exerted upon tungsten matrix by the infiltrant under rocket firing conditions.

It has been reported that improved strength, shock resistance, and high-temperature microstructural stability can be obtained by using thoriated tungsten as the matrix (Cannon, 1968). In addition to silver and copper as mentioned above,
tin, lead (Resnick et al., 1963), zinc (Smith, 1965), magnesium (Sturiale et al., 1966), Ag–15 Mn, and Mn–4 Cu (Kotfila, 1968) can also be used as infiltrants in a tungsten matrix.

For rocket nozzle applications, the thermophysical as well as the mechanical properties of the metal-infiltrated tungsten are important. The former are the basis for evaluating effective transpiration cooling, and the latter relate to structural integrity during service. Among all the above-mentioned composite materials, only W–10% Ag by weight has been extensively evaluated. Figure 8.24 shows the tensile strength and 0.2% yield strength of W–10% Ag at a strain rate of 0.05 min⁻¹ as functions of temperature (Dotson and Kotfila, 1967). Note that at temperatures

Fig. 8.24. Tensile (top) and 0.2% offset yield (bottom) strength with 95% confidence limits as functions of temperature for 10% silver-infiltrated tungsten. Strength properties for 85% dense pressed-and-sintered tungsten are shown for comparison (Dotson and Kotfila, 1967).
above 1649°C (3000°F), an expanded stress scale is used. It is evident that the inflitrant does not contribute to the strength of the composite.

Figure 8.25 shows the ductility of the W–10% Ag composite at different strain rates as functions of temperature. The brittle-ductile transition temperature increases with strain rate; above this temperature, the ductility is primarily independent of strain rate. Two minima in both elongation and reduction in area, are observed in the 816–1093°C (1500–2000°F) and 1649–1927°C (3000–3500°F) ranges. The ductility minimum in the former range may be associated with melting of the silver inflitrant, which could conceivably increase stress concentrations in the irregularly shaped pores. A change in the fracture mode from transgranular to intergranular is observed in the latter temperature range, which probably accounts for the second minimum. In general, the ductility is lower than that of unalloyed tungsten, and that is especially true at high temperatures. This is probably attributable primarily to the notch effect of the pores in the matrix. The compressive yield strength of the composite is compared with that of uninflitrated tungsten in Fig. 8.26. The relationship of the compressive yield strength and the tensile yield strength for both inflitrated and uninflitrated tungsten is shown in the upper part of the figure. The thermal properties of inflitrated and uninflitrated tungsten are summarized in Fig. 8.27.
Some mechanical properties of copper infiltrated tungsten are reported by Aerojet General Corporation (1963). Simulated rocket firing tests for silver-infiltrated tungsten (Price, 1963) and composites with zinc, magnesium, and tin as infiltrants (Sturiale et al., 1966) have been reported. Some machining data of silver- and copper-infiltrated tungsten have been discussed in Sec. 5.11.1. The machining characteristics of silver infiltrated tungsten have been investigated by Aerojet General (1965), and optimum shop turning conditions are recommended. When compared with mild steel, silver-infiltrated tungsten offers greater tool life, better surface finish, and a faster metal-removal rate. However, silver-infiltrated tungsten shows a greater tendency for chipping, spalling, and chatter.

![Graph of mechanical properties](image)

Fig. 8.26. The compressive 0.2% offset yield strength of 10% silver-infiltrated tungsten as a function of temperature. The ratio of compressive to tensile yield strength is shown in the upper part of the graph (Dotson and Kotfila, 1967).
Fig. 8.27. Thermal expansion, thermal conductivity, and enthalpy of 10% silver-infiltrated tungsten and 85% dense pressed and sintered tungsten (Dotson and Kotfila, 1967).

8.4.3. Tungsten-Fiber-Reinforced Composites

Because of the extraordinary strength of whiskers or fibers of any material, fiber-reinforced composites have been of interest in the materials industry. The greatest success in this field has been in the reinforcement of plastic with fiber glass. The fibers used for reinforcement are usually brittle but of high tensile strength and have large elastic moduli. The matrix serves to bind together the fibers and separate them so that a crack cannot propagate across the composite entirely in the brittle
phase. Furthermore, the matrix should have a lower modulus of elasticity than the fibers, so that under load the matrix can deform elastically and thus transfer stress to the fibers. The distance of separation of fibers is immaterial, but rather the volume fraction of the fibers is the determining factor for the strength of the composite (Kelly and Davies, 1965).

Tungsten whiskers, at a diameter of 3–8 μm, have an ultimate tensile strength of up to 2812 kg/mm² (4000 ksi) (Starliper and Kenworthy, 1968). However, due to the difficulty in producing whiskers, the common tungsten-fiber metal composite is made of drawn tungsten wire about 0.076–0.178 mm (0.003–0.007 in.) in diameter, with copper as the matrix (McDanel et al., 1963). The wire may be extended through the whole length of the composite, in which case it is called continuous fiber; alternatively, short sections or chopped lengths of the wire may be used, in which case they are called discontinuous fibers. To prepare the composite, the fibers, continuous or discontinuous, are placed inside a container in an axial orientation, which is essential for axial composite strengthening. Copper is added and infiltrated to form the matrix in either a vacuum or hydrogen atmosphere at a temperature of 1204°C (2200°F) for approximately 1 hr.

It has been found that there is no difference in strength between a continuous and discontinuous fiber composite, provided that the fibers are of the same diameter. The strength of composites of copper reinforced with continuous or discontinuous tungsten fibers is a linear function of fiber content and is given by the equation (McDanel et al., 1963; Umakoshi et al., 1974)

$$\sigma_e = \sigma_f V_f + \sigma_m V_m$$

where $V_f$ is the volume fraction of the fiber, $V_m$ is the volume fraction of the matrix, $\sigma_e$ is the tensile strength of the composite, $\sigma_f$ is the tensile strength of the fiber, and $\sigma_m$ is the stress on matrix at the fracture strain of the fiber. The tensile strength vs. fiber volume percent is shown in Fig. 8.28 (McDanel et al., 1963). Composite strength $\sigma_e$ at 600°C (1112°F) vs. volume fraction of the fibers with a length-to-diameter ratio as the third variable is shown in Fig. 8.29 (Kelly and Tyson, 1965).

Small percentages of nickel, cobalt, aluminum, titanium, zirconium, chromium, or niobium are added to copper for the composite matrix by Petrasek and Weeton (1963). They conclude that three types of reactions occur at the matrix–fiber interface: (1) diffusion–penetration reaction accompanied by a recrystallization of the grains at the periphery of the tungsten fiber, (2) formation of a two-phase zone, (3) solid solution reaction without subsequent recrystallization. Reactions of types 2 and 3 do not seriously affect the properties of the fiber or composites. The most damaging type of reaction is the diffusion–penetration accompanied by recrystallization.

Using thoriated and nonsag tungsten wires (see Sec. 5.6) as fibers, Petrasek and Signorelli (1969) explored the strengthening effect on nickel-base superalloys for turbine bucket applications. They concluded that the 100-hr stress rupture strength obtained for the composites at 1093°C (2000°F) was 34.5 kg/mm² (49,000 psi), as compared to 8.09 kg/mm² (11,500 psi) for the best cast nickel alloys, and that above 149°C (300°F), the impact resistance of the composite compares favorably with that
Fig. 2.8. Tensile strength of tungsten-fiber-reinforced copper composites (McDannels et al., 1963). (a) Continuous reinforcement with 0.78-mm (0.030-in.)-diameter tungsten fibers; (b) continuous reinforcement with 0.127-mm (0.005-in.)-diameter tungsten fibers. (O) McDannels et al. (1963). (C) Arch et al. (1959). McDannels et al. (1959, 1960).
of superalloys, but considerably lower impact strength values are obtained below 149°C (300°F).

Tungsten-fiber-reinforced composites with aluminum, cobalt, or some superalloys such as Monel and S-816 were studied by Starliper and Kenworthy (1968), who stated that none of these composites was considered satisfactory for high-temperature use, chiefly because of reactions at the matrix metal–tungsten interface. Cobalt or “H” Monel matrices showed poor bonding characteristics with the tungsten fibers.

It has been reported (Morris and Steigerwald, 1967) that the fatigue properties of pure silver are improved by reinforcement with continuous or discontinuous tungsten filaments. The degree of increase in fatigue strength at $10^{-7}$ cycles show a dependence on volume fraction of the filaments.

A composite system with Nb–42 Ti–4 Cr–4 Al–1 V matrices and W–3 Re fiber was investigated (Klein and Metcalfe, 1973) for gas turbine applications at temperatures above 1093°C (2000°F). In the coated condition, the composite with 27 vol% fiber reinforcement had excellent stress rupture strength [100-hr rupture strength of 17.6 kg/mm² (25 ksi) at 1204°C (2200°F)], elevated temperature tensile strength [23.2 kg/mm² (33 ksi) at 1427°C (2600°F)], and isothermal oxidation life [greater than 1100 hr at 1093°C (2000°F)].

A more ductile matrix material, Nb–15 Ti, was also investigated (Klein and Metcalfe, 1974) for turbine applications. The coated niobium alloy–tungsten fiber composites are actually three-component systems, which include, in addition to the alloy matrix and the tungsten filament, a silicide coating. Difficulties have been encountered for the improvement in cyclic oxidation resistance. The 1-hr rapid heating cycles with air-blast cooling generate high transient strains because of the
differential expansions of the three components in the composite system. Another problem area, typical of unidirectionally reinforced composites, is low off-axis strength, especially at elevated temperatures.

A unique composite material, known as wire-wound tungsten, has been developed by United Technology Center (Hill and Banta, 1972). The primary objective has been to produce rocket-nozzle throat inserts capable of withstanding long-duration, multirestart, high-pressure firings in solid-propellant and hybrid motors. The composites are prepared by winding the tungsten wire over a properly shaped mandrel in a prearranged order of helical and hoop sequences. After each winding, a layer of plasma-sprayed tungsten is used to encapsulate the wire and to provide a laminate base for the next wire-winding sequence. Fabrication by this method ensures a good balance of hoop and longitudinal strength and also provides for interruption of stress paths and attendant retardation of crack propagation. Wire-wound tungsten exhibits room-temperature tensile strength of 2.0 kg/mm² (2.8 ksi), as compared with 38.7 kg/mm² (55 ksi) for pressed and sintered tungsten of an equivalent density, approximately 85%. However, in compression, wire-wound tungsten exhibits room-temperature ultimate strength of 21.1 kg/mm² (30 ksi). These data indicate that composites are most useful in compression applications.

A tungsten matrix with additions of oxides, borides, nitrides, and carbides that are elongated into fibers by hot extrusion has shown very good stress rupture properties. Interested readers should refer to Blankenship (1968) and Quatinetz et al. (1965).

8.5. TUNGSTEN AS AN ALLOYING ELEMENT

Tungsten is generally a powerful strengthener and grain refiner when used as an alloying element in other metals, especially at elevated temperatures. These metals include stainless steels, tool steels, refractory alloys, and heat-resisting and corrosion-resisting superalloys.

8.5.1. Tungsten as an Alloying Element in Steels

Tungsten consumption as an alloying element in steels in the United States used to be as high as 45% of the total consumption (Li and Wang, 1955) and, in 1972, the estimated tungsten contained in steel amounted to 1,420,000 kg (3,130,000 lb) as compared to the total consumption of 7,370,000 kg (16,260,000 lb) (National Materials Advisory Board, 1973).

A closed gamma “loop” exists in the binary iron–tungsten system (Hansen, 1958), and tungsten is a powerful ferrite stabilizer, only about 6% tungsten being required to prohibit the formation of austenite at any temperature. In the iron–carbon–tungsten ternary system, about 12% of tungsten is required to completely eliminate austenite as a pure phase, although in high-carbon steels, austenite-carbide structures may appear and, therefore, may be hardenable (Roberts et al., 1962). Tungsten has a great potency to move the eutectoid to a lower concentration.
of carbon and thereby increase the amount of undissolved or excess carbide in the hardened steel. The presence of increasing quantities of alloy carbides in tool-steel compositions leads to improvements in wear resistance, a most important property of successful tool performance.

A fine grain structure is highly desirable in tool steel to minimize the possibility of distortion or cracking during hardening and for maximum toughness. The excess carbide is primarily responsible for retarding grain growth during austenitizing. Tungsten, next to vanadium, is one of the most potent elements for restricting grain growth. With a high-speed steel containing 18% tungsten, 4% chromium and 1% vanadium, a fine grain size is retained up to the melting point of the steel (Roberts et al., 1962).

Most alloy elements, including tungsten, added to tool steels tend to move the isothermal transformation curve to longer times for greater hardenability with less severe quenching mediums. The alloying additions also tend to lower the $M_s$ (martensite start) temperature. This effect is complicated by the formation of complex carbides that may remain undissolved at the hardening temperature. Thus, a carbide-forming alloy addition may actually raise the $M_s$ temperature by decreasing the amount of carbon dissolved at a given hardening temperature. Tungsten, like other alloying elements added to steels, can change the curve for hardness vs. tempering temperature with resultant retarded softening or secondary hardening. These effects strongly depend on the carbon and other alloy dissolved in the austenite during prior hardening and are reduced by excess carbide remaining in the structure.

Compared to other alloying elements, tungsten is the most potent in imparting hot hardness to steel and is only second to vanadium in rendering wear resistance and toughness to the material.

Table 8.5 shows the composition of principal types of tool steels that contain tungsten (Lyman et al., 1961, p. 638). It is apparent that tungsten is an important alloying element in various types of tool steels, especially high-speed and hot-work tool steels. For details, the reader is referred to the work of Roberts et al. (1962). Small amounts of tungsten are used in some stainless and heat-resisting steels (Gregg, 1934; Lyman et al., 1961, pp. 409, 780). Steels containing 5–7% tungsten and 0.70–0.75% carbon are used as permanent magnets, and cobalt magnet steels with more coercive force contain 3.75–8.25% of tungsten (Gregg, 1934; Lyman et al., 1961, pp. 409, 780).

### 8.5.2. Tungsten as an Alloying Element in Refractory Metals

Tungsten forms solid solutions at all compositions with niobium, tantalum, and molybdenum (English, 1961). Because of the similarities of tungsten and molybdenum, these metals can be alloyed at all compositions. Some tungsten-base alloys of this type have been mentioned in Sec. 8.2.1.

Tungsten is added to niobium or tantalum to improve the high-temperature strength and creep properties. However, the percentage is generally limited, for example, to 10% in tantalum and to 15% in niobium, above which the fabricability of
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* Lyman et al., 1961.  \(^b\) Readily available.  \(^c\) Available as free-cutting grade.
Table 8.6. Tungsten-Containing Niobium and Tantalum Alloys

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<td>Bentle and Chandler, 1968</td>
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<td>Baker, 1968</td>
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the alloy is poor. A list of these alloys is given in Table 8.6; for their properties, the reader is referred to the references given in the last column of the table.

8.5.3. Tungsten as an Alloyn Element in Other Metals

There are essentially two classes of alloys in this category. The first is heat-resistant alloys, usually called superalloys, and the second is hard-facing and wear-resistant alloys (produced under the trade name Stellites), or Co–Cr–W alloys.

Superalloys have been developed since the 1930s in the United States primarily for application in gas turbines for aircraft, space vehicles, marine craft, and industry. They are generally classified as nickel-, cobalt-, and iron-base alloys; the typical compositions of those which contain tungsten are shown in Tables 8.7 and 8.8 (Sims and Hagel, 1972). It is apparent from these tables that most superalloys contain
### Table 8.7. Chemical Composition of Tungsten-Containing Cast Superalloys

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<th>Ti</th>
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<td>25.5</td>
<td>54.0</td>
<td>7.5</td>
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<td>0.50/0.25</td>
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* Sims and Hagel, 1972.
### Table 8.8. Chemical Composition of Tungsten-Containing Wrought Superalloys

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<thead>
<tr>
<th>Alloy designation</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Cb</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>B</th>
<th>Zr</th>
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<td>Hastelloy alloy X</td>
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<td>18.0</td>
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<td>Udiment 520</td>
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*a* Sims and Hagel, 1972.
<table>
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<tr>
<th>Item</th>
<th>Soft grades&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Medium grades&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Hard grades&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>Tungsten (%)</td>
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<td>Molybdenum (max) (%)</td>
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<td>1.5</td>
<td>1.5</td>
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<tr>
<td>Carbon (%)</td>
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<td>2.45</td>
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<tr>
<td>Manganese (max) (%)</td>
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<td>Silicon (max) (%)</td>
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<td>1.5</td>
<td>1.0</td>
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<td>Nickel (max) (%)</td>
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<tr>
<td>Cobalt (%)</td>
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<td>bal.</td>
<td>bal.</td>
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<td>Hardness (R&lt;sub&gt;s&lt;/sub&gt;)</td>
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<tr>
<td>Chill cast</td>
<td>49</td>
<td>51</td>
<td>55</td>
</tr>
<tr>
<td>Sand cast</td>
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<td>48</td>
<td>52</td>
</tr>
<tr>
<td>Hot rolled</td>
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<td>43</td>
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<tr>
<td>Tensile strength (kg/mm&lt;sup&gt;2&lt;/sup&gt;)</td>
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<td>Compressive strength (kg/mm&lt;sup&gt;2&lt;/sup&gt;)</td>
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<td>218</td>
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<td>Sand cast</td>
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<td>Hot rolled</td>
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<td>169</td>
<td>229</td>
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<tr>
<td>Izod impact strength</td>
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<td></td>
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<tr>
<td>(kg/m unnotched)</td>
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<tr>
<td>Chill cast</td>
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<td>1.59</td>
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</tr>
<tr>
<td>Sand cast</td>
<td>0.346</td>
<td>0.97</td>
<td>0.346</td>
</tr>
<tr>
<td>Hot rolled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
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<td>8.81</td>
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<td>8.64</td>
</tr>
<tr>
<td>Electrical resistivity (μΩ-cm)</td>
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<td></td>
</tr>
<tr>
<td>14.2</td>
<td>14.1</td>
<td>14.1</td>
<td>16.1</td>
</tr>
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</table>

* Fritzien and Elbaum, 1961.
* bal. = balance.
either tungsten or molybdenum, which play an important role in maintaining their high temperature strength. For details and properties, the reader is referred to the recent work of Sims and Hagel (1972).

The Co–Cr–W alloys are used as hard-facing materials and cutting tools. They are generally classified into soft, medium, and hard grades, the nominal compositions and major properties of which are shown in Table 8.9 (Fritzlen and Elbaum, 1961). For more information, the reader is referred to the work of Centre d’Information du Cobalt (1960). The detailed applications of these alloys will be discussed in Sec. 10.5.
Tungsten Carbides and the Hard Metal Industry

9.1. INTRODUCTION

Tungsten carbide, \( \text{WC}_2 \), was first prepared and identified by Moissan (1893, 1896, 1897) by melting tungsten as well as by reducing \( \text{WO}_3 \) with carbon or calcium carbide in a carbon arc furnace. Later, from a melt of \( \text{WO}_3 \), iron, and carbon, Williams (1898) was able to isolate double carbides and gray crystals, the latter of which had a composition of 93.5% tungsten and 6.1% carbon corresponding to the composition of \( \text{WC} \). Other early work (Schenck et al., 1931; Li and Wang, 1955) suggested the existence of the compounds \( \text{W}_3\text{C} \), \( \text{W}_3\text{C}_4 \), and later \( \text{W}_5\text{C}_2 \) and \( \text{W}_3\text{C}_2 \); but more recent work has not confirmed their existence (Kieffer and Benesovsky, 1963).

9.2. PHASE EQUILIBRIUM

The rather complex phase relationships in the tungsten–carbon system were clarified in detail only recently (Doloff and Sara, 1961; Rudy et al., 1966; Rudy, 1969). The constitution diagram presented by the last work is reproduced in Fig. 9.1. The system contains three intermediate phases, \( \text{W}_2\text{C} \), \( \text{WC} \), and \( \alpha\text{-WC}_{1-x} \), of which \( \alpha\text{-WC}_{1-x} \) is stable at high temperatures only. The structure and lattice parameters of tungsten carbides are shown in Table 9.1 (Rudy, 1969).

According to Orton (1961), \( \text{W}_2\text{C} \) is unstable below approximately 1250°C, decomposing into tungsten and the monocarbide. There seems to be some uncertainty regarding a polymorphic phase change of \( \text{W}_2\text{C} \) at high temperatures. Skaupy (1927), and Becker (1928a, b, c) observed the formation of \( \beta\text{-W}_2\text{C} \), which is unstable below 2400°C. This was not confirmed by Sykes (1930) and Doloff and Sara (1961).

The cubic "WC" phase observed by Kirner (Kieffer and Benesovsky, 1963) is apparently the same compound, designated as \( \beta\text{-W}_2\text{C} \) by Lautz and Schneider (1961) and by Goldschmidt and Brand (1962). This phase is now designated as \( \alpha\text{-WC}_{1-x} \), which is unstable below 2530°C, decomposing into \( \text{W}_2\text{C} \) and WC; above
Fig. 9.1. Constitution diagram for the tungsten–carbon system. The temperature figures refer to mean values and estimated overall uncertainty (Rudy, 1969).

Table 9.1. Structure and Lattice Parameters of Tungsten Carbides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₂C</td>
<td>Hex, L'3 type</td>
<td>a = 2.992, c = 4.722b</td>
</tr>
<tr>
<td></td>
<td>Hex, C6 type⁶</td>
<td>a = 2.985, c = 4.716 at 29.5 at % C⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = 3.000, c = 4.730 at 32.8 at % C⁴</td>
</tr>
<tr>
<td></td>
<td>Orth. D₁₅₋₇-Pb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2100–2480°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = 4.728, b = 6.009, c = 5.193 at 32.6 at % C⁶</td>
</tr>
<tr>
<td>α-WC₁₋ₓ</td>
<td>Fcc, B₁ type</td>
<td>a = 4.234; a = 4.215b; c = 4.220g</td>
</tr>
<tr>
<td>WC</td>
<td>Hex, D₃₋₁-P6m2</td>
<td>a = 2.900, c = 2.831b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = 2.9063, c = 2.8368f</td>
</tr>
</tbody>
</table>

⁴ Rudy (1969).
⁵ Westgren and Phragmen (1926).
⁶ Butorina and Pinsky (1960).
⁷ Rudy et al. (1966).
⁸ Rudy and Windisch (1967).

Formulae: aₜₘᵢₜ = cₜₘᵢₜ, bₜₘᵢₜ = 2aₜₘᵢₜ, cₜₘᵢₜ = 3aₜₘᵢₜ.
² Kieffer and Benesovsky (1963).
³ Dolloff and Sara (1961).
⁴ Sara (1965).
⁵ Metcalfe (1946).
Tungsten Carbides and the Hard Metal Industry

2700°C, the phase extends to the ideal composition WC (Dolloff and Sara, 1961; Sara, 1965).

There is general agreement that the solid solubility of carbon in tungsten is very small, <0.1 at % (Kieffer and Benesovsky, 1963).

9.3. CHEMICAL AND PHYSICAL PROPERTIES

9.3.1. Chemical Reactivity

Ditungsten carbide, W₂C, is fairly resistant to acids. It is, however, dissolved by hot HNO₃ and also by a 1:4 mixture of HNO₃ and HF (Ruff and Wunsch, 1914) at room temperature. It reacts at 200°C with chlorine to form WCl₆ and graphite (Becker and Hoelbling, 1927). It is attacked by fluorine at room temperature (Schwarzkopf and Kieffer, 1953). Under oxygen atmosphere, it is oxidized to WO₃ at 500°C.

Tungsten monocarbide, WC, is also highly resistant to acids. Unlike W₂C, it is not attacked by a 1:4 HNO₃–HF mixture at room temperature, and starts to react only at temperatures from 600 to 800°C. With fluorine, it reacts and forms a flame at room temperature. Upon heating in air, it is slowly oxidized to WO₃. Table 9.2 (Kosolapova, 1971) shows the extent of chemical attack in various chemical reagents.

9.3.2. Physical Properties

Ditungsten carbide, W₂C, with 3.16% carbon has an x-ray density of 17.34 g/cm³ and a measured value of 17.2 g/cm³ (Becker, 1928a). It has a Mohs hardness of +9. Schwarzkopf and Kieffer (1953) reported the microhardness on fused WC–W₂C at 3000 kg/mm² (50-g load), but more recently, Jones (1965) reported a hardness of 2250 kg/mm² for WC when W₂C was present. Dolloff and Sara (1961) reported a microhardness of 1450 kg/mm² for isolated W₂C.

The modulus of elasticity of W₂C at room temperature is 42,800 kg/mm² (60.5 × 10⁶ psi) according to Koester and Rauscher (1948). The linear coefficients of thermal expansion have been determined by Becker (1928a) as 1.2 × 10⁻⁶/°C in the direction of the a-axis and 11.4 × 10⁻⁶/°C in the direction of the c-axis.

Becker (1928a, b) reported that the resistivity of W₂C at room temperature is 80 μΩ-cm and, at approximately 2000°C, 125 μΩ-cm. Kosolapova (1971) reported a room-temperature resistivity of 75.7 ± 1 μΩ-cm and that the thermal coefficient of electrical resistivity is 1.95 × 10⁻³/°C. He also lists the Richardson constant for thermionic emission at 190 A/cm-deg. Matthias and Hulm (1952) found the superconductivity critical temperature to be 2.74 K.

Tungsten monocarbide, WC, with 6.13% carbon, has an ideal crystallographic (x-ray) density of 15.77 g/cm³ and measured values ranging from 15.5 to 15.7 g/cm³ (Ruff and Wunsch, 1914; Westgren and Phragmen, 1926; Becker, 1928a). WC has a Mohs hardness of +9. Engle (1942), by extrapolating WC–Co hardness curves,
Table 9.2. Resistance to Chemical Attack of Tungsten Carbide in Various Media\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>24 hr at 20–25°C</th>
<th>2 hr at boiling point of the medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (density 1.19)</td>
<td>97</td>
<td>48</td>
</tr>
<tr>
<td>HCl (1:1)</td>
<td>96</td>
<td>92</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} (density 1.84)</td>
<td>91</td>
<td>1</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} (1:4)</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>HNO\textsubscript{3} (1.43)</td>
<td>63</td>
<td>1</td>
</tr>
<tr>
<td>HNO\textsubscript{3} (1:1)</td>
<td>72</td>
<td>10</td>
</tr>
<tr>
<td>H\textsubscript{3}PO\textsubscript{4} (1.7)</td>
<td>91</td>
<td>93</td>
</tr>
<tr>
<td>H\textsubscript{3}PO\textsubscript{4} (1:3)</td>
<td>96</td>
<td>90</td>
</tr>
<tr>
<td>HClO\textsubscript{4}</td>
<td>98</td>
<td>40</td>
</tr>
<tr>
<td>HClO\textsubscript{4} (1:3)</td>
<td>98</td>
<td>93</td>
</tr>
<tr>
<td>H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (saturated solution)</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>HCl + HNO\textsubscript{3} (3:1)</td>
<td>28</td>
<td>3</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} + HNO\textsubscript{3} (1:1)</td>
<td>92</td>
<td>42</td>
</tr>
<tr>
<td>HNO\textsubscript{3} + HF (4:1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} + H\textsubscript{3}PO\textsubscript{4} (1:1)</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} + H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (1:1)</td>
<td>95</td>
<td>70</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4} + H\textsubscript{3}PO\textsubscript{4} (1:1)</td>
<td>94</td>
<td>95</td>
</tr>
<tr>
<td>NaOH 20% solution</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>10% solution</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>20% + bromine water (4:1)</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>20% + H\textsubscript{2}O\textsubscript{2} (4:1)</td>
<td>88</td>
<td>87</td>
</tr>
<tr>
<td>20% + K\textsubscript{3}[Fe(CN)\textsubscript{6}] (10% solution)</td>
<td>68</td>
<td>68</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Kosolapova (1971).
\textsuperscript{b} Powders with a particle size of 40–50 \(\mu\)m were used for obtaining the results.

established a Rockwell A hardness of 94 for WC. Schwarzkopf and Kieffer (1953) have reported a microhardness (50-g load) of 2400 kg/mm\textsuperscript{2}, whereas Hinnueber (1950) reported a microhardness (20-g load) of 2500 kg/mm\textsuperscript{2}. Takahashi and Freise (1965) using single crystals of WC have measured the anisotropy of microhardness as: (001) plane, 2100±40 kg/mm\textsuperscript{2}; (1100) plane, 1080±50 kg/mm\textsuperscript{2}; (1101) plane, 1060±20 kg/mm\textsuperscript{2}.

The room-temperature modulus of elasticity, as measured by different authors (Koester and Rauscher, 1948; Toth, 1971; Kosolapova, 1971), ranges from 68,200 to 72,100 kg/mm\textsuperscript{2} (97–102 × 10\textsuperscript{6} psi). Toth (1971) reports a shear modulus of 26,700 kg/mm\textsuperscript{2} (38 × 10\textsuperscript{6} psi). Doi \textit{et al.} (1970) have obtained an elastic modulus of 71,000 kg/mm\textsuperscript{2}, a shear modulus of 30,400 kg/mm\textsuperscript{3}, a compressive modulus of 39,200 kg/mm\textsuperscript{3}, and a Poisson ratio of 0.194 by extrapolating curves of these properties established for WC–Co alloys.

The linear coefficient of thermal expansion has been reported by Becker (1928a) to be \(5.2 \times 10^{-6}/^\circ\text{C}\) in the \(a\)-axis direction and \(7.3 \times 10^{-6}/^\circ\text{C}\) in the \(c\)-axis direction.
Toth (1971) reports the same value in the \( a \)-axis direction, but a value of \( 4.2 \times 10^{-6} \degree/\circ C \) in the \( c \)-axis direction.

The electrical resistivity at room temperature is listed by Toth (1971) as 25 \( \mu \Omega \)-cm, while Bachman and Williams (1971) have reported a value of from 17 to 19 \( \mu \Omega \)-cm in the \( c \)-axis direction at room temperature. The magnetic susceptibility of WC according to Klemm and Schuth (1931) is \( +0.005 \times 10^{-6} \). Measurements by Willens et al. (1967) indicate WC becomes superconducting at 10\(^{\circ}K\).

Plastic flow has been observed in WC by several authors. Takahashi and Freise (1965) and French and Thomas (1965) identified the [1100] prism planes as slip planes and the [0001] and \( \frac{1}{3} \langle 11\overline{2}0 \rangle \) were suggested as Burgers vectors. Luyckx (1970) deduced the slip system \( \frac{1}{3} \langle 11\overline{2}3 \rangle \) [0001] by means of transmission electron microscopy. Johansson and Lehtinen (1971) confirmed the existence of \( \frac{1}{3} \langle 11\overline{2}3 \rangle \) Burgers vectors and further found that they are dissociated into superdislocations having unit Burgers vectors \( \frac{1}{6} \langle 20\overline{2}3 \rangle \) and \( \frac{1}{3} \langle 02\overline{2}3 \rangle \).

### 9.4. PREPARATION OF TUNGSTEN CARBIDES

There are five general methods of producing tungsten carbides — reduction of the oxide, isolation from alloys, deposition from the vapor phase, electrolysis of fused salts, and synthesis from the elements. The simplest method of producing tungsten monocarbide of good purity and controlled stoichiometry is by direct combination of the pure elements. This method is therefore the most important commercially.

#### 9.4.1. Direct Reduction

The direct reduction of \( \text{WO}_3 \) with carbon by fusion in the carbon arc furnace was accomplished by Moissan in 1896. By melting \( \text{WO}_3 \) as well as tungsten with either carbon or calcium carbide, he obtained a tungsten–carbon regulus containing 3.05–3.22 % carbon, which he identified as \( \text{W}_2\text{C} \) (theoretical, 3.16% C). This classical method of preparing tungsten carbide permits the ready preparation of \( \text{W}_2\text{C} \)–WC with about 3.5–4% of free graphite.

Tungsten carbides can also be prepared by direct reduction of tungstic acid with an excess of carbon by heating at temperatures below the melting point. To produce oxide-free end products, however, it is necessary to heat above 1500\(^{\circ}C\). Schwarzkopf and Kieffer (1953) have pointed out that to obtain a stoichiometric carbon content using this method, it is necessary to take into account that the amount of carbon required is only 80–90% of the amount theoretically necessary according to the equation \( \text{WO}_3 + 4\text{C} = \text{WC} + 3\text{CO} \). This is due to the fact that CO also takes part in the reaction.

In the reduction of \( \text{WO}_3 \) to WC, the influence of the gas atmosphere is very important. Depending on the temperature, the reaction occurs as follows:

\[
\text{WO}_3 + 4\text{C} = \text{WC} + 3\text{CO} \tag{9.1}
\]

\[
2\text{WO}_3 + 5\text{C} = 2\text{WC} + 3\text{CO}_2 \tag{9.2}
\]
For each reaction temperature, the required quantity of carbon to be added must be determined. For a 1-hr carburization at 1100°C (2010°F) an addition of 3 moles of carbon black per mole of WO₃ has proven most favorable.

Li and Dice (1950) suggested the production of monocarbide from ore containing tungsten oxide by reduction with carbon, and Chrétien and Josien (1952) have described the preparation of monocarbide by carbon reduction of wolframite ore at 1400°C. In the latter case, the product contains W₂C, but WC can be separated by leaching with a maximum yield of 83%.

Tokyo Tungsten (Ito et al., 1970) has recently patented a method for producing uniform WC by reducing WO₂ with calcium and carburizing at temperatures above 1500°C. General Electric (Palm, 1969) has recently received a patent for the direct production of WC from scheelite. Matsumoto and Matsufuji (1972) have reported the feasibility of producing a mixture of W₂C and WC by direct reduction and carburization using lampblack in air. The product is deemed useful as a WC hard-facing material where composition and purity are not as critical as for metal-cutting tools. McKenna (1965) has patented a process to produce tungsten monocarbide directly from a charge of tungsten ore with metallic aluminum and calcium carbide. The process produces WC with less than 2% iron. By suitable leaching treatments, the iron concentration can be reduced to 0.2%.

9.4.2. Isolation from Alloys

By dissolution of a melt of WO₃, iron, and carbon in acid, Williams (1898) isolated double carbides and relatively pure crystals of a composition of 93.5% tungsten and 6.1% carbon, which corresponded to the formula WC. Arnold and Read (1914) also isolated tungsten monocarbide by electrolytic dissolution of tungsten steels. Westgren and Phragmen (1936) subsequently used this technique to isolate tungsten monocarbide from highly carburized ferrotungsten steel melts.

Tungsten carbides and tungsten–titanium mixed carbides have been produced commercially from a molten metal bath following the method of McKenna (1937). This method involves the introduction of tungsten, titanium, and carbon into a molten nickel bath and heating the melt to 2000°C. After cooling, the menstruum is dissolved in acid. The carbides thus isolated are essentially free of graphite, oxygen, and nitrogen.

9.4.3. Deposition from the Vapor Phase

Deposition from the vapor phase is one of the most promising methods of producing high-purity tungsten carbides. Takahashi and Itoh (1972) have prepared both WC and W₂C by chemical vapor deposition from a gas mixture containing tungsten hexachloride, propane, hydrogen, and argon on a graphite substrate in the temperature range 1220–1500°C. An adherent coating of W₂C was obtained at relatively high flow rates of H₂ and WCl₆. Appropriate gaseous concentration for the growth of WC were as follows: WCl₆, 1.0–1.5 mole %; C₃H₈, 1.7–2.8 mole %; H₂, 10–20 mole %; Ar, 75–85 mole %; and total flow rate of 1.7 ml/sec. Tarver (1968) obtained a patent for the chemical vapor deposition of W₂C in the manufacture of coated articles.
Campbell et al. (1949) reported the deposition of tungsten carbide layers at 300–800°C from a mixture of tungsten carbonyl–hydrogen. Hurd et al. (1952) demonstrated that WC powder of a particle size suitable for the manufacture of cemented carbide (1–20 μm) could be produced by pyrolysis of W(CO)_6 and subsequent carburization of the metal with CO–CO_2 mixtures. This method, however, has not yet found commercial application.

### 9.4.4. Electrolysis of Fused Salts

Gomes and Wong (1969) have prepared WC by molten salt electrolysis using sodium tungstate in the electrolyte and carbon from the graphite anode as constituent sources. Optimum results were obtained with an electrolyte consisting of 83 mole % sodium chloride and 5.7 mole % each of sodium tungstate, sodium carbonate, and sodium hydroxide with a temperature of 1000–1025°C, and an anode current density of 37 A/dm². The yield was approximately 0.45 g/A-hr. The product had a carbon concentration of 5.4% and it is believed to contain W_2C.

Weiss (1946) and Andrieux and Weiss (1948) deposited W_2C and WC from carbonate–fluoride–metal oxide–salt melts by electrolysis. The CO_2:WO_3 ratio in the electrolyte controls the carbon content of the deposited product. If the ratio is between 3.3 and 6, W_2C (3.16% carbon) is formed, but if the ratio is 12 or greater, WC (6.13% carbon) will be deposited. At intermediate values, mixtures of both carbides are formed.

### 9.4.5. Synthesis from the Elements

#### 9.4.5.1. In a Carbon-Containing Gas

Considerable work has been done on the carburization of tungsten metal with hydrocarbon gases, carbon monoxide, or other gas mixtures. Much of this work was done in connection with the production of tungsten carbide wire, which at one time was of interest for incandescent lamp filaments. Schwarzkopf and Kieffer (1953) have summarized much of this work.

Hilpert and Ornstein (1913) have carburized metallic tungsten powder with carbon monoxide and methane–hydrogen mixtures and found that specimens carburized at 850°C (1580°F) formed WC, while specimens carburized at 1000°C (1830°F) had a higher carbon content. More recently, Kim and Chang (1968) have studied the carburization of tungsten powder with CO in the temperature range of 1150–1350°C. For the reaction \( W + 2CO = WC + CO_2 \), they obtained an equilibrium constant of \( \log K = 10.950/T − 10.11 \) and the Gibbs free energy change was calculated to be \( \Delta G = -50.129 + 46.37T \) cal/g-mole.

#### 9.4.5.2. Synthesis with Solid Carburizers

**A. By Fusion**

The commercial production of tungsten–carbon alloys by fusion has been a general practice in the industry since the early 1930s. In this process, a mixture of
carbon-reduced tungsten powder and carbon or lampblack is charged into a graphite tube furnace, which is held at a temperature of 3000–3200°C. The product is a molten mixture of WC and W₂C, usually in the proportion of 70% W₂C and 30% WC, which is sometimes cast directly into wear part shapes but most often is quenched in an oil bath or onto a cold plate and subsequently ground into powder. The powder is commonly used in hard-facing welding electrodes and other wear applications.

B. By Carburizing below the Melting Point

Tungsten monocarbide used in preparing cemented carbide is produced primarily by carburizing hydrogen-reduced tungsten powder with carbon black. The carburization is usually carried out under hydrogen in either a carbon-tube furnace or a high-frequency induction furnace using a graphite susceptor.

In the carburization process, the presence of a gas with a definite partial pressure of carbon is essential for the formation of the carbide. For example, in a graphite-tube furnace, carbides are readily formed by carburization with carbon under hydrogen, while carbide formation proceeds slowly in the carbon-free, tungsten-tube furnace. The carburizing atmosphere is produced by reaction of hydrogen with the hot carbon tube to form a hydrocarbon.

Huettig and Fattinger (1950) have studied the extent of reaction of a mixture of tungsten and carbon with a molar ratio of 1:1 under different atmospheres, and their results are shown in Table 9.3. It can be seen that the reaction under vacuum is rather slow, and this is understandable, because at relatively low temperature, the reaction proceeds for the most part via the gaseous phase. Hydrogen halide compounds show some reaction-promoting effects.

In the commercial production of tungsten monocarbide, tungsten powder is mixed with 6.2–6.9% carbon. This amount of carbon is 2–10% in excess of the stoichiometric amount in WC(6.13%) required for reducing the oxygen content. The mixture is usually blended in a rotary blender containing steel or carbide balls. Typically one-half of the tungsten will be added to all of the carbon and blended for

<table>
<thead>
<tr>
<th>Reaction atmosphere (reaction time 4 hr)</th>
<th>Total carbon (%)</th>
<th>Free carbon (%)</th>
<th>Combined carbon (%)</th>
<th>Loss in weight (%)</th>
<th>Extent of reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ + 0.5% propane</td>
<td>6.03</td>
<td>0.85</td>
<td>5.18</td>
<td>0.15</td>
<td>81</td>
</tr>
<tr>
<td>Vacuum</td>
<td>6.03</td>
<td>3.2</td>
<td>2.83</td>
<td>0.8</td>
<td>46.7</td>
</tr>
<tr>
<td>H₂ + HCl (6:1:3) + 0.5% propane</td>
<td>6.1</td>
<td>0.75</td>
<td>5.35</td>
<td>1.2</td>
<td>87.6</td>
</tr>
<tr>
<td>H₂ + HI (6:1:3) + 0.5% propane</td>
<td>6.05</td>
<td>0.4</td>
<td>5.65</td>
<td>0.9</td>
<td>93.5</td>
</tr>
<tr>
<td>H₂ + HBr (6:1:3) + 0.5% propane</td>
<td>6.1</td>
<td>0.71</td>
<td>5.39</td>
<td>1.3</td>
<td>88.5</td>
</tr>
</tbody>
</table>

* Huettig and Fattinger, 1950.
several hours followed by the addition of the remaining one-half tungsten and an additional several hours of blending. Careful blending procedures are required, particularly in the case of coarse tungsten powder, due to the great disparity in density of the constituents and due to the size effects of the particles.

If a tube furnace (Fig. 9.2) is used, the tungsten–carbon mixture is put into graphite boats and passed through the furnace continuously. The furnace may be either gas fired or electrically heated in the temperature range 1400–1600°C. Hydrogen is usually introduced into the discharge end of the tube and is burned off at the charging end.

The reduction conditions in the furnace and the characteristics of the starting metal powder have a marked influence on the properties of the carbide produced. The temperature of carburization particularly has a direct effect on the carbide particle size. Table 9.4 shows the relationship between carburization temperature and Fisher subsieve size of the carbide produced where the starting tungsten had a Fisher size of 1.2 μm.

A typical graphite-tube furnace is 63.5–127 mm (2 1/2–5 in.) in diameter, having a hot zone 406–432 mm (16–17 in.) long, with an overall length of 1219 mm (48 in.)

<table>
<thead>
<tr>
<th>Fisher subsieve size of tungsten carbide (μm)</th>
<th>Carburizing temperature (°C)</th>
<th>Retention time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2</td>
<td>1400–1450</td>
<td>3</td>
</tr>
<tr>
<td>3–5</td>
<td>1450–1500</td>
<td>1 1/2</td>
</tr>
<tr>
<td>6–8</td>
<td>1500–1550</td>
<td>1 1/2</td>
</tr>
</tbody>
</table>

* Data from Teledyne Wah Chang Huntsville.
and is equipped with a gear driven or other type of push rod. The cycle time from charging to discharging is 4–5 hr in the hot zone of the furnace.

An alternative to the graphite-tube furnace is the high-frequency induction furnace. This type of furnace consists basically of an induction coil and a graphite crucible susceptor surrounded by insulation. The carbon–tungsten mixture is loaded inside graphite trays, which are, in turn, placed inside the susceptor. Openings in the susceptor are provided for the admission and discharge of hydrogen gas. The charge is usually rapidly heated to the carburizing temperature, where it is held for about 2 hr. The carbide is then cooled under hydrogen atmosphere for about 10 hr before being discharged. The sintered carbide removed from the furnace is then crushed in a hammer mill, ground in a ball mill, and then screened to assure particle separation.

9.5. CEMENTED TUNGSTEN CARBIDES

Sintered tungsten carbide tools were actually produced and used in commercial applications using the methods described by Voigtlander and Lohmann (1915, 1916a, b), and thus, they are usually credited with the first commercial production of sintered tungsten carbide. Schroeter (1925), found that by mixing tungsten carbide powder with powdered cobalt and heating this mixture until the cobalt melted, a material was produced that retained the wear resistance of tungsten carbide with strength enough to withstand the shock involved in cutting tool and rock-drilling applications. The first large-scale production of a cemented tungsten carbide with 6% cobalt started in Europe in 1926. In the United States, Schroeter's patents were assigned to General Electric, and production started here in 1928.

Even today, over half of the sintered carbide produced is similar to that described by Schroeter. These straight cemented tungsten carbide grades, as they are called, exhibit superior performance in the machining of cast iron and nonferrous and nonmetallic materials. Early in the application of straight cemented carbides in cutting steels, however, performance was found to be less than desirable, because the steel chips being removed tended to weld to the carbide tool causing a crater to form and early tool failure.

Further developments in the industry were primarily modifications of Schroeter's compositions made by replacing either a portion or all of the tungsten carbide with other carbides, such as titanium carbide, tantalum carbide, and molybdenum carbide. Schwarzkopf (1929) found that solid solutions of more than one carbide produced a superior tool material, particularly for cutting steels. Schwarzkopf's patent (1929) covering the use of solid solutions marked the starting point of the development of multicarbide cutting tools for the high-speed machining of steel.

Today in the United States, approximately 60% of the tungsten metal produced goes into the production of tungsten carbide (see Chapter 11), and of this, nearly two-thirds goes into the manufacture of cemented carbide cutting tools. In addition to cutting tools, cemented carbide is used in mining and drilling tools, dies, bearings,
and numerous wear applications. For an approximate breakdown of the usage, the reader is referred to Table 11.8.

9.5.1. Manufacture of Cemented Carbides

One of the first and most important steps in the preparation of cemented carbides is the milling of the constituent carbides with a cobalt binder. The purpose of milling is not only to reduce the carbide particle size, but also to produce a uniform and fine distribution of the cobalt binder. In industrial practice, the carbide mixtures are wet milled using either rotary, vibratory, or attrition mills, with rotary mills being the most common. Milling is usually performed in a hydrocarbon liquid using straight tungsten carbide balls. The time of milling may vary from one day to several days, depending upon the particle size and distribution desired. Insufficient milling can lead to high porosity and a resulting decrease in strength of the finished product, while overmilling can result in too fine a particle size and excessive impurity pickup.

In the case of straight carbide grades, all constituents are usually added at the start of milling. In the case of steel cutting grades, however, the solid solution carbides containing TiC and/or TaC are usually milled for some time prior to adding the straight tungsten carbide.

Following milling, the milling fluid is decanted or siphoned off, and the carbide slurry is dried in vacuum dryers, in low-temperature furnaces, or, more commonly today, by spray drying. The milled carbide is screened either wet or dry to remove cobalt flakes and any agglomerates.

Prior to pressing, a binder material such as paraffin, camphor, wax, or methylene glycol may be added to the carbide powder for the purpose of imparting strength to the pressed part and to act as a lubricant. Paraffin, which is commonly used in the United States, can be added in the molten state during vacuum drying, by spraying on the dry powder, or as a 5–10% solution in a suitable hydrocarbon solvent before spray drying. The waxed powder is then dried and put into a granular form to produce good flow and fill properties during pressing. One method is first to homogenize the powder in a high-energy blender, followed by pressing at less than one-third of final pressure and granulating by pushing the pressed mass through an approximately sized metal sieve. The granules are then sized, with the fine and coarse granules being reprocessed.

A second method of producing granules is incorporated in the process of spray drying. In this process, a slurry of carbide, a hydrocarbon solvent (usually the milling slurry), and wax is sprayed upward in a tank into a flow of hot gas coming from the top of the tank. The slurry dries into nearly perfect spheres, which fall to the bottom of the tank where they are collected. This method of granulation not only has production advantages but also produces a granule with excellent flow and fill characteristics.

Standard cutting tool shapes and other high-volume parts are then pressed in automatic hydraulic or mechanical presses using carbide-lined dies. Pressures of 21.1–42.2 kg/mm² (30–60 ksi) are employed. The parts are pressed sufficiently over size to allow for shrinkage during sintering and for any subsequent grind-off. The
exact amount of shrinkage depends upon the carbide grade and the pressing pressure but will usually be in the neighborhood of 15–20\%.

For parts that are not pressed to size or that are low-volume items, the carbide is usually pressed into large ingots or blocks from which the parts can be cut and shaped. Some cutting and shaping can be done with carbide in the as-pressed condition, but generally shaping is done after a presinter operation, which imparts some strength to the compact. The blocks or ingots are usually compacted in split die molds with side rams. Pressures as high as 42.2 kg/mm\(^2\) (60 ksi) are used to compact ingots, but for large parts [>102-mm (>4-in.) diameter] pressures of the order of 7–14 kg/mm\(^2\) (10–20 ksi) are more common.

Another compacting method generally used for large pieces is isostatic pressing. In this method, powders are charged into a closed flexible container, which is then suspended in a liquid in a closed pressure vessel. Pressures in the range of 20–30 kg/mm\(^2\) (28.4–42.7 ksi) are applied. Following pressing, the compacts are processed in a manner similar to the mechanical or hydraulic pressed parts mentioned previously. For more details about the operation of isostatic pressing, the reader is referred to Sec. 4.2.2.

For the production of large parts, such as dies, drawing tools, and shell cores, hot pressing techniques are often used. In this process the powder mixture is compacted and simultaneously sintered in graphite molds at a pressure of 0.56–2.1 kg/mm\(^2\) (0.8–3 ksi) and at a temperature of 1300–1600\°C.

Presintering and sintering are usually required after cold compacting. Presintering is a low-temperature heat treatment performed for the purpose of removing wax binder and to impart sufficient strength to the compact to permit preforming or shaping operations if they are required. The presintered compact attains a consistency similar to that of ordinary blackboard chalk and can be readily shaped by such techniques as drilling, slicing, grinding, or turning.

A presinter cycle consists of heating the compacts slowly to a temperature of about 400\°C and holding for a period of time sufficient to remove the wax binder. Once wax removal is complete, the temperature is increased to 800–1150\°C and held for a predetermined time period to allow for some degree of sintering to occur. If the compacts do not require preforming, this presintering step is not necessary, and the compacts can be final sintered upon removal of the wax binder.

Sintering of WC–Co compacts is performed with the cobalt binder in the liquid phase (Co–W–C eutectic) at temperatures from 1350 to 1550\°C. The exact sintering temperature depends upon the carbide composition, the average particle size, and the particle size distribution. Higher sintering temperatures are generally used for the steel-cutting grades, which contain titanium and tantalum carbides. Lower sintering temperatures are used for the straight WC–Co carbide grades and particularly those having a fine grain size.

Sintering time is also important because it can affect the mechanical properties just as sintering temperature does. Mechanical properties improve during the initial stages of sintering but will decrease at later stages. The decrease in properties is associated with grain growth, grain coalescence, and possible departure from stoichiometry (Gurland, 1960).

In spite of the high pressures employed in compacting, it is not possible to get
much better than 60% theoretical density in the unsintered condition. At the sintering temperature, densification to theoretical density takes place, practically eliminating any pore volume. The linear shrinkage occurring during sintering depends on several factors, including composition, compacting pressure, average particle size, and particle size distribution, but will generally be in the range of from 15 to 20%. In recent years, isostatic hot pressing has been used if porous free material is needed.

9.5.2. Properties of Cemented Carbides

9.5.2.1. Strength-Controlling Factors

The mechanical properties of cemented tungsten carbides depend primarily on composition, binder content, average particle size, and particle size distribution. It is by varying these parameters that carbide producers formulate grades to fit specific applications. Other factors, such as compacting pressure, sintering time and temperature, microstructure, porosity level, impurity concentration, and surface condition also affect properties of the final product. These latter factors are controlled primarily by processing techniques and will not be further considered here. In the case of throw-away inserts, coatings of TiC, TiN, Ti(C,N), Hf(C,N), or Al₂O₃ may be applied by the chemical vapor deposition process to reduce cratering.

9.5.2.2. Effect of Binder Content

Both in the straight and multicarbide grades, binder content is the most important variable in determining transverse rupture strength, hardness, and other strength properties. Within the range of 3–25% cobalt for commercial straight carbides, hardness and elastic modulus increase with decreasing cobalt content. Compressive strength also increases with decreasing cobalt, but at a concentration of 6% and lower there is little further increase. Until recently, most compressive strength studies showed a decrease in strength below 6% cobalt, but Lueth and Hale (1970) have shown this decrease to be associated with test procedures rather than with the actual strength of the carbide.

Transverse rupture strength and toughness increase with increasing cobalt content up to a maximum at approximately 25% cobalt (Gurland, 1963; Kreimer and Alekseeva 1962). The effect of cobalt content on these properties for alloys with a 2-μm particle size is shown in Fig. 9.3. The properties and applications of different grades of cemented carbides are shown in Table 9.5. To a certain degree, the sintering temperature and the cooling rate affect the toughness, because some carbide may be retained in the binder as a solid solution.

9.5.2.3. Effect of Particle Size

The effect of carbide particle size on mechanical properties has been studied extensively by Exner and Gurland (1970), Gurland (1963), Gurland and Bardzil (1955), and by Kreimer and Alekseeva (1962). Hardness and compressive strength
decrease with increasing particle size. Transverse rupture strength has a pronounced maximum, which varies depending on cobalt content and carbide particle size. This effect was first demonstrated by Gurland and Bardzil (1955) and is shown for a 12% cobalt alloy in Fig. 9.4.

The combined effect of cobalt content and carbide particle size is best illustrated in terms of the average thickness of the cobalt layers. Gurland and Bardzil have shown that, to a first approximation, hardness of carbide alloys is an exponential function of cobalt mean free path as shown in Fig. 9.5. Compressive strength also decreases with increasing mean free path, while transverse rupture strength exhibits a maximum as shown in Fig. 9.6. The maximum marks a change in fracture mode from a continuous crack for thin layers of cobalt to interrupted cracking or crack arrest for thicker cobalt layers.

Lueth (1972) has measured fracture toughness parameters as a function of binder film thickness. He has shown that the critical strain energy release rate increases approximately linearly with binder film thickness. The results of Lueth's study are listed in Table 9.6.

9.5.2.4. Effect of Carbide Composition

The carbon level in the cemented carbide is extremely important for good strength and wear properties. Wood (1970) states that for a 6% cobalt alloy, the
<table>
<thead>
<tr>
<th>Composition</th>
<th>Steel cutting</th>
<th>Cast iron and nonferrous cutting</th>
<th>Noncutting applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate grain size (µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC (%)</td>
<td>TiC (%)</td>
<td>TaC (%)</td>
<td>Co (%)</td>
</tr>
<tr>
<td>1-2</td>
<td>64</td>
<td>25.5</td>
<td>4.5</td>
</tr>
<tr>
<td>1-2</td>
<td>71</td>
<td>12.5</td>
<td>12.0</td>
</tr>
<tr>
<td>1-2</td>
<td>76</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>1-2</td>
<td>72</td>
<td>8</td>
<td>11.5</td>
</tr>
<tr>
<td>1-2</td>
<td>79</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>2-4</td>
<td>57</td>
<td>—</td>
<td>27</td>
</tr>
<tr>
<td>1-2</td>
<td>92</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>1-2</td>
<td>91</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>2-3</td>
<td>97</td>
<td>—</td>
<td>3</td>
</tr>
<tr>
<td>2-3</td>
<td>94</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>2-3</td>
<td>94</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>2-3</td>
<td>94</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>2-4</td>
<td>91</td>
<td>—</td>
<td>9</td>
</tr>
<tr>
<td>1-3</td>
<td>89</td>
<td>—</td>
<td>11</td>
</tr>
<tr>
<td>2-3</td>
<td>90</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>2-4</td>
<td>90</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>1-4</td>
<td>87</td>
<td>—</td>
<td>13</td>
</tr>
<tr>
<td>2-4</td>
<td>84</td>
<td>—</td>
<td>16</td>
</tr>
<tr>
<td>2-5</td>
<td>75</td>
<td>—</td>
<td>25</td>
</tr>
</tbody>
</table>

* Data from supplier's sales or technical brochures.
Fig. 9.4. Effect of grain size on transverse rupture strength of cemented tungsten carbide (Exner and Gurland, 1970), (1) Fischmeister and Exner (1961), (2) Gurland and Bardzil (1955).

Fig. 9.5. Rockwell hardness as a function of mean free path for cemented tungsten carbide (Gurland and Bardzil, 1955).
carbon limits should be 5.68–5.79%, a range of only 0.11% carbon. Undercarburized 
material results in the formation of the extremely brittle η phase (a double carbide of 
variable composition) during sintering, while an excess of carbon results in retained 
free carbon, which weakens the alloy and has harmful effects on abrasive wear 
properties.

Even within the acceptable carbon range, properties are affected by changes in 
carbon content. Suzuki and Kubota (1966) found that dissolved tungsten in the 
binder phase changes from a minimum 2–3% in high-carbon two-phase alloys to a 
maximum of 7–9% in low-carbon two-phase alloys. The effect this has on transverse 
rupture, hardness specific gravity, and lattice parameter of the binder phase is shown 
in Fig. 9.7. Based on these findings and by optimization of the carbon level, Suzuki 
et al. (1969) have prepared alloys having transverse rupture strength as high as 
370 kg/mm² for a 10% cobalt alloy.

9.5.2.5. Effect of Adding (W,Ti)C Solid Solution and TaC

The primary advantage of adding (W,Ti)C solid solution and TaC is to improve 
cratering and edge-wear resistance in steel-cutting applications. Increasing TiC 
content also tends to increase oxidation resistance, hardness, and hot strength, but 
has an adverse effect on transverse rupture strength, impact resistance, and 
compressive strength.

Increasing the TaC content in multcarbides further improves steel-cutting 
performance, particularly edge-wear resistance. Unlike TiC, however, TaC does not 
appreciably effect hardness and tends to improve toughness and transverse rupture
Table 9.6. Effect of Binder Film Thickness on the Mechanical Properties of Cemented Tungsten Carbide

<table>
<thead>
<tr>
<th>Co (wt %)</th>
<th>Grain size desired (μm)</th>
<th>Transverse rupture strength [kg/mm² (ksi)]</th>
<th>Compressive yield, 0.002% offset [kg/mm² (ksi)]</th>
<th>Ultimate Compressive strength [kg/mm² (ksi)]</th>
<th>Critical strain energy release rate [kg/cm² (psi)]</th>
<th>Critical stress intensity parameter [kg/mm² (ksi)]</th>
<th>Hardness (Rockwell A)</th>
<th>Modulus of elasticity × 10^6 [kg/mm² (ksi)]</th>
<th>Binder film thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.5</td>
<td>302 (430)</td>
<td>111 (158)</td>
<td>465 (662)</td>
<td>0.13 (1.9)</td>
<td>8.8 (12.5)</td>
<td>89.0</td>
<td>58.4 (83.1)</td>
<td>0.29</td>
</tr>
<tr>
<td>15</td>
<td>2.5-3.0</td>
<td>295 (420)</td>
<td>71.7 (102)</td>
<td>391 (556)</td>
<td>0.23 (3.25)</td>
<td>10.5 (15.0)</td>
<td>87.0</td>
<td>50.9 (72.4)</td>
<td>0.65</td>
</tr>
<tr>
<td>15</td>
<td>7-8</td>
<td>273 (388)</td>
<td>54.8 (78)</td>
<td>322 (458)</td>
<td>0.46 (6.5)</td>
<td>15.5 (22.0)</td>
<td>85.0</td>
<td>50.5 (71.9)</td>
<td>1.4</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>239 (340)</td>
<td>155 (221)</td>
<td>498 (709)</td>
<td>0.06 (0.88)</td>
<td>5.9 (8.4)</td>
<td>90.5</td>
<td>56.9 (81.0)</td>
<td>0.16</td>
</tr>
<tr>
<td>9</td>
<td>2.5-3.0</td>
<td>215 (306)</td>
<td>149 (212)</td>
<td>444 (631)</td>
<td>0.12 (1.7)</td>
<td>8.2 (11.6)</td>
<td>88.9</td>
<td>55.7 (79.2)</td>
<td>0.38</td>
</tr>
<tr>
<td>9</td>
<td>7-8</td>
<td>239 (340)</td>
<td>99.8 (142)</td>
<td>362 (515)</td>
<td>0.34 (4.78)</td>
<td>13.4 (19.0)</td>
<td>87.3</td>
<td>53.4 (76.0)</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>138 (196)</td>
<td>295 (420)</td>
<td>605 (860)</td>
<td>0.04 (0.58)</td>
<td>4.6 (6.5)</td>
<td>92.8</td>
<td>67.1 (95.5)</td>
<td>0.09</td>
</tr>
<tr>
<td>3</td>
<td>2.5-3.0</td>
<td>176 (250)</td>
<td>197 (280)</td>
<td>487 (693)</td>
<td>0.07 (0.98)</td>
<td>6.7 (9.6)</td>
<td>91.3</td>
<td>66.6 (94.7)</td>
<td>0.14</td>
</tr>
<tr>
<td>6</td>
<td>7-8</td>
<td>209 (298)</td>
<td>134 (190)</td>
<td>398 (566)</td>
<td>0.14 (1.98)</td>
<td>9.1 (13.0)</td>
<td>88.6</td>
<td>59.4 (84.5)</td>
<td>—</td>
</tr>
</tbody>
</table>

strength. The trends in the effects of these alloying constituents can be seen from the commercial carbide property data of Table 9.5.

9.6. **RECLAMATION OF TUNGSTEN CARBIDES**

The quantity of tungsten-containing scrap recycled to the United States domestic market represents approximately 20% of the total consumption. Among different kinds of scraps reclaimed, tungsten carbides are the largest portion of the total (see Sec. 11.2.2). The current processes used for recycling cemented tungsten carbides are the coldstream process, the zinc process, and the leach–milling process. These are described in detail in Sec. 2.8.2. Other processes of recycling by chemical methods, which are applied to other scraps as well as to tungsten carbides, are described in Sec. 2.8.3.
Applications of Tungsten

10.1. INTRODUCTION

Tungsten wire has been used primarily in the electric lamp industry since Coolidge's (1909) powder metallurgy method was developed. High-speed steel-cutting tools gained industrial acceptance in the 1900s and accounted for the major consumption of tungsten before World War II. Tungsten carbides were commercially available as early as 1915 and became dominant in the consumption of tungsten during World War II. In the same period of time, the substitution of molybdenum for tungsten in high-speed steel alloyment took place, reducing tungsten consumption in the steel industry.

The consumption of tungsten ore and concentrates by end use, 1940–1974, in the United States is shown in Table 10.1; that of tungsten intermediate products is shown in Tables 10.2 through 10.4. In the following sections, the applications of tungsten will be discussed in detail according to the product forms.

10.2. UNALLOYED TUNGSTEN

In this section, unalloyed tungsten is defined as metallic tungsten (without any intentional alloying additives) in the form of mill products, as sintered slabs, and on forms consolidated by other means. However, the traditional doped wire and thoriated and zirconiated wire (see Secs. 5.6.3 and 5.6.4), are also included in this category.

10.2.1. Tungsten Wire

The major uses for unalloyed tungsten are in the wire form for incandescent lamp filaments (Figs. 10.1 and 10.2), heating elements in fluorescent lamps, lamp support wire, electronic emitters, electronic heater and grid wire (Fig. 10.3), vacuum metallizing wire (Fig. 10.4), and heating elements for high-temperature furnaces (see Sec. 5.6). In general, material employed in incandescent filaments should have a high melting point, a favorable radiation range, low vapor pressure, and high shock
### Table 10.1. United States Consumption of Tungsten Ore and Concentrates by End Use, 1940–1976*

<table>
<thead>
<tr>
<th>Year</th>
<th>Ferrotungsten</th>
<th>Direct to steel</th>
<th>Metal powder and other uses</th>
<th>Total†</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>4.3</td>
</tr>
<tr>
<td>1941</td>
<td>5.68</td>
<td>1.5</td>
<td>0.4</td>
<td>7.58</td>
</tr>
<tr>
<td>1942</td>
<td>5.36</td>
<td>1.4</td>
<td>1.2</td>
<td>7.90</td>
</tr>
<tr>
<td>1943</td>
<td>5.40</td>
<td>1.2</td>
<td>2.0</td>
<td>8.76</td>
</tr>
<tr>
<td>1944</td>
<td>5.13</td>
<td>1.1</td>
<td>2.5</td>
<td>8.72</td>
</tr>
<tr>
<td>1945</td>
<td>3.2</td>
<td>0.82</td>
<td>2.4</td>
<td>6.40</td>
</tr>
<tr>
<td>1946</td>
<td>1.0</td>
<td>0.82</td>
<td>1.1</td>
<td>3.0</td>
</tr>
<tr>
<td>1947</td>
<td>1.6</td>
<td>0.59</td>
<td>1.3</td>
<td>3.5</td>
</tr>
<tr>
<td>1948</td>
<td>1.8</td>
<td>0.82</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>1949</td>
<td>1.0</td>
<td>0.4</td>
<td>0.82</td>
<td>2.3</td>
</tr>
<tr>
<td>1950</td>
<td>0.5</td>
<td>0.82</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td>1951</td>
<td>1.0</td>
<td>0.59</td>
<td>3.6</td>
<td>5.18</td>
</tr>
<tr>
<td>1952</td>
<td>0.95</td>
<td>n.a.</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>1953</td>
<td>1.3</td>
<td>n.a.</td>
<td>2.2</td>
<td>3.5</td>
</tr>
<tr>
<td>1954</td>
<td>0.59</td>
<td>n.a.</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>1955</td>
<td>1.4</td>
<td>n.a.</td>
<td>2.7</td>
<td>4.1</td>
</tr>
<tr>
<td>1956</td>
<td>1.5</td>
<td>n.a.</td>
<td>2.7</td>
<td>4.1</td>
</tr>
<tr>
<td>1957</td>
<td>0.95</td>
<td>n.a.</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>1958</td>
<td>0.64</td>
<td>n.a.</td>
<td>1.8</td>
<td>2.4</td>
</tr>
<tr>
<td>1959</td>
<td>1.4</td>
<td>n.a.</td>
<td>3.1</td>
<td>4.4</td>
</tr>
<tr>
<td>1960</td>
<td>0.95</td>
<td>n.a.</td>
<td>4.3</td>
<td>5.27</td>
</tr>
<tr>
<td>1961</td>
<td>0.95</td>
<td>n.a.</td>
<td>4.1</td>
<td>5.04</td>
</tr>
<tr>
<td>1962</td>
<td>1.0</td>
<td>n.a.</td>
<td>5.18</td>
<td>6.22</td>
</tr>
<tr>
<td>1963</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.04</td>
</tr>
<tr>
<td>1964</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.58</td>
</tr>
<tr>
<td>1965</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>6.31</td>
</tr>
<tr>
<td>1966</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>8.22</td>
</tr>
<tr>
<td>1967</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>6.31</td>
</tr>
<tr>
<td>1968</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.0</td>
</tr>
<tr>
<td>1969</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.95</td>
</tr>
<tr>
<td>1970</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>7.58</td>
</tr>
<tr>
<td>1971</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5.27</td>
</tr>
<tr>
<td>1972</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>6.40</td>
</tr>
<tr>
<td>1973</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>6.99</td>
</tr>
<tr>
<td>1974</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>7.36</td>
</tr>
<tr>
<td>1975</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>6.37</td>
</tr>
<tr>
<td>1976</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>7.32</td>
</tr>
</tbody>
</table>


* n.a. = not available.

* For the period 1952–1962, this column includes scheelite used directly in steel bath; separate figures are not available.

* Totals may not add due to rounding.
Table 10.2. United States Consumption of Tungsten Intermediate Products by End Use, 1956–1962*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High speed</td>
<td>1.27</td>
<td>0.95</td>
<td>0.50</td>
<td>0.95</td>
<td>0.77</td>
<td>0.64</td>
<td>0.82</td>
</tr>
<tr>
<td>Hot-work and other tool</td>
<td>0.23</td>
<td>0.18</td>
<td>0.18</td>
<td>0.27</td>
<td>0.18</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td>Alloy, other than tool*</td>
<td>0.23</td>
<td>0.14</td>
<td>0.14</td>
<td>0.23</td>
<td>0.14</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>High-temperature nonferrous alloys*</td>
<td>0.14</td>
<td>0.14</td>
<td>0.09</td>
<td>0.23</td>
<td>0.23</td>
<td>0.18</td>
<td>0.27</td>
</tr>
<tr>
<td>Other nonferrous alloys*</td>
<td>0.32</td>
<td>0.23</td>
<td>0.23</td>
<td>0.41</td>
<td>0.27</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Tungsten metal</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Wire, rod, and sheet</td>
<td>0.54</td>
<td>0.50</td>
<td>0.41</td>
<td>0.59</td>
<td>0.59</td>
<td>0.64</td>
<td>0.77</td>
</tr>
<tr>
<td>Other</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.09</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Carbide (cemented or sintered)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Made from hydrogen-reduced powder</td>
<td>0.77</td>
<td>0.82</td>
<td>0.54</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
<td>1.41</td>
</tr>
<tr>
<td>Made from crystalline powder</td>
<td>0.14</td>
<td>0.14</td>
<td>0.09</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.64</td>
</tr>
<tr>
<td>Other carbides (cast or fused)</td>
<td>0.64</td>
<td>0.54</td>
<td>0.32</td>
<td>0.45</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>Chemicals*</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Total</td>
<td>4.36</td>
<td>3.68</td>
<td>2.50</td>
<td>4.45</td>
<td>4.13</td>
<td>4.10</td>
<td>5.36</td>
</tr>
</tbody>
</table>

* Includes steel mill rolls, stainless, and other steels.
* Includes cutting and wear-resistant alloys.
* Includes diamond drill bit matrices, electrical contacts, and welding rods.
* Includes fluorescent powders and organic and inorganic pigments.

Resistance. Tungsten is the most practical material for this application.

Osmium has the highest optical emission up to 1927°C (3500°F) among all metallic materials, but tungsten can withstand higher temperature than osmium and thus gives more luminosity. In a vacuum lamp operating at 2141°C (3886°F), the tungsten filament has luminosity of 10 lumens/W; with a double-spiral filament in a gas filled lamp, the luminosity of tungsten is 20–30 lumens/W at 2907°C (5264°F). In contrast, carbon filament at 1847°C (3356°F) is rated at 3.2 lumens/W, and tantalum, about 6.3 lumens/W at 1977°C (3590°F) (Agte and Vacek, 1954).

At first sight, tungsten does not appear to be a good choice for use as an electron emitter, since there are many more electropositive metals whose emissions at a given temperature are considerably higher. The reason that tungsten is still practically the only material used in this field is due to its extraordinarily low vapor pressure. In commercial emitters where life is an important consideration, the criterion of
### Table 10.3. United States Consumption of Tungsten Intermediate Products by End Use, 1963–1968

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-speed</td>
<td>0.86</td>
<td>0.73</td>
<td>0.77</td>
<td>1.0</td>
<td>0.73</td>
<td>0.91</td>
</tr>
<tr>
<td>Hot-work and other tool</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.36</td>
<td>0.41</td>
<td>0.27</td>
</tr>
<tr>
<td>Alloy, other than tool&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.23</td>
<td>0.27</td>
<td>0.45</td>
<td>0.54</td>
<td>0.32</td>
<td>0.14</td>
</tr>
<tr>
<td>High-temperature nonferrous alloys&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.27</td>
<td>0.27</td>
<td>0.32</td>
<td>0.41</td>
<td>0.41</td>
<td>0.32</td>
</tr>
<tr>
<td>Other nonferrous alloys&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.32</td>
<td>0.27</td>
<td>0.27</td>
<td>0.18</td>
<td>0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>Tungsten metal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wire, rod, and sheet</td>
<td>0.59</td>
<td>0.68</td>
<td>0.91</td>
<td>1.14</td>
<td>0.77</td>
<td>0.91</td>
</tr>
<tr>
<td>Other</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Carbide (cemented or sintered)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Made from hydrogen-reduced powder</td>
<td></td>
<td></td>
<td></td>
<td>2.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Made from crystalline powder</td>
<td>1.0</td>
<td>1.41</td>
<td>1.91</td>
<td></td>
<td>2.1</td>
<td>2.32</td>
</tr>
<tr>
<td>Other carbidess&lt;sup&gt;d&lt;/sup&gt; (cast or fused)</td>
<td>0.5</td>
<td>0.27</td>
<td>0.36</td>
<td>0.5</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>Chemicals&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.05</td>
<td>0.09</td>
<td>0.05</td>
<td>0.09</td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td>Unspecified</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.64</td>
<td>0.32</td>
</tr>
<tr>
<td>Total</td>
<td>4.77</td>
<td>5.04</td>
<td>6.17</td>
<td>7.31</td>
<td>6.22</td>
<td>5.95</td>
</tr>
</tbody>
</table>


<sup>b</sup> Includes steel mill rolls, stainless, and other steels.

<sup>c</sup> Includes cutting and wear-resistant alloys.

<sup>d</sup> Includes diamond drill bit matrices, electrical contacts, and welding rods.

<sup>e</sup> Includes fluorescent powders and organic and inorganic pigments.

Usefulness is the ratio of emission to rate of evaporation rather than of emission alone. Furthermore, tungsten can be used at higher temperature than most other materials, and thus, the filament is kept reasonably free from gas contamination, which inhibits emission. In order to improve electron emission, thoriated tungsten is used in most cases, because higher emission is achieved due to the enhancement of the thorium coating on the surface of the filament (see Sec. 5.6.4). Tungsten is used for heater wires of the oxide-coated metal cathodes in electronic vacuum tubes. It is also used for grid wires in these vacuum tubes.

In vacuum, or under an inert or reducing atmosphere, tungsten is used as heating elements in the form of wire, as well as rod, strip, or tube, for high-temperature furnaces. Only at temperatures below 2000°C is molybdenum generally the preferred material for this application because of its electrical and mechanical properties and because of its lower cost than tungsten.
### Table 10.4. United States Consumption of Tungsten Intermediate Products by End Use, 1969–1976

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless and heat resistant alloy (excludes stainless and heat resistant)</td>
<td>0.157</td>
<td>0.114</td>
<td>0.085</td>
<td>0.079</td>
<td>0.096</td>
<td>0.117</td>
<td>0.075</td>
<td>0.057</td>
</tr>
<tr>
<td>Tool</td>
<td>0.886</td>
<td>0.672</td>
<td>0.645</td>
<td>0.658</td>
<td>0.917</td>
<td>0.931</td>
<td>0.382</td>
<td>0.485</td>
</tr>
<tr>
<td>Cast iron</td>
<td>—</td>
<td>0.0005</td>
<td>0.007</td>
<td>0.006</td>
<td>0.003</td>
<td>0.0005</td>
<td>—</td>
<td>0.0005</td>
</tr>
<tr>
<td>Superalloys</td>
<td>0.173</td>
<td>0.120</td>
<td>0.095</td>
<td>0.195</td>
<td>0.275</td>
<td>0.276</td>
<td>0.099</td>
<td>0.109</td>
</tr>
<tr>
<td>Cutting and wear/ resistant alloys</td>
<td>3.305</td>
<td>3.19</td>
<td>2.31</td>
<td>3.02</td>
<td>4.54</td>
<td>5.54</td>
<td>3.372</td>
<td>4.236</td>
</tr>
<tr>
<td>Other alloys</td>
<td>0.468</td>
<td>0.249</td>
<td>0.365</td>
<td>0.554</td>
<td>0.586</td>
<td>0.754</td>
<td>0.348</td>
<td>0.437</td>
</tr>
<tr>
<td>Mill products made from metal powder</td>
<td>1.317</td>
<td>1.50</td>
<td>0.926</td>
<td>1.15</td>
<td>1.21</td>
<td>1.21</td>
<td>0.679</td>
<td>1.090</td>
</tr>
<tr>
<td>Chemical and ceramic uses</td>
<td>0.184</td>
<td>—</td>
<td>0.173</td>
<td>0.081</td>
<td>0.202</td>
<td>0.072</td>
<td>0.130</td>
<td>0.316</td>
</tr>
<tr>
<td>Miscellaneous and unspecified</td>
<td>0.536</td>
<td>1.04</td>
<td>0.395</td>
<td>0.224</td>
<td>0.183</td>
<td>0.125</td>
<td>0.099</td>
<td>0.101</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>7.29</td>
<td>6.99</td>
<td>5.08</td>
<td>6.04</td>
<td>8.17</td>
<td>9.35</td>
<td>5.25</td>
<td>6.94</td>
</tr>
</tbody>
</table>


![Fig. 10.1. Tungsten lamp filament, single- and double-coiled. In this photograph, the wire sizes range from 13.2 μm to 1.22 mm in diameter, with their capacities ranging from 7.5 to 10,000 W. (Courtesy of General Electric Company, Cleveland, Ohio.)](image-url)
Fig. 10.2 A 1000-W incandescent lamp with the coiled tungsten filament mounted in position. (Courtesy of General Electric Company, Cleveland, Ohio.)

Fig. 10.3 Lamp and electronic components. In the upper left-hand corner are a complete electrode and its components for a Lucalox high-pressure sodium vapor lamp. Through the center is a coil for a traveling-wave tube, and beneath it, on the extreme left and right, are three fluorescent lamp electrodes. In the lower left center are three mercury lamp electrodes, and in the lower right center, against the black background are two $\text{Al}_2\text{O}_3$-coated television gun heaters. (Courtesy of General Electric Company, Cleveland, Ohio.)
10.2.2. Tungsten Rods

Tungsten rods are essentially used for lamp filament supports, glass-to-metal seals, electrical contacts, electrodes for arc lamps, and in welding and electric discharge machining (Fig. 10.5). Tungsten is used in glass-to-metal seals because its thermal expansion coefficient is very low and comparable with that of the glass. At low voltage and current applications, 54% Fe–29% Ni–17% Co alloy (Kovar) may be used as a substitute. The disadvantage of Kovar is that its thermal coefficient of expansion remains low only up to 450°C (842°F).

Tungsten is used for electrodes because of its resistance to arc erosion, welding, and pitting. In this area of application, thoriated and zirconiated tungsten rods are generally preferred. Thoriated tungsten carries 50% more current than pure tungsten; both thoriated and zirconiated tungsten start easier, give a more stable arc, and are less likely to spit tungsten into the deposit (see Sec. 5.6.4).

The general advantages for using tungsten as electric contacts are its adequate electrical conductivity, its high hardness, and its resistance to wear and arc erosion. The resistance to oxidation of tungsten is poor, but for some applications, particularly where the current load is not heavy, such as in the automotive ignition system, tungsten contacts are widely used. For other applications where higher conductivity and better oxidation resistance are required, silver- or copper-infiltrated tungsten is employed. This will be further discussed in Sec. 10.3.2.

Tungsten contacts are usually made by sawing swaged rod into thin slices. The
Fig. 10.5. Electrodes for d.c. xenon high-pressure arc lamps. The cathodes are typically made from thoriated tungsten and the anodes from pure tungsten. (Courtesy of General Electric Company, Cleveland, Ohio.)

polished contact face perpendicular to the direction of swaging gives better arc erosion resistance than that of other orientations. Tungsten is used for lamp filament supports because of its high strength at elevated temperatures.

10.2.3. Other Forms of Mill Products

In addition to tungsten wire and rod, tungsten in other forms is also used in various parts of vacuum tubes. For example, it is used in flexible parts of tubes, such as spring contacts, because of the elasticity of wrought tungsten to about 500°C. Tungsten is also used in x-ray and transmitter tubes as anodes of various shapes.

Fig. 10.6. Tungsten targets used in x-ray tubes. (Courtesy of General Electric Company, Cleveland, Ohio.)
(Fig. 10.6) because of its ability to withstand heavy current loads and its high atomic number.

In addition to heating elements, tungsten and molybdenum are also used in radiation shields for high-temperature furnaces. Tungsten, together with tungsten alloys and composites, is also used as a counterweight material for ailerons in airplanes and for helicopter propellers, as nozzle inserts for rockets, as control instrumentation components and gyroscope rotors for missiles, as semiconductor supports, as projectile cores, and as nuclear shielding material.

### 10.3. TUNGSTEN ALLOYS AND COMPOSITES AND TUNGSTEN-CONTAINING REFRACTORY ALLOYS

Tungsten-base alloys are generally developed to improve ductility or high-temperature strength of the metal and are used as substitutes for unalloyed tungsten in some applications in spaceship or nuclear industries. However, some new applications have emerged for some newly developed alloys with unusual properties.

Tungsten composites such as heavy alloys and metal infiltrated tungsten, have been developed for special industrial applications. Niobium and tantalum are alloyed with tungsten to improve the elevated-temperature strength of these metals for various applications. These will be discussed in the following sections.

#### 10.3.1. Tungsten Alloys

Tungsten–molybdenum alloys (see Sec. 8.2.1) are used as substitutes for unalloyed tungsten because of their improved mechanical properties. The family of tungsten–rhenium alloys has excellent low-temperature ductility and high-temperature strength. In addition to the high-temperature applications in space vehicles and tubing in nuclear reactors, these alloys are also used as thermocouples in vacuum or hydrogen furnaces and combustion chambers of turbine engines or reactors; electrical contacts, especially in high-humidity and corrosive environments; as lamp and electronic tube wires (see Sec. 8.2.2), and as x-ray targets. The commonly used thermocouples for elevated temperatures are of the compositions W/W–25 Re and W–3 Re/W–25 Re (Fig. 10.7).

#### 10.3.2. Tungsten Composites

Heavy alloys, also called heavy metals, are used as gyroscope rotors (Fig. 10.8) in inertial guidance systems and navigation equipment; as rim components of flywheels or rotating members in governors; as counterweights in static and dynamic balancing applications in airplanes and as actuators on the winding mechanism in self-winding watches, where space is limited; as shielding or capsule material for radioactive materials; as tool shanks, holders, and boring bars; as electrodes in the resistance welding of copper wire and rods; as backup disks for semiconductors; as tooling material for brass and aluminum die casting; as floats in
Fig. 10.7. Tungsten/tungsten–rhenium thermocouples made by capacitance discharge welding. The 0.127-mm (0.005-in.) couple on the left is insulated, but the 0.381-mm (0.015-in.) couple on the right is bare. (Courtesy of General Electric Company, Cleveland, Ohio.)

Fig. 10.8. Gyroscope rotors made of heavy alloys. (Courtesy of Teledyne Powder Alloys, Clifton, New Jersey.)

flow meters; and as projectile cores (see Sec. 8.5.1 for details).

Silver- or copper-infiltrated tungsten is used for electrical contacts, semiconductor supports (Fig. 10.9), and more recently, it has been applied as a major constructional material for rocket nozzles (Figs. 10.10 and 10.11).

10.3.3. Tungsten-Containing Refractory Alloys

Refractory metals such as niobium and tantalum possess good ductility but have poor tensile and creep strength at elevated temperatures as compared with tungsten. With addition of tungsten in these metals, elevated-temperature properties are improved. They are used as high-temperature gas turbine vanes, where the temperature is beyond the capability of superalloys; as rocket nozzles, flame shields, and other parts in space applications (Figs. 10.12 and 10.13); as x-ray targets in certain applications; and as chemical-resistant tubing or containers in very corrosive environments.
Fig. 10.9. Pressed and sintered tungsten disks are used as substrates for silicon diodes like the one at the bottom (a cut-away view) and for silicon control rectifiers like that at the top of the picture. (Courtesy of General Electric Company, Cleveland, Ohio.)

Fig. 10.10. Silver-infiltrated tungsten rocket valve body. (Courtesy of Teledyne Wah Chang Albany, Oregon.)
10.4. TUNGSTEN STEELS

Tungsten is an important alloying element in four types of tool steels — high-speed steel, hot-work steel, cold-work steel, and shock-resistant steel (Table 8.6). In addition, tungsten is also used in some stainless, heat-resistant, and magnet steels. These will be discussed in the following sections.
10.4.1. **High-Speed Steel**

The development of high-speed tool steel at the turn of the century spurred the advancement of modern machining technology. For the first quarter of the century, high-speed steel was the only cutting material (Figs. 10.14 and 10.15); later, cast alloys such as Stellite and tungsten carbides were developed. During World War II, tungsten carbides gradually became a more important cutting material than high-speed steel. At the same time, substitution of molybdenum for tungsten in high-speed steel occurred, and consumption of tungsten in this area of application was reduced to a place second to that for tungsten carbides.

On the other hand, the different cutting materials do not compete in all applications. For example, for soft metals such as low-carbon steels, high-speed steel tools may be used; while for alloy steels or superalloys of high hardness, tools of tungsten carbide are employed. For cutting a metal with a Brinnell hardness of 200, high-speed steel is used for speeds up to about 30.5 m/min (100 ft/min), and Stellite are used for speeds between 30.5 and 45.6 m/min (100 and 150 ft/min). In general, for single-point machine tools and forming tools, tungsten carbide is used; while for drills, taps, and reamers, high-speed steels are applied. This is because the drills, taps, and reamers generally do not attain high cutting speeds. As high-speed steels themselves can be machined and otherwise shaped more easily than other cutting materials, the steel is also used in making tools with complicated shapes. High-speed steels are used as threading tools, broaches, gear cutters, power tools, wood-working tools, and some long-run punches and dies.

10.4.2. **Other Tungsten Steels**

Hot-work steels are used extensively for extrusion dies, hot-drawing dies, shear blades, hot cutoff tools, gripper dies, forging dies, hot-heading punches, piercers, ball
Fig. 10.14. Various forms of high-speed steel cutting tools.

Fig. 10.15. Various forms of high-speed steel cutting tools.
dies, trimmer dies, or for other occasions where resistance to abrasion and shock is required.

Cold-work steels have longer lives and better nondeforming qualities than low-carbon steels. These steels are generally used for blanking, forming, coining, and trimming dies used in the cold-forming of metals, thread roller dies, bushings, cold-forming rolls, gauges, master tools, broaches, taps, etc.

A tungsten–chromium steel is one of the shock-resisting steels, used for heavy-duty shear blades, punches, and pneumatic tools such as chisels, rivet sets, rivet busters, and backing-out punches.

A few percent of tungsten is used in some heat-resisting and stainless steels. The tungsten addition imparts increased corrosion resistance, and strength at high temperatures, making these materials desirable for such applications as distilling tubes in oil refineries, turbine materials for aircraft, and engine exhaust valves.

Tungsten magnet steels once enjoyed wide acceptance, with a variety of such steels available (see Sec. 8.6.1), but they have now been largely replaced by alnico and other alloys.

10.5. HEAT- AND WEAR-RESISTANT ALLOYS

There are essentially two classes of alloys in this category. The first is the heat-resistant alloys, usually called superalloys, and the second is hard facing or wear-resistant alloys, known under the trade name Stellites and called cobalt–chromium–tungsten alloys.

10.5.1. Super alloys

Superalloys are generally classified into three types — nickel-base, iron-base, and cobalt-base. The most important applications of superalloys are gas turbine vanes and buckets for aircraft, marine vehicles, and stationary power units. They are also used in furnace combustion tubes, muffles, cracking and reformer tubes, and other high-temperature applications.

10.5.2. Hard-Facing and Wear-Resistant Alloys

These alloys are produced in the form of welding rod or powder atomized from a homogeneous melt and are readily weldable by gas or arc welding processes. They are widely used for valves, valve seats, bearings for screw conveyors, elevators, rock crushers, mixing equipment, marine propeller shafts, and automotive water or fuel pump shafts. Knives and blades for cutting cold or hot materials are frequently hardfaced with these alloys.

In addition to serving as hard facing material, the cobalt–chromium–tungsten alloys are used in the massive form. Since many of the commercial grades are not amenable to hot rolling or forging, they must be used as cast, and the shapes finished by grinding when necessary.

One of the principal uses of the cast materials is for metal-cutting tools (Fig.
10.12. Compared to high-speed steels, they are harder and more wear resistant but more costly. The cutting speed used for these cast alloys is between that for high-speed steel and that for tungsten carbides. They are also used for wear- and corrosion-resistant parts, as pump sleeves, valves, and valve seats, and as high-temperature tooling such as extrusion dies and mill guides. For more information, the reader is referred to the work by Centre d’Information du Cobalt (1960).

10.6. TUNGSTEN CARBIDES

In the industry, tungsten carbides are generally divided into two categories. The first and most important group is termed cemented tungsten carbide. These materials are in the form of WC, produced from hydrogen-reduced powder, cemented with cobalt as a binder, with or without other carbides (see Chapter 9). The cobalt content usually varies from 3 to 22%, depending on the toughness required for the specific applications. Increasing the cobalt content increases the toughness but decreases the hardness of the tooling material. The second group is called fused or cast carbide, because it is produced by a melting and casting technique derived from carbon-reduced powder. This cast material includes W₂C and a eutectic of WC and W₂C, which is harder but more brittle than the cemented carbide mentioned above.

10.6.1. Cemented Tungsten Carbide

The major usage of cemented carbide is in the cutting tool application, which includes turning, facing, milling, boring, reaming, threading, filing, broaching, shearing, and glass cutting. Cemented tungsten carbide was first marketed in 1926 under the trade name Widia. In the United States, Carboloy was the first

Fig. 10.16. Disposable tungsten carbide tool bits, with a clamping mechanism at right.
commercial product, appearing in 1928. Many improvements and modifications of the original compositions were made, particularly the addition of carbides of titanium, tantalum, and molybdenum and coating with TiC, TiN, Ti(C,N), HfN, Hf(C,N), and Al₂O₃. Modern carbide tools can cut materials of ordinary hardness at speeds up to 305 m/min (1000 ft/min). Consumption of carbide cutting tools was probably stimulated by the development of disposable carbide inserts, which appeared in 1954–1956 (Fig. 10.16). These inserts, instead of being brazed in position, are clamped or screwed into a steel shank and have a number of cutting edges. After each edge becomes dull, the insert is turned to another edge, and after all edges are used, the insert is recycled rather than reground.

Other large uses of cemented tungsten carbide include swaging dies, drawing dies, and other metal-deformation applications, such as cold heading and Sendzimir mill rolls. Tungsten carbide is also used exclusively in tooling for mining drills, which include oil well, coal mining, and tunnel boring applications. Since World War II, substantial amounts of tungsten carbide have been used in projectile cores for armor-piercing weapons.

10.6.2. Fused or Cast Carbide

This material is usually produced by melting a mixture of tungsten powder, graphite, and a considerable percentage of scrap tungsten carbide (see Chapter 9). The fused carbide, in the form of castings or crushed particles, as well as cemented carbide mentioned above, are used for wear-resistant applications such as spraying, injection, and blasting nozzles; as guide sleeves in machines; as thread guides in textile machinery; as micrometer anvils; in burnishing tools; as centers for lathes and grinders; as ball-point tips, Brinell balls, dies for extruding, swaging, and wire drawing; as teeth and jaws for excavators; and as rest pads and rollers.

Tire studs produced largely from recycled tungsten carbide and cased in metal or plastic sheaths are used for snow tires. These studs were introduced in Europe in 1960 and appeared on the United States market in 1963. Between 1964 and 1967, United States sales of tire studs increased from 32 to 435 million units, which means that about 6.6 million snow tires sold in 1967 were studded. By March 1968, only seven sunshine states prohibited studs (Burrows, 1971).

10.7. CHEMICAL USES

Tungsten bronze, tungstates of the alkali and alkaline earth metals, is used as a substitute for bronze in paints for ornamental purposes. Sodium tungstate is also used to produce phosphotungstic acid and phosphotungstomolybdic acid-type organic dyes and pigments, which are brilliant, light resistant, and insoluble in water and linseed oil. These pigments can be used in oil and water paints, printing inks, plastics, rubber, paper, waxes, etc. Calcium and magnesium tungstates are used as phosphors in fluorescent lights and television tubes.

Ammonium tungstate and other compounds, e.g., WO₃ or WS₂, are used as catalysts in the petroleum industry for hydro treating, hydrocracking, dehy-
drogenation, isomerization, polymerization, reforming, hydration, dehydration, hydroxylation, epoxidation, etc. W(CO)$_6$, WF$_6$, WCl$_6$, etc., are used for chemical vapor deposition to provide a hard acid-resistant tungsten coating on bearings, dies, rolls, gauges, etc. (see Sec. 4.4.6).

Tungsten selenide, WSe$_2$, is used as a dry lubricant employed under high temperature and high vacuum conditions. Wilkinson Sword Ltd. reportedly uses tungsten sulfide, WS$_2$, to form a self-lubricating surface on their razor blades (Tungsten News, 1967).
Industry and Future Outlook of Tungsten

11.1. INTRODUCTION

The resources or mines of tungsten are unevenly scattered throughout the world. Furthermore, with a few exceptions, most consumer countries rely essentially upon their ore supply from those countries who themselves consume tungsten very little.

For some applications of tungsten, such as high-speed steels, major substitutions may gradually emerge in the foreseeable future; and for still other applications, such as lamp filaments, no substitutes are in sight, and a steadily and gradually increasing trend can be predicted. Since the applications of tungsten have been discussed in detail in Chapter 10, this chapter will deal with the industrial structure, the potential substitutes, and the outlook for the future.

11.2. INDUSTRIAL STRUCTURE

11.2.1. Mining

The estimated world tungsten reserves and approximate annual production with consumption for specific countries are shown in Table 11.1. Some major world tungsten mines and their production have been shown in Table 1.2, and the production of some countries based on available data in recent years is shown in Table 11.2. The world production of tungsten is nearly divided between the West and East, as revealed in Table 11.2.

In early years, United States production attained high rates when the prices for tungsten concentrates were high. In 1955, specifically, a record high production of 7,170,000 kg (15,800,000 lb) of tungsten was produced due to the government procurement incentive program effected between 1950 and 1956. Some 740 mines and prospects were active with some 10 large mines operating. With the cessation of the government incentive program, followed by falling prices, the number declined rapidly to four major mines by December 1957 and two by mid-1958. In the period 1962–1972, domestic production provided about 60% of the required consumption. The remainder came from imports and from the government stockpile, as shown in Table 11.3.
### Table 11.1. World Tungsten Reserves, Annual Production, and Consumption

<table>
<thead>
<tr>
<th>Country</th>
<th>Estimated reserves(^b) (1,000,000 kg of contained tungsten)</th>
<th>Annual mine production(^c) (1,000,000 kg of contained tungsten)</th>
<th>Annual consumption(^b) (1,000,000 kg of contained tungsten)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>n.a.</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>Australia</td>
<td>34.5</td>
<td>1.36(^e)</td>
<td>0.05</td>
</tr>
<tr>
<td>Austria</td>
<td>_d</td>
<td>0.14</td>
<td>1.68</td>
</tr>
<tr>
<td>Bolivia</td>
<td>39.5</td>
<td>1.86</td>
<td>n.a.</td>
</tr>
<tr>
<td>Brazil</td>
<td>18.2</td>
<td>1.14</td>
<td>0.18</td>
</tr>
<tr>
<td>Burma</td>
<td>31.8</td>
<td>0.27</td>
<td>n.a.</td>
</tr>
<tr>
<td>Canada</td>
<td>216.4</td>
<td>1.59</td>
<td>0.23(^e)</td>
</tr>
<tr>
<td>China</td>
<td>955.0</td>
<td>8.00</td>
<td>0.64(^e)</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>n.a.</td>
<td>n.a.</td>
<td>1.36(^e)</td>
</tr>
<tr>
<td>France</td>
<td>_d</td>
<td>0.18</td>
<td>1.32</td>
</tr>
<tr>
<td>East Germany</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.36</td>
</tr>
<tr>
<td>West Germany</td>
<td>n.a.</td>
<td>n.a.</td>
<td>3.23</td>
</tr>
<tr>
<td>India</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.14</td>
</tr>
<tr>
<td>Japan</td>
<td>2.3</td>
<td>0.68</td>
<td>3.18</td>
</tr>
<tr>
<td>North Korea</td>
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<td>2.14(^e)</td>
<td>1.59(^e)</td>
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<td>1.91</td>
<td>n.a.</td>
</tr>
<tr>
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<td>0.14</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mexico</td>
<td>_d</td>
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<td>n.a.</td>
</tr>
<tr>
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<td>0.09</td>
<td>n.a.</td>
</tr>
<tr>
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<td>_d</td>
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</tr>
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<td>n.a.</td>
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<td>0.32</td>
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</tr>
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<td>n.a.</td>
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<td>n.a.</td>
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<td>0.14</td>
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<td>n.a.</td>
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<td>1.59</td>
<td>n.a.</td>
</tr>
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<td>n.a.</td>
<td>n.a.</td>
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<td>United States</td>
<td>108.2</td>
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<tr>
<td>U.S.S.R.</td>
<td>159.1</td>
<td>6.73(^e)</td>
<td>6.55(^e)</td>
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<tr>
<td>Others</td>
<td>111.0</td>
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<td>0.14</td>
</tr>
<tr>
<td>World total</td>
<td>1881.8</td>
<td>35.6</td>
<td>34.5</td>
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\(^b\) n.a., not available.
\(^c\) Approximate average of 4-year period.
\(^d\) Included in "Others" below.
\(^e\) Estimated.

The cost of imported concentrates is highly variable and relatively unaffected by domestic demand. European–Japanese consumption is approximately twice that of the United States, and almost all of their needs is from imports. The prices as published by the *London Metal Bulletin*, which represents the Western world market excluding the United States, compared with the prices published by *Metals Week* (New York) for the United States market are shown in Fig. 11.1.
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<td>(37.900)</td>
<td>(37.600)⁴</td>
<td>(37.200)⁴</td>
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<td>(11.052)</td>
<td>(10.263)⁴</td>
<td>(9.573)⁴</td>
<td>(10.263)</td>
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<td>(7.275)</td>
<td>(7.480)</td>
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<td>(9.650)</td>
<td>(10.150)⁴</td>
<td>(10.650)⁴</td>
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<td>(0.001)</td>
<td>(0.001)</td>
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<td>(0.109)</td>
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<td>(5.262)⁴</td>
<td>(5.149)⁴</td>
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<td>1.669</td>
<td>1.280</td>
<td>1.075</td>
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<td>(0.008)</td>
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<td>(8.000)</td>
<td>(8.500)</td>
<td>(8.980)</td>
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<td>(2.150)</td>
<td>(2.150)⁴</td>
<td>(2.150)⁴</td>
<td>(2.150)</td>
</tr>
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<td>Hong Kong</td>
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<td>(0.005)</td>
<td>(0.005)</td>
<td>(0.005)</td>
<td>(0.005)</td>
</tr>
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<td>0.017</td>
<td>0.015</td>
<td>0.025⁵</td>
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<td>Japan</td>
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<td>0.769</td>
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<td>0.125</td>
<td>0.013</td>
<td>0.106</td>
</tr>
<tr>
<td>Republic of Korea</td>
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<td>1.731</td>
<td>1.915</td>
<td>2.180</td>
<td>2.533</td>
</tr>
<tr>
<td>Thailand</td>
<td>2.533</td>
<td>3.343</td>
<td>2.602</td>
<td>2.204</td>
<td>1.773</td>
</tr>
<tr>
<td>Europe</td>
<td>(9.178)</td>
<td>(9.606)</td>
<td>(10.236)⁴</td>
<td>(10.280)</td>
<td>(10.726)</td>
</tr>
<tr>
<td>Austria</td>
<td>0.047</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>(0.075)</td>
<td>(0.075)</td>
<td>(0.080)</td>
<td>(0.080)</td>
<td>(0.080)</td>
</tr>
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<td>France</td>
<td>0.300</td>
<td>0.561</td>
<td>0.695</td>
<td>0.593</td>
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<td>Portugal</td>
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<td>1.403</td>
<td>1.502</td>
<td>1.478</td>
<td>1.467⁷</td>
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<td>Spain</td>
<td>0.407</td>
<td>0.362</td>
<td>0.312</td>
<td>0.347</td>
<td>0.351⁴</td>
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<td>Sweden</td>
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<td>—</td>
<td>0.234</td>
<td>0.166</td>
<td>0.151</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>0.005</td>
<td>(0.005)</td>
<td>0.015³</td>
<td>0.016</td>
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<tr>
<td>U.S.S.R.</td>
<td>(7.000)</td>
<td>(7.200)</td>
<td>(7.400)</td>
<td>(7.600)</td>
<td>(7.800)</td>
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<td>Netherlands (excluded from totals)</td>
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<td>0.194</td>
<td>0.289</td>
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<td>0.646</td>
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<td>1.529</td>
<td>1.239</td>
<td>1.125</td>
<td>1.533</td>
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<td>New Zealand</td>
<td>0.004</td>
<td>0.008</td>
<td>0.001</td>
<td>0.004</td>
<td>(0.005)</td>
</tr>
</tbody>
</table>


Symbols: Parentheses indicates estimated value, dash indicates nil or negligible.

³ Preliminary or provisional.

⁴ Revised.
11.2.2. Tungsten Products and Manufactures

The general processes through which intermediate and final products of tungsten are manufactured are shown schematically in Fig. 11.2. The two groups of ores — scheelite and wolframite — find slightly different applications. Scheelite may be added directly to the steel bath in the production of steel, or it may be used to produce ferrotungsten, which, in turn, is used as a part of the charge in steelmaking. Wolframite and scheelite can be processed into various intermediate chemical forms from which final products are made. The most important of these are sodium tungstate, and ammonium paratungstate.

Sodium tungstate is consumed in various chemical uses or is frequently processed into synthetic scheelite for charging in the steel bath. Ammonium paratungstate is a widely traded intermediate product and is used to make metallic tungsten powder by hydrogen or carbon reduction. Carbon-reduced powder is used in the production of high-temperature nonferrous alloys and of crushed cast carbide powder for wear-resistant applications. At one time, this powder was used in the production of steels by the crucible melting process. By World War II, however, most steels were being made in electric furnaces, which could utilize ferrotungsten. Hydrogen-reduced powder is used to produce tungsten carbide powder, mill products of metallic tungsten, tungsten alloys, and composites and refractory alloys that contain tungsten. The major companies and their product lines in the Western world are shown in Table 11.4.

11.2.3. Scrap Recycling

For completeness of discussion and overall material balance, the recycling of tungsten scrap should be also discussed. The quantity recycled to the United States domestic market represents approximately 20% of the total consumption. They can be divided into four categories — tungsten carbide, tungsten metal and alloys, tungsten steels, and sludges.
Fig. 11.1. Prices of tungsten concentrates, United Kingdom and United States (a metric ton unit equals 10 kg WO₃, and a short ton unit equals 20 lb WO₃) (UNCTAD, 1965–1975).
Fig. 11.2. Tungsten production processes and product applications.
Table 11.4. Major Companies and Their Product Lines in Some Western Countries

<table>
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<tr>
<th>Company</th>
<th>Ore</th>
<th>Concentrate</th>
<th>Sodium tungstate</th>
<th>H₂-reduced powder</th>
<th>C-reduced powder</th>
<th>Tungsten metal⁴</th>
<th>Ferrotungsten</th>
<th>WC powder</th>
<th>Final products containing:</th>
<th>WC</th>
<th>Tungsten⁵</th>
<th>WO₃</th>
<th>H₂WO₄</th>
<th>High-speed steel</th>
<th>Nonferrous alloys</th>
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<td></td>
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<td></td>
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<td>x</td>
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<td>Teledyne</td>
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<td>x</td>
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<td>Radium, Wippenfurth</td>
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</tr>
</tbody>
</table>

* Including Cleveland Wire and Carboloy.
⁴ Including light bulbs.
⁵ Wire, rod, and sheet.
Tungsten carbide scrap is obtained primarily from the tool users. In the early years, few users found it economical to recover brazed bits, but as a result of the development of clamped or "disposable" inserts for cutting tools in the mid 1950s, the recycling of used inserts is now feasible. One recycling process reduces the pieces to powder form of a few microns in particle size. Alternative methods involve chemical treatment to remove the binding materials, e.g., cobalt, and leave the tungsten carbide particles intact (see Sec. 2.8). The residual particles are washed and reduced in hydrogen or used as tungsten carbide powder. Estimates of the quantity of tungsten carbide scrap available in the market vary from 340,000 to 1,300,000 kg (750,000 to 2,800,000 lb) of tungsten per year in the United States (Charles River Associates, 1969).

Pure tungsten metal scrap is derived essentially from lamp filaments, alumina-coated wire, x-ray targets, and welding rods. These sources account for 140,000–270,000 kg (400,000–600,000 lb) of tungsten per year in the United States.

Tungsten steel scrap is recovered from machine shops and tool makers in the form of turnings, borings, and stock remnants, which can be added directly to the steel bath. It is estimated that this category amounts about 900,000 kg (2,000,000 lb) of steel containing 15% tungsten and 7,300,000 kg (16,000,000 lb) of steel containing 5% tungsten. Thus, the total estimated steel scrap amounts to 500,000 kg (1,100,000 lb) of contained tungsten in the United States.

Sludges and chemical forms of tungsten are recycled from spent catalysts, contaminated grinding sludges, etc. An estimated 70,000–90,000 kg (150,000–200,000 lb) of tungsten is recovered annually from such residues. Generally, the tungsten is regenerated as synthetic scheelite and treated as tungsten concentrate.

11.3. TUNGSTEN CONSUMPTION AND POTENTIAL SUBSTITUTES

The world tungsten consumption in recent years is shown in Table 11.5. The consumption in the United States, according to the product form is shown in Tables 10.2 and 10.3. It is apparent from these tables that although unalloyed tungsten consumption in the electrical and electronic applications is quite stable, the major market today still rests upon tungsten carbide, followed by tungsten steels in the second place.

Since the specific applications of various tungsten products have been discussed in detail in Chapter 10, only important consumption items and the potential substitutes will be elaborated in the following sections.

11.3.1. Unalloyed Tungsten

The major use for unalloyed tungsten is in wire form in electrical lamps and electronic vacuum tubes. Although the use of wire in electronic applications is declining as vacuum tubes are replaced to some extent by semiconductors, the steady growth of lamp applications is more than offsetting this decline. There is no known substitute for tungsten wire in this area.
## Table 11.5. World Consumption of Tungsten Ores and Concentrates

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<td>Actual consumption</td>
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</tr>
<tr>
<td>Australia</td>
<td>0.040</td>
<td>0.040</td>
<td>0.040</td>
<td>0.040</td>
</tr>
<tr>
<td>Austria</td>
<td>1.553</td>
<td>1.413</td>
<td>1.122</td>
<td>1.050</td>
</tr>
<tr>
<td>Czechoslovakia(^b)</td>
<td>1.318</td>
<td>1.364</td>
<td>1.364</td>
<td>1.318</td>
</tr>
<tr>
<td>France</td>
<td>1.121</td>
<td>1.243</td>
<td>1.752</td>
<td>1.853</td>
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<tr>
<td>Japan</td>
<td>2.081</td>
<td>2.331</td>
<td>3.614</td>
<td>3.030</td>
</tr>
<tr>
<td>Portugal</td>
<td>0.226</td>
<td>0.309</td>
<td>0.320</td>
<td>0.378</td>
</tr>
<tr>
<td>Sweden</td>
<td>1.467</td>
<td>1.382</td>
<td>1.465</td>
<td>1.723</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>2.190</td>
<td>3.275</td>
<td>3.608</td>
<td>3.708</td>
</tr>
<tr>
<td>United States</td>
<td>5.283</td>
<td>6.412</td>
<td>6.994</td>
<td>7.408</td>
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<tr>
<td>Apparent consumption, excluding stock variations(^d)</td>
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</tr>
<tr>
<td>Argentina</td>
<td>0.038</td>
<td>0.044</td>
<td>0.052</td>
<td>0.050</td>
</tr>
<tr>
<td>Belgium—Luxembourg</td>
<td>0.030</td>
<td>0.049</td>
<td>0.157</td>
<td>0.165</td>
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<tr>
<td>Brazil</td>
<td>0.210</td>
<td>0.225</td>
<td>0.255</td>
<td>0.236</td>
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<tr>
<td>Bulgaria</td>
<td>0.034</td>
<td>0.032</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>Canada(^b)</td>
<td>0.200</td>
<td>0.250</td>
<td>0.240</td>
<td>0.277</td>
</tr>
<tr>
<td>People's Republic of China(^e)</td>
<td>1.818</td>
<td>2.045</td>
<td>2.045</td>
<td>2.045</td>
</tr>
<tr>
<td>East Germany(^e)</td>
<td>0.341</td>
<td>0.318</td>
<td>0.295</td>
<td>0.273</td>
</tr>
<tr>
<td>West Germany</td>
<td>2.420</td>
<td>2.506</td>
<td>3.150</td>
<td>2.407</td>
</tr>
<tr>
<td>Hungary(^e)</td>
<td>0.023</td>
<td>0.023</td>
<td>0.023</td>
<td>0.023</td>
</tr>
<tr>
<td>India</td>
<td>0.187</td>
<td>0.192</td>
<td>0.151</td>
<td>0.175</td>
</tr>
<tr>
<td>Italy</td>
<td>0.057</td>
<td>0.047</td>
<td>0.090</td>
<td>0.075</td>
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<tr>
<td>North Korea(^e)</td>
<td>1.591</td>
<td>1.591</td>
<td>1.591</td>
<td>1.591</td>
</tr>
<tr>
<td>South Korea(^e,(^f))</td>
<td>—</td>
<td>—</td>
<td>0.250</td>
<td>0.636</td>
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<tr>
<td>Netherlands</td>
<td>0.279</td>
<td>0.719</td>
<td>0.896</td>
<td>1.735</td>
</tr>
<tr>
<td>Poland</td>
<td>1.762</td>
<td>1.815</td>
<td>2.340</td>
<td>1.695</td>
</tr>
<tr>
<td>Romania(^e)</td>
<td>0.014</td>
<td>0.014</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td>Republic of South Africa</td>
<td>0.265</td>
<td>0.361</td>
<td>0.260</td>
<td>0.362</td>
</tr>
<tr>
<td>Spain</td>
<td>0.092</td>
<td>0.129</td>
<td>0.130</td>
<td>0.125</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>31.097</td>
<td>34.810</td>
<td>38.975</td>
<td>39.008</td>
</tr>
</tbody>
</table>

\( ^b  \) Estimate.  
\( ^c  \) Revised.  
\( ^d  \) Production plus imports minus exports to obtain the estimated value.  
\( ^f  \) Data represents tungsten concentrates consumed to produce ammonium paratungstate at plant adjacent to Sang Dong Mine.

Other applications for unalloyed tungsten such as glass-metal sealing rods, cathode material, electrical contacts, and heating elements may be partially replaced by molybdenum, but molybdenum has its limitations, as already mentioned in the previous chapter. Furthermore, the cost of tungsten material is rather small as compared to the cost of fabrication to the final mill product form; and the cost of the final tungsten product is still a very small percentage of the cost of the device that
contains tungsten. The fluctuations of the price of tungsten is of little concern for the manufacturer, and a gradual growth in the applications in these areas can be expected.

Tungsten in still other applications, such as counterweights for aircrafts, may partially be substituted for by heavy alloys and depleted uranium; tungsten in rocket nozzles, semiconductor supports, and electrical contacts may be partially substituted for by silver- or copper-infiltrated tungsten.

11.3.2. Tungsten Alloys and Composites and Tungsten-Containing Refractory Alloys

Tungsten alloys are generally developed as substitutes for unalloyed tungsten with better low-temperature ductility or high-temperature strength. Furthermore, they extend the field of applications of tungsten. Tungsten–rhenium alloys have gained recognition as thermocouples, rotating anodes, in space vehicles and tubing for reactors, etc. However, the very high cost and the scarcity of rhenium prohibit the extensive application of these alloys.

A potential substitute in counterweights and balancing applications for heavy alloys is depleted uranium, which has comparable density. When nuclear power plants become more widely accepted in the industry, the depleted uranium will become more available for these applications.

With a combination of good conductivity and erosion resistance, silver- or copper-infiltrated tungsten is still the best material for electrical contacts without any possible substitutes in sight. Silver-infiltrated tungsten also enjoys its unique position for application in rocket nozzles because of the transpiration cooling behavior of the material (see Sec. 8.5.2).

As the aircraft and spaceship industry advances, higher temperatures are required for their engine parts, and, hence, there is a need for more refractory alloys, including molybdenum-, tantalum-, and niobium-base alloys. Tungsten additions to these alloys usually increase their tensile and creep strength at elevated temperatures. A steady and gradual increase in consumption of tungsten should be expected in this area.

11.3.3. Tungsten Steels

The substitution of tungsten carbide for tungsten high-speed steels has been taking place in machining applications, but gradually. This is partly due to the fact that the new cutting materials can only be used effectively at higher speeds, and hence, they have not been employed on the older equipment. A survey conducted by the American Machinist (1966) revealed that in 1963 about 64% of cutting machines used in the United States were 10 years old and 21% were over 20 years old. This substitution trend will probably continue, which means that the demand for tungsten high-speed steels still will grow with durable goods production, but at a lower rate than that of tungsten carbides.

The all-molybdenum high-speed steels, such as M1 and M10 (Table 11.6), have a slightly lower hot-hardness and wear-resistance than tungsten steels.
### Table 11.6. Compositions of Readily Available High-Speed Steels

<table>
<thead>
<tr>
<th>AISI²</th>
<th>W</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>18.00</td>
<td>0.70ᵃ</td>
<td>4.00</td>
<td>1.00</td>
<td>0.75</td>
<td>0.30</td>
<td>0.30</td>
<td></td>
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<tr>
<td>T2</td>
<td>18.00</td>
<td>0.60ᵃ</td>
<td>4.00</td>
<td>2.00</td>
<td>0.85</td>
<td>0.30</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td>18.50</td>
<td>0.70ᵃ</td>
<td>4.25</td>
<td>1.00</td>
<td>0.75</td>
<td>0.30</td>
<td>0.30</td>
<td>5.00</td>
</tr>
<tr>
<td>T5</td>
<td>18.50</td>
<td>0.80ᵃ</td>
<td>4.25</td>
<td>2.00</td>
<td>0.80</td>
<td>0.30</td>
<td>0.30</td>
<td>8.00</td>
</tr>
<tr>
<td>T6</td>
<td>19.50</td>
<td>0.70</td>
<td>4.25</td>
<td>1.80</td>
<td>0.80</td>
<td>0.30</td>
<td>0.30</td>
<td>12.00</td>
</tr>
<tr>
<td>T15</td>
<td>13.00</td>
<td>0.50ᵃ</td>
<td>4.50</td>
<td>5.00</td>
<td>1.55</td>
<td>0.30</td>
<td>0.30</td>
<td>5.00</td>
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<table>
<thead>
<tr>
<th></th>
<th>W</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
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</thead>
<tbody>
<tr>
<td>M1</td>
<td>1.50</td>
<td>8.50</td>
<td>4.00</td>
<td>1.00</td>
<td>0.80</td>
<td>0.30</td>
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<tr>
<td>M10</td>
<td>8.25</td>
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<td>4.00</td>
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<td>0.30</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>AISI</th>
<th>W</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>6.00</td>
<td>5.00</td>
<td>4.00</td>
<td>2.00</td>
<td>0.85</td>
<td>0.30</td>
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</tr>
<tr>
<td>M3a</td>
<td>6.00</td>
<td>6.00</td>
<td>4.00</td>
<td>2.50</td>
<td>1.05</td>
<td>0.30</td>
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<tr>
<td>M3b</td>
<td>6.00</td>
<td>6.00</td>
<td>4.00</td>
<td>3.00</td>
<td>1.15</td>
<td>0.30</td>
<td>0.30</td>
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</tr>
<tr>
<td>M4</td>
<td>6.00</td>
<td>6.00</td>
<td>4.50</td>
<td>4.00</td>
<td>1.30</td>
<td>0.30</td>
<td>0.30</td>
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</tr>
</tbody>
</table>

ᵃ Roberts et al., 1962.
ᵇ American Iron and Steel Institute classification.
ᶜ Optional.

Furthermore, molybdenum steels have a greater tendency to decarburize, requiring the use of special salt baths for heat treatment. On the other hand, the molybdenum steels are slightly tougher and considerably cheaper than tungsten steels. The consumer may also compromise by using such tungsten–molybdenum steels as M2, M3, and M4, the properties and prices of which fall in between those of the tungsten and the molybdenum high-speed steels.

The relative consumption of these high-speed steels in the period of 1945–1963 is shown in Table 11.7. In the future, the substitution of molybdenum for tungsten in high-speed steels may be expected to be sensitive to changes in the relative prices of tungsten and molybdenum and to changes in the availability of molybdenum. Other tool steels that contain tungsten probably will follow the same pattern as tungsten high-speed steels.

### 11.3.4. Heat- and Wear-Resistant Alloys

This category consists essentially of nickel- or cobalt-base alloys used for cutting tools and heat- and wear-resistant parts. Among these, superalloys used as gas turbine vanes and buckets probably will enjoy a faster growing rate than the others; cast alloys that are used as cutting tools probably will show little growth, due to their competition with tungsten carbides and tungsten high-speed steels.
Table 11.7. United States Consumption of High-Speed Steel, 1945–1963

<table>
<thead>
<tr>
<th>Year</th>
<th>Tungsten steels</th>
<th>Tungsten-molybdenum steels</th>
<th>Molybdenum steels</th>
<th>Total</th>
</tr>
</thead>
<tbody>
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<td>1945</td>
<td>13,660</td>
<td>8,104</td>
<td>1,026</td>
<td>22,791</td>
</tr>
<tr>
<td>1946</td>
<td>8,781</td>
<td>6,207</td>
<td>387</td>
<td>15,375</td>
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<tr>
<td>1947</td>
<td>10,325</td>
<td>4,754</td>
<td>304</td>
<td>15,383</td>
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<tr>
<td>1948</td>
<td>8,596</td>
<td>6,870</td>
<td>680</td>
<td>16,146</td>
</tr>
<tr>
<td>1949</td>
<td>4,833</td>
<td>3,125</td>
<td>164</td>
<td>8,122</td>
</tr>
<tr>
<td>1950</td>
<td>7,632</td>
<td>7,716</td>
<td>928</td>
<td>16,276</td>
</tr>
<tr>
<td>1951</td>
<td>6,808</td>
<td>15,441</td>
<td>2,326</td>
<td>24,501</td>
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<tr>
<td>1952</td>
<td>2,379</td>
<td>15,465</td>
<td>2,573</td>
<td>20,417</td>
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<tr>
<td>1953</td>
<td>3,124</td>
<td>15,837</td>
<td>3,389</td>
<td>22,349</td>
</tr>
<tr>
<td>1954</td>
<td>2,309</td>
<td>9,415</td>
<td>2,264</td>
<td>13,988</td>
</tr>
<tr>
<td>1955</td>
<td>3,041</td>
<td>15,928</td>
<td>3,723</td>
<td>22,692</td>
</tr>
<tr>
<td>1956</td>
<td>3,285</td>
<td>15,822</td>
<td>2,948</td>
<td>22,056</td>
</tr>
<tr>
<td>1957</td>
<td>2,537</td>
<td>13,144</td>
<td>3,013</td>
<td>18,694</td>
</tr>
<tr>
<td>1958</td>
<td>1,575</td>
<td>5,317</td>
<td>3,797</td>
<td>10,694</td>
</tr>
<tr>
<td>1959</td>
<td>2,119</td>
<td>8,646</td>
<td>7,597</td>
<td>18,365</td>
</tr>
<tr>
<td>1960</td>
<td>1,736</td>
<td>6,793</td>
<td>6,453</td>
<td>14,982</td>
</tr>
<tr>
<td>1961</td>
<td>1,534</td>
<td>6,860</td>
<td>5,679</td>
<td>14,118</td>
</tr>
<tr>
<td>1962</td>
<td>1,684</td>
<td>8,502</td>
<td>7,818</td>
<td>18,004</td>
</tr>
<tr>
<td>1963</td>
<td>1,745</td>
<td>8,169</td>
<td>7,635</td>
<td>17,550</td>
</tr>
</tbody>
</table>


11.3.5. Tungsten Carbides

For cutting tools, and wear-resistant applications, a number of new materials have been developed, but at the present time, none of these has supplanted tungsten carbides in any volume. Only TiC, TaC, MoC, and aluminum oxide ceramics have gained some market acceptance.

The first aluminum oxide cutting tool materials were produced in Germany in 1930–1940 and in Russia in 1948–1951 (Kieffer and Ettmayer, 1974) and were then introduced in the United States in 1955. These ceramics may be substituted for tungsten carbides in applications involving machining with high speeds and light cuts. However, for heavy cuts or in mining applications, the ceramics are too brittle and insufficient in toughness.

Compared with tungsten carbides, titanium carbide can be produced at a relatively low cost and cemented with molybdenum and nickel to become a strong tool material. In emergencies, titanium carbide could be substituted for most cutting tool applications but would give poorer performance in some cases. Even in the absence of an emergency, 20–40% of the tungsten carbide tools could be substituted on an economic basis. On the other hand, coating of tungsten carbide tools with titanium carbide or nitride has gained wide acceptance in the industry. These cutting tools may eventually become dominant in the tool market.

Only recently, it has been discovered that hexagonal molybdenum monocarbide can be stabilized up to 1200°C and can be used with tungsten carbide in all
proportions in tool applications (Kieffer, 1976; Rudy, 1976). The substitution of molybdenum for tungsten in this area may be expected to be sensitive to changes in the relative prices of tungsten and molybdenum as mentioned for high-speed steel applications.

The abrasion resistance of cemented TiC is not equivalent to that of tungsten carbide; the former could be used in an emergency in some wear- and abrasion-

<p>| Table 11.8. United States Estimated Tungsten Contained in Products and Demand, All Categories* |
|--------------------------------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Product category</th>
<th>Average growth rate (%) increase per year</th>
<th>Amount of contained tungsten (10^6 kg)</th>
<th>1972</th>
<th>1977</th>
<th>1982</th>
<th>1987</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1972–1987</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cemented tungsten carbide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cutting tools</td>
<td>8.2</td>
<td>1.18</td>
<td>1.82</td>
<td>2.63</td>
<td>3.86</td>
<td></td>
</tr>
<tr>
<td>Wear parts</td>
<td>8.9</td>
<td>0.45</td>
<td>0.91</td>
<td>1.27</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>Mining tools</td>
<td>6.5</td>
<td>0.77</td>
<td>1.04</td>
<td>1.73</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>Tire studs</td>
<td>4.7</td>
<td>0.09</td>
<td>0.14</td>
<td>0.18</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Armor-piercing projectiles</td>
<td>1.5</td>
<td>0.18</td>
<td>0.23</td>
<td>0.23</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>12.7</td>
<td>0.045</td>
<td>0.09</td>
<td>0.18</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7.6</td>
<td>2.72</td>
<td>4.23</td>
<td>6.22</td>
<td>8.17</td>
<td></td>
</tr>
<tr>
<td>Cast tungsten carbide, W2C</td>
<td>0.3</td>
<td>0.45</td>
<td>0.64</td>
<td>0.86</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless</td>
<td>5.0</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Tool</td>
<td>2.5</td>
<td>1.40</td>
<td>1.78</td>
<td>1.57</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.42</td>
<td>1.82</td>
<td>1.60</td>
<td>2.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast alloys and superalloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard-facing alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard-facing rod</td>
<td>4.0</td>
<td>0.09</td>
<td>0.10</td>
<td>0.12</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Spray-welding powder</td>
<td>4.0</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Cast alloys</td>
<td>1.5</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Superalloys</td>
<td>10.0a</td>
<td>0.55</td>
<td>0.66</td>
<td>1.06</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>Heat-resisting alloys</td>
<td>5.5</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Highly corrosion-resisting alloys</td>
<td>2.0</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.76</td>
<td>0.90</td>
<td>1.34</td>
<td>2.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tungsten mill products</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wire, rod, plate, and sheet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(electrical and electronic)</td>
<td>4.7</td>
<td>0.59</td>
<td>0.77</td>
<td>0.95</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Heavy alloys (tungsten composites)</td>
<td>2.3</td>
<td>0.23</td>
<td>0.25</td>
<td>0.30</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Electrical contacts (infiltrated tungsten)</td>
<td>5.2</td>
<td>0.16</td>
<td>0.20</td>
<td>0.27</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Other (pressed and sintered)</td>
<td>2.5</td>
<td>0.23</td>
<td>0.26</td>
<td>0.29</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.21</td>
<td>1.48</td>
<td>1.81</td>
<td>2.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical uses</td>
<td>7.0</td>
<td>0.32</td>
<td>0.45</td>
<td>0.63</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Grand total contained tungsten</td>
<td>6.0</td>
<td>6.88</td>
<td>9.52</td>
<td>12.46</td>
<td>16.45</td>
<td></td>
</tr>
<tr>
<td>Process loss (% of total demand)</td>
<td>0.52</td>
<td>0.70</td>
<td>0.95</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total demand</td>
<td>6.0</td>
<td>7.40</td>
<td>10.29</td>
<td>13.41</td>
<td>17.68</td>
<td></td>
</tr>
</tbody>
</table>


resistant applications if tungsten or cobalt became scarce, but TiC is not a feasible substitute for tungsten carbides in mining applications. Diamonds are occasionally used as cutting tools, especially for applications in which a perfect finish is necessary at any cost. However, the cost and brittleness of diamonds preclude their use for substitution of tungsten carbides in heavy cutting.

The principle substitute materials for tungsten carbides in drawing dies are diamonds and tool steels. The use of tungsten carbides in this application may be quite sensitive to the price of tungsten. Wrought depleted uranium alloys, when they are abundantly available, are possible alternatives to tungsten carbides for projectile core applications.

11.3.6. Chemical Uses

The major established and steady chemical uses of tungsten without possible substitutes are in dyes, phosphors, reagents, and corrosion inhibitors. The use of tungsten chemicals for catalysts and chemical vapor deposition is probably unpredictable.

11.4. FUTURE OUTLOOK

The trend of applications of tungsten products and their potential substitutes have already been discussed under specific subsections of Sec. 11.3. According to the National Materials Advisory Board (1973), the estimated tungsten consumption in the United States for the period 1972–1987 is shown in Table 11.8. The overall future for tungsten is summarized as follows:

The greatest application of all forms of tungsten products is for cutting tools. The growth in consumption of tungsten-containing cutting tools should be at approximately the same rate as that of durable goods production. During the last decade, some new materials and techniques have been developed for machining, and tungsten may lose part of its cutting tool market.

Other important applications for tungsten are in its unalloyed form used in electrical and electronic devices, and in nonferrous alloys used in heat- and wear-resistant parts. Consumption of these products are expected to closely relate to the production of electrical machinery and durable goods.

With the exception of some minor applications, such as tire studs, there is no evidence of important new applications being developed in recent years. It appears that demand for tungsten as a whole will be fairly closely related to the general economic growth. For a detailed analysis of the industry and quantitative calculations of the market, including the past and the future, the reader is referred to the recent work of Burrows (1971).
Appendix I

Metallographic Preparation of Tungsten, Its Alloys, and Tungsten Carbides

1.1. METALLOGRAPHIC PREPARATION FOR OPTICAL MICROSCOPIC EXAMINATION

1.1.1. Sectioning and Mounting

Sectioning or cutting of massive tungsten, its alloys, and tungsten carbides is generally performed on a cut-off wheel. The selection and operation of the cut-off wheels have been described in Sec. 5.11.2. Improper operation during cutting may result in microcracks, called heat checks, in the specimen.

Large sizes of specimen such as plate, bar, rod, or wire not less than 0.1 mm in diameter can conveniently be mounted in any good thermosetting phenolic molding material such as Bakelite. Finer wires, coils, and powder also may be mounted using either Bakelite or Formvar, Type 95/E, in the powder form. Other methods used for mounting fine specimens are (1) to embed the specimen in fused glass (Smithells, 1953), and (2) to prepare the specimen by sintering tungsten with copper powder (Schröter, 1931).

1.1.2. Grinding

Grinding of the mounted specimen can be performed either on a diamond wheel or using the conventional belt-and-sand method. The former may be especially suitable for cemented tungsten carbide. Diamond wheels used for rough grinding are usually of 120 grit and those for finer grinding, 15 μm. The conventional belt-and-sand method consists of the following three steps: (1) coarse grinding on wet, 120- or 180-grit SiC belt; (2) intermediate grinding on numbers 1 and 2 SiC paper; (3) fine grinding on numbers 0, 00, 000 emery paper, or on 240-, 400-, and 600-grit wet or dry metallographic disks.

Coarse grinding establishes a plane surface and removes the heat-affected zone and cold-working effects of sectioning. Wet grinding prevents the specimen from heating and washes off the debris and abrasive particles from the belt. Intermediate and fine grinding are necessary to eliminate any cold-working effects of the coarse grinding and to produce a smoother surface.
During grinding, the direction of grinding is changed 90° between the use of each grit size to insure the complete elimination of the previous grinding marks. A still finer grinding is recommended by some. This operation involves a slurry of loose 600-grit SiC–water mixture, which is placed on a polishing wheel covered with either canvas or silk cloth, rotating at a speed of 500 rpm.

1.1.3. Polishing

There are alternatives of methods of polishing as follows.

1.1.3.1. Chemical–Mechanical Method

In this method, the specimen is polished in two steps — rough and final polishing. Rough polishing is carried out on a high-speed (1150–1750 rpm), 4-in. (102-mm) wheel covered with Buehler Metcloth and silk cloth using a slurry of 8–10 g Linde A alumina (0.3 μm), 10 ml 20% chromic acid, and 150 ml water. During polishing, the specimen should be etched intermittently to remove scratches and flowed metal. However, it should be in the unetched condition before final polishing. The etching solution will be discussed in Sec. 1.1.4.

Final polishing is performed on a slow-speed (250–550 rpm), 8-in. (204-mm) wheel with Buehler Metcloth lapping; 0.5 g Linde B alumina (0.05 μm) is placed on the lap and moistened with a solution consisting of 3.5 g K₃Fe(CN)₆, 0.2–0.3 g NaOH, and 150 ml water.

Newton and Olson (1968) claimed that for single-crystal tungsten, better results were obtained by using a solution of 1 part NH₄OH, 1 part 30% H₂O₂, and 1 part H₂O with 1 μm alumina abrasive placed on a polishing wheel covered with a polyethylene lap that has a kitten-ear broadcloth covering. A finer abrasive, 0.05 μm alumina, may be used for final polishing if necessary. With polycrystals of tungsten, a dilute solution, 2 parts H₂O, 1 part NH₄OH and 1 part H₂O₂, may be used to prevent grain boundary etching.

1.1.3.2. Electromechanical Method

There are also two steps involved in this method. Rough polishing is performed on a high-speed, e.g., 1150 rpm, 4-in. (102-mm) wheel, with a slurry of 8–10 g Linde A alumina (0.3 μm), 5 g K₃Fe(CN)₆, and 150 ml water. During polishing, 20–25 V d.c. is applied between the specimen (anode) and the lapping wheel (cathode). The degree of etching varies with the pressure applied during polishing. The rough polishing operation should be finished with light pressure in order to minimize the extent of etching.

In final polishing, a slow-speed, e.g., 550 rpm, 8-in. (204-mm) wheel with Buehler Microcloth lapping may be used. The paste is made by placing 0.5 g Linde B alumina (0.05 μm) on the lap, which is lightly moistened with a solution of 3.5 g K₃Fe(CN)₆, 0.2–0.3 g NaOH, and 150 ml water. The specimen is polished on the final lap for not more than 5 sec with light pressure.
I.1.3.3. Mechanical Method

The grinding process prior to this method of polishing is generally performed on a diamond wheel as mentioned in Sec. I.1.2. The polishing is usually carried out in two steps. In the first step, the operation is executed on a slow-speed wheel with a nylon cloth covering using a paste of diamond dust (2.5–6 μm) and oil of lavender. For the final polishing, a finer diamond dust (0–2 μm) is used.

For best observation, especially for cemented tungsten carbide, a differential interference contrast microscope can be used. In this case, no etching agent is required and an uneven attack at grain boundaries or inclusions is avoided.

I.1.3.4. Electropolishing Method

The electrolytes commonly used with descriptions of current or voltage applied in each case are as follows: (1) 93.75 vol % methanol, 1.25 vol % HF, and 5 vol % H₃SO₄; 15–20 V for 15–20 sec; (2) 25 ml H₂SO₄ and 175 ml CH₃OH; 4 A/in.² (0.62 A/cm²) for 15–30 sec; (3) 60 ml perchloric acid, 350 ml butyl Cellosolve (2-butoxyethanol), and 590 ml methanol; 15–20 V for 15–20 sec; (4) 100 g NaOH and 1000 ml water; 0.03–0.06 A/cm² at 6 V and 20°C for 20–30 min.

I.1.4. Etching

Etching agents are applied during polishing, as for chemical–mechanical polishing described in Sec. I.1.3, or after polishing in order to reveal the grain structure and details of the specimen for microscopic observation. The only method of polishing without the aid of etching is the mechanical process as mentioned above. Different etching solutions may be used for specific conditions. Those commonly used are: (1) A solution of 5 parts HNO₃, 5 parts HF, and 15 parts lactic acid; (2) a solution of 10 gm K₃Fe(CN)₆, 10 g KOH or NaOH, and 100 ml water; (Murakami’s reagent).

The etching solutions mentioned above can be diluted by adding larger amounts of water and smaller amounts of HF in solution (1), or alkali in solution (2). Etching reagents are generally applied by swabbing for 5–10 sec. If stain etching is desired, immersion can also be used. After etching, the specimen should be rinsed in water, then alcohol, and air dried.

I.2. METALLOGRAPHIC PREPARATION FOR ELECTRON MICROSCOPIC EXAMINATION

Specimen preparation for scanning electron microscope examination and replica preparation for transmission electron microscope examination for tungsten, its alloys, and tungsten carbides are not different from those for other metals and specimens. The reader is referred to the textbooks on these subjects, e.g., the work by Thomas (1962).
However, the preparation of thin foil specimens for transmission electron microscope examination for tungsten are somewhat different in details, and will be discussed below. As a rule, the bulk sample of tungsten is sectioned or sliced on an ordinary or diamond-impregnated copper cut-off wheel and then ground to a thickness of 0.254 mm (0.010 in.). This is further thinned by chemical etching, ion bombardment, or electropolishing.

The reagents used for chemical etching have been described in Sec. I.1.4. The ion bombardment process has been described by Thomas (1962). However, these two methods are usually slow and tedious. The electropolishing techniques have been found to be the most convenient and successful way of finally thinning specimens.

The general methods used in electropolishing include the window method (Thomas, 1962) and jet polishing (DuBose and Stiegler, 1967). In the jet polishing method, specimens are cut to a thickness of about 0.51 mm (0.020 in.) with a maximum diameter of 3.18 mm (0.125 in.). These are then “dimpled” on both sides by the electrolytic jet technique to reduce the center of the specimen to about 0.051 mm (0.002 in.). The shape of the dimple bottom can be controlled by varying the current density. Under appropriate conditions, large, flat-bottomed dimples can be obtained. Final polishing is accomplished in a standard electrolytic polishing cell in which breakthrough in the dimpled region is detected by a photocell device. Incident light is piped to the specimen and the light transmitted through the hole is delivered to the photocell by a fiber optics system. Activation of the photocell stops the polishing action in the final step.

The electrolyte used for jet as well as cell polishing contains 32 g Na₃PO₄ and 250 ml water, with a current density of 16 mA/mm² at 400 V for the jet and 2 mA/mm² at 12 V for the cell polishing. The operation is carried out at room temperature, and the removal rate in the jet polishing step is about 0.025 mm/min (0.001 in./min).
Appendix II

Analytical Chemistry of Tungsten

In this appendix, only those procedures more generally employed and proven to be successful for analyzing tungsten ores and tungsten-containing materials are described in some detail. For others and alternatives, the reader is referred to the literature (for a review, see Wuensch, 1977).

II.1. DETECTION OF TUNGSTEN

II.1.1. Reduction of Tungsten Oxide

When an ore of tungsten is heated with aqua regia, lemon yellow tungstic acid is obtained. When tungstic acid is treated with hydrochloric acid and zinc, aluminum, or tin, it turns a beautiful blue color because of its reduction to the intermediate oxide (see Sec. 7.1.1.).

II.1.2. Preparation of Ore for Detection of Tungsten

Mix the pulverized ore with several times its volume of sodium carbonate add a little water to make a paste, and fuse in a loop of platinum wire. Pulverize the bead and dissolve in a little water. The presence of tungsten in the solution may be detected by the following sensitive tests.

II.1.2.1. Spot-Test Paper

On spot-test paper, add one drop of concentrated hydrochloric acid, one drop of the solution in the center of the moist area, one drop of 2 N potassium thiocyanate solution, and one drop of 1 N stannous chloride in concentrated hydrochloric acid. When tungsten is present, the middle of the moist spot turns greenish blue (Li and Wang, 1955).

II.1.2.2. Precipitation Reaction

To a drop of the solution in a micro-test tube, add a drop of diphenylene
Table II.1. Most Sensitive Emission Lines of Tungsten

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>Excitation potential (V)</th>
<th>Relative intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Arc</td>
</tr>
<tr>
<td>4302.108</td>
<td>3.2</td>
<td>60</td>
</tr>
<tr>
<td>4294.614</td>
<td>3.2</td>
<td>50</td>
</tr>
<tr>
<td>4008.753</td>
<td>3.4</td>
<td>45</td>
</tr>
<tr>
<td>3613.790</td>
<td>&gt;9.2</td>
<td>10</td>
</tr>
<tr>
<td>3215.560</td>
<td>5.3</td>
<td>10</td>
</tr>
<tr>
<td>2589.167</td>
<td>&gt;10.6</td>
<td>15 (double line)</td>
</tr>
<tr>
<td>2397.091</td>
<td>&gt;10.9</td>
<td>18</td>
</tr>
<tr>
<td>2944.395</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2946.981</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

hydrochloride. The presence of tungsten is indicated by precipitation or cloudiness in the tube (Li and Wang, 1955).

II.1.3. Emission Spectroscopy

The identification and analysis of tungsten can be accomplished by emission spectroscopy. The most sensitive lines are listed in Table II.1 (Harrison, 1939).

II.1.4. Atomic Absorption

In atomic absorption, a sensitivity of about 11 µg/ml for 1% absorption has been reported using the 255.1 nm (nanometer) line. For this and other lines with corresponding sensitivities, the reader is referred to Perkin-Elmer (1973).

II.2. DETERMINATION OF TUNGSTEN

In the determination of tungsten, the type of sample and the level of accuracy and precision needed will dictate the procedure used. For instance ores and mill tailings with low concentrations of tungsten usually call for a spectrophotometric or equally sensitive method of determination, while a gravimetric procedure is preferred for tungsten concentrates.

II.2.1. Gravimetric Procedures

Gravimetric procedures are generally used for samples containing 5% or more tungsten. Several reagents have been proposed and are used, and procedures mostly involve the precipitation of tungsten with final weighing as the trioxide. Among these are cinchonine (Furman, 1962; Li and Wang, 1955), α-benzoinoxime (Knowles, 1932), tannic acid–antipyrene (Peterson and Anderson 1943), and N-benzol-N-phenylhydroxylamine (Kaimal and Shome, 1964). Cinchonine is the most widely
used reagent and gives very reliable results when the procedure is performed carefully. Tungsten is determined as WO₃ in a range of approximately 0.5 to > 90%.

**Cinchonine Procedure**

The following describes the most commonly used gravimetric procedure for determination of tungsten:

Weigh 0.5 to 2 g (depending on the tungsten content) of the finely ground material, at least 200 mesh, into a 400-ml beaker. Moisten the sample with 5 ml water and add 100 ml HCl. Cover the beaker and digest on a low- to medium-heat hot plate for at least 1 hr. Stir from time to time with a glass rod to prevent crust formation. Remove watch glass and evaporate on down to about 50 ml. Add 40 ml HCl and 15 ml HNO₃ and evaporate to approximately 15 ml. Add water to 150 ml, boil for a few minutes, and let stand for several hours, preferably over night.

Filter and wash with HCl (1:9). To the filtrate add 2 ml cinchonine solution (12.5 g cinchonine dissolved in 100 ml 6 N HCl), stir and reserve as precipitate one. Wash the residue on the filter back into the original beaker, using about 25–50 ml water. Add 5 ml NH₄OH, cover, and heat gently until all the yellow tungstic acid is dissolved. Filter while hot through the original filter, receiving the filtrate in a clean 400-ml beaker. Wash with a hot solution of NH₄OH (1:9). Partially cover the beaker with the filtrate in it, and boil to remove excess ammonia. Volume should be reduced to about 25 ml. Dilute to 300 ml with hot water, add 2 ml HCl and 8 ml of cinchonine solution, stirring vigorously to coagulate the precipitate. Reserve as precipitate two.

Ignite the residue from the last filtration in a platinum dish at 750°C. Transfer ash to a zirconium crucible and mix with five to six times its weight of Na₂O₂ and fuse. Cool and leach cake in a 250-ml beaker with hot water. Boil to dissolve the fused mass, and then after settling, filter into a 400-ml beaker. Wash with a dilute Na₂CO₃ solution and discard the residue. To the filtrate add 5 ml HCl in excess and boil to expel gases. Add 4 ml cinchonine solution, stir, and reserve as precipitate three.

Filter precipitates one, two, and three onto a filter paper containing some pulp. Wash beaker and filter with cinchonine wash solution and wipe inside of beaker with a rubber policeman to recover any adhering precipitate. Finally, wash the filter once with cold water. Transfer the filter with precipitate to a previously ignited (750°C) and weighed platinum dish.

Dry on a hot plate then in a muffle furnace at 300°C. After paper has charred, transfer to a 750°C muffle furnace and ignite for 1.5–1.75 hr with the muffle door slightly open, so that air for oxidation can enter. Cool, add enough HF to wet the WO₃, some HNO₃ to assure complete oxidation, and one drop of H₂SO₄. Evaporate to dryness on hot plate, expel residual H₂SO₄ by heating in a muffle at 300°C, and finally, ignite at 750°C again for approximately 15 min. Cool in desiccator and weigh. Weight difference is WO₃.

If the sample being analyzed contains molybdenum, its level should be determined as MoO₃ and deducted from the weight of the WO₃.

**II.2.2. Spectrophotometric Procedures**

Low levels of tungsten can be accurately determined by spectrophotometric techniques in a variety of samples, with thiocyanate and dithiol being the most popular reagents. Methods utilizing various reagents including the two mentioned for ores and other types of samples are well described (Furman, 1962; Snell and Snell, 1957; Sandell, 1959), with the preparation and separation procedures included.

A method using thiocyanate for analyzing tungsten ores claims to be good between 0.0003% and 1.5% tungsten in the presence of up to 10% arsenic, 3%
antimony, 0.5% molybdenum, 0.3% chromium, and up to 0.1% each of vanadium, selenium, and tellurium (Busev et al., 1970). Another method using thiocyanate is good to as low as 2.1 mg tungsten with an average error of ±0.3 mg. A complete review of the use of thiocyanate is available (Fogg et al., 1970) along with specific methods such as for tungsten in natural water and seawater (Polydovskaya, 1967) and others (Cronthamel and Johnson, 1954; Babko and Drako, 1957; Hiroshi, 1955).

3,4-Dimercaptotoluene (dithiol) as a colorimetric reagent was used to do a geochemical field survey for determining tungsten in soils, sediments, and rocks (Bowden, 1964; Stanton, 1970) and for the determination of molybdenum and tungsten good to about 10–80 mg of molybdenum and 10–100 mg of tungsten. The blue–green molybdenum complex is extracted with chloroform and read at 680 nm, while the tungsten complex is extracted and read at 640 nm.

**Dithiol Procedure**

This method covers the determination of 10–80 mg of molybdenum and 10–100 mg of tungsten in ores, oxides, and residues. Sample size is adjusted to maintain Mo and W concentrations in the above ranges.

**A. Reagents Required**

Ammonium bisulfate solution: Dissolve 300 g of ammonium bisulfate in one liter of 36 N sulfuric acid (concentrated).

Dithiol (3,4-dimercaptotoluene): Dissolve 20 g sodium hydroxide in 500 ml water. Liquify 5 g 3,4-dimercaptotoluene by running warm water over the vial. Break the neck of the vial, quickly add the contents to the beaker, and stir to effect dissolution. Add 10 ml mercaptoacetic (thioglycolic) acid. Dilute to 1 liter with water and store in a refrigerator. The reagent is stable for at least 1 month.

Molybdenum standard 10 mg/ml: Dissolve 1.000 g molybdenum powder in 10 ml 12 N hydrofluoric acid; add dropwise 16 N nitric acid. Dilute to 1 liter. Dilute a 10-ml portion of this solution to 1 liter.

Titanium(III) chloride stock solution: Weigh 32 g titanium metal into a 4-liter beaker and add 2680 ml of hydrochloric acid. Cover and place on a low-heat hot plate until all reaction ceases. Cool and transfer to a suitable storage bottle. Store in a coldbath.

Titanium(III) chloride working solution: Dilute 670 ml of the stock solution to 1 liter with water. Store in a coldbath.

Tungsten standard, 10 mg/ml: Dissolve 0.1794 g sodium tungstate dihydrate (Na₂WO₄·2H₂O) in 1 liter of water. Dilute a 50 ml portion of this solution to 500 ml.

**B. Dissolution of Samples**

Metal samples are dissolved in the appropriate mineral acid. Ore samples low in tungsten or molybdenum can be dissolved by fusion with sodium peroxide. These samples are then digested to known volumes and a proper portion is taken and transferred to a 125-ml Erlenmeyer flask containing 10 ml ammonium bisulfate solution. This is then allowed to stand until dense fumes of sulfur trioxide appear, then cooled to room temperature. The sample is now ready for color development, extraction, and measurement.

**C. Molybdenum Color Development**

Add 10 ml hydrochloric acid, 5 drops 48% HF, and 10 ml 3,4-dimercaptotoluene to the sample solution at room temperature and swirl occasionally for 15 min.
D. Extraction

Add 25.0 ml chloroform by pipette, stopper the flask, and shake vigorously for 1 min. Transfer the solution to a dry glass funnel in which a piece of phase-separating paper has been dry set and for which a 25-ml volumetric flask is placed under the stem to catch the organic phase. Stopper the volumetric flask. The color is stable for at least 24 hr.

E. Photometry

Read the absorbance of molybdenum at 680 nm. For the tungsten determination, return the molybdenum-free aqueous portion to the 125-ml Erlenmeyer flask, add 5 ml ammonium bisulfate solution, and let stand until heavy fumes of sulfur trioxide appear.

F. Tungsten Color Development

Add 25 ml titanium(III) solution to the sample. Add concentrated hydrofluoric acid dropwise until the solution turns green. Add 10 ml of 3,4-dimercaptotoluene solution to the sample and place in a boiling water bath for 20 min. Swirl after 10 min. Add concentrated hydrofluoric acid dropwise as needed to maintain green color. Cool the solution to below room temperature. Proceed as in the extraction of molybdenum.

G. Calibration Curve

Plot the adsorbance readings of the solutions against the concentration of molybdenum or tungsten per 25 ml of solution.

II.2.3. Titration Procedures

Some volumetric procedures have been developed that are in general more rapid, but they are limited in use to specialized cases, such as a polarographic determination of small amounts of tungsten in ores (Love, 1955). Another method involving the reduction of tungsten before titration was used for tungsten–nickel alloys (Luke, 1961) and in ores (Busev et al., 1970). This method consisted of bypassing a solution of tungsten through a Jones reductor or similar system and catching the reduced tungsten in ferric iron solution and titrating it with standard dichromate solution.

Indirect procedures using a compleximetric technique have also been proposed (Bibinov et al., 1969). One involves the precipitation titration of lead tungstate using 4-(2-pyridylazo)resorcinol (PAR) as an indicator (Lassner and Scharf, 1960). The insolubility of lead tungstate was also used in a coulometric titration in which the titrant was electrically generated lead (Tutundzic and Stojkovic, 1966).

II.2.4. Atomic Absorption Procedures

Tungsten has been determined by atomic absorption using nitrous oxide–acetylene flame. Reasonable sensitivity can be obtained (Slavin, 1968), and optimum conditions and sensitivity data for aqueous solutions have been outlined (Perkin-Elmer, 1973).

A method for the analysis of ores and concentrates has been proposed for samples containing 200 ppm or greater amounts of tungsten. A HF–HNO₃
digestion was used, and relative standard deviations of 1.3–3.5% for determinations of 0.5 to 40.7% were obtained (Quin and Brooks, 1973).

Another scheme using atomic absorption for the analysis of ores uses a preconcentration and separation step (Rao, 1970). Greater sensitivity is claimed by extracting the phosphotungstate with a diisobutyl ketone solution of methyltricaprylammonium chloride. Good recoveries were made on standard samples in the 0.5–5% range using U.S.B.M. (U.S. Bureau of Mines) Nos. 6-10, 6-95E, and 5-2742.

A review of other methods with a list of references can be found in a nonferrous analytical review (Butler and Kniseley, 1973).

II.2.5. Emission Spectroscopy Procedures

These methods are used primarily for the determination of tungsten at the trace level. Spectrographic lines studied for this purpose have been already listed in the detection section of this chapter (Sec. II.1.3). Methods for the determination of tungsten in metals, alloys, and geochemical samples are given in reviews (Bachman and Banks, 1969; Butler and Kniseley, 1973).

II.2.6. X-Ray Fluorescence Procedures

In some cases, x-ray fluorescence techniques can be used to advantage. Sample preparation and standardization are very critical in most cases, but when these problems are solved, x-ray methods are usually much more rapid and precise. Wet techniques are long and laborious and generally not used for trace determinations of tungsten. Lassner (1966) compared x-ray fluorescence methods to conventional wet methods and pointed out the particular efficiency of x-ray fluorescence for qualitative analysis of small amounts of substance and for samples that are difficult to analyze by other techniques.

Sample preparation using a lithium metaborate fusion has been suggested, especially for geochemical analysis by x-ray fluorescence (Ingamells, 1970). A rapid ore analysis having good agreement with chemical assays was obtained by overcoming heterogeneity effects with proper grinding of the sample (Carr-Brion and Payne, 1968).

Fagel et al. (1958) used bromine as an internal standard to analyze solutions of tungsten ores. Another proposed method for ores uses nondispersive x-ray fluorescence; practically no matrix effects are claimed for this method (Lubecki and Vogg, 1973).

High-temperature alloys (Tompkins et al., 1962) and steels (Rhodes et al., 1971) have been successfully analyzed for tungsten by x-ray fluorescence methods.

II.3. DETERMINATION OF IMPURITIES IN TUNGSTEN

II.3.1. Emission Spectroscopy

Emission spectroscopy provides an accurate and rapid method for the determination of impurities in tungsten and tungsten alloys. Farrar et al. (1962)
described 12 different spectrochemical procedures in which 61 elements are measurable; 56 of the elements are determinable in the range of 0.1–3 ppm. Three direct-reading, optical emission spectrometric techniques have been developed that claim relative standard deviations of 0.005–0.03% for major and 0.02–0.026% for minor elements (Knott et al., 1972).

A germanium carrier-distillation procedure is applicable to the determination of 13 elements in tungsten powder, a silver chloride carrier-distillation procedure provides for the determination of 24 elements in tungstic oxide, and a sustaining arc method can determine 26 elements in tungstic oxide. These procedures have been reported (Gabler and Peterson, 1965). Fifteen elements were determined in samples of metal in the form of rods and powder, in tungsten anhydride, in tungsten acid, and in ammonium paratungstate (Filimonov et al., 1960). Dyck (1965) was able to markedly improve the detection limits for impurities in tungsten by diluting with graphite.

Chaney and Peterson (1963) describe a semiquantitative spectrographic determination of twenty-nine elements in tungsten designed to give estimates of impurities up to 500 ppm. Limits of detectability range from 0.3 ppm for the more sensitive elements to 100 ppm for the less sensitive ones. A method has been suggested by ASTM (1971a) for the determination of 14 trace elements in tungsten using various sample preparation and excitation conditions.

The following is a suggested procedure for the determination of impurities in oxides, metal powder, ammonium paratungstate, tungstic acid, tungsten carbide, and certain ores that have been converted to oxides. It covers the elements and ranges indicated in Table II.2.

To oxidize metal samples, dissolve solids and coarse tungsten with 30% hydrogen peroxide and take to dryness. For powders and fine turnings, place about 1 g of sample in a platinum crucible and burn off in a muffle furnace at a maximum temperature of 700°C. When the sample is completely oxidized, cool and transfer to a 4 × 2 in. plastic vials to which has been added two ½-in. plastic ball pestles, and ball mill for about a minute. Ammonium paratungstate samples are treated the same as powders.

### Table II.2. Ranges of Impurities in Tungsten-Containing Materials for Spectrographic Analysis

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Content (ppm)</th>
<th>Impurity</th>
<th>Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td></td>
<td>Group II</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>10–250</td>
<td>Manganese</td>
<td>1–250</td>
</tr>
<tr>
<td>Boron</td>
<td>0.5–5</td>
<td>Nickel</td>
<td>10–250</td>
</tr>
<tr>
<td>Calcium</td>
<td>10–250</td>
<td>Silicon</td>
<td>10–1000</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1–50</td>
<td>Tin</td>
<td>10–250</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1–50</td>
<td>Titanium</td>
<td>10–250</td>
</tr>
<tr>
<td>Chromium</td>
<td>5–250</td>
<td>Vanadium</td>
<td>5–250</td>
</tr>
<tr>
<td>Copper</td>
<td>1–100</td>
<td>Bismuth</td>
<td>25–250</td>
</tr>
<tr>
<td>Iron</td>
<td>25–1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>5–250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>1–250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Group III</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molybdenum</td>
<td>50–1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tantalum</td>
<td>50–1000</td>
</tr>
</tbody>
</table>
**Table II.3. Instrument Parameters Used in Procedure for Spectrographic Analysis**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>For group I elements</th>
<th>For group II elements</th>
<th>For group III elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>15 (ac)</td>
<td>7 (dc)</td>
<td>19 (ac)</td>
</tr>
<tr>
<td>Slit width (μm)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Rotating sector</td>
<td>2-step, 100 and</td>
<td>2-step, 100 and</td>
<td>2-step, 100 and</td>
</tr>
<tr>
<td>50% transmittancea</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Primary filter</td>
<td>None</td>
<td>80% transmittanceb</td>
<td>None</td>
</tr>
<tr>
<td>Arc preburn (sec)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Arc exposure (sec)</td>
<td>33</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Analytical gap (mm)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

*a* A spectograph having a reciprocal linear dispersion of about 5 Å/mm in the first order has been found adequate for this procedure.

*b* Transmission values should be adjusted to give intensities of about 10–90% transmittance for the full range of standards used.

For group I impurities (Table II.2), prepare a buffer mixture consisting of 1 part AgCl to 2 parts SP-1C graphite. Weigh 100 mg of sample and 150 mg of the buffer into a 1 × ½ in. plastic vial containing two ½-in.-diameter plastic balls. Cap and agitate on Wig-L-Bug for about 1 min. Weigh 75 mg of the oxide–buffer mixture into each of two electrodes, ASTM type S-12 with a 0.5-in. cup.

For group II impurities, weigh 270 mg of sample and 30 mg AgCl into a 1 × ½ in. plastic vial containing two ½-in.-diameter plastic balls. Cap and agitate as before. Fill the crater of two ASTM type S-3 electrodes with the sample–AgCl mixture and firmly tamp the mixture into the electrode.

For group III impurities, make a buffer mixture consisting of 1 part BaF to 1 part SP-2X graphite. Weigh 40 g of sample and 40 mg of buffer and mix the two as described above. Fill the crater of two ASTM type S-4 electrodes with the sample–buffer mixture and firmly tamp.

Produce and record the spectrum of each sample or standard in accordance with parameters listed in Table II.3. Develop the spectrographic film or plate in a photoprocessor at 20°C for 3 min using Kodak D-19 developer. Fix the plates in Kodak Rapid Fixer for 3 min. Wash the plates for 3 min in water and dry.

Measure the line intensities with a densitometer. Calibrate the film emulsion in accordance with ASTM E116 (Recommended Practice for Photographic Photometry in Spectrochemical Analysis). Use the analytical lines recommended in Table II.4.

**II.3.2. Interstitials**

Included in the interstitial determinations are the elements carbon, hydrogen, nitrogen, and oxygen. Kallmann *et al.* (1965) evaluated the determination of these elements using several different techniques. Carbon was done by combustion followed by a coulometric, conductometric, or thermoconductometric finish. Hydrogen determination was completed using vacuum extraction and vacuum fusion. Nitrogen was determined primarily with various micro-Kjeldahl procedures and as a by-product from vacuum fusion versions of hydrogen or oxygen. Oxygen determination was made using the aforementioned vacuum fusion technique along with inert gas fusion and neutron activation. They were able to obtain satisfactory results for a variety of techniques.

Molybdenum, tantalum, and tungsten were analyzed for oxygen, hydrogen, and nitrogen by vacuum fusion (Fagel *et al.*, 1959), and a technique using an iron flux
Table 11.4. Analytical Lines Used in Procedure for Spectrographic Impurities

<table>
<thead>
<tr>
<th>Element</th>
<th>Analytical line (Å)</th>
<th>Internal standard (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3082.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2567.99</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2496.78</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>3067.70</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>4226.73</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>2288.02</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>2521.36</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2843.25</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>3247.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3273.96</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2489.75</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>2833.07</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>2795.53</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2593.73</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>3012.00</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>2514.33</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>2863.33</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>3349.41</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>3185.40</td>
<td></td>
</tr>
<tr>
<td>All of the above elements</td>
<td></td>
<td>2447.93 (Ag)</td>
</tr>
<tr>
<td>Mo</td>
<td>3158.17</td>
<td>3156.60</td>
</tr>
<tr>
<td></td>
<td>3358.12</td>
<td>3350.50</td>
</tr>
<tr>
<td></td>
<td>3240.49</td>
<td>3240</td>
</tr>
<tr>
<td>Ta</td>
<td>2714.67</td>
<td>2713</td>
</tr>
</tbody>
</table>

for determining the same elements was claimed by Mikhilova et al. (1957) and Lassner and Woefel (1960).

Two methods for determining small amounts of carbon in tungsten metal have been published, both using combustion of the sample to carbon dioxide with a conductimetric titration for a readout (Gordon et al., 1964; Sheherbakov and Yurkevich, 1959). Total carbon in tungsten and tungsten alloys have been done by combustion and absorption of CO₂ with a gravimetric finish (ASTM, 1969). A newer technique entails the use of a gas chromatograph as a read-out after combustion of the sample. The following procedures are examples of this.

II.3.2.1. Determination of Carbon

Described below are two methods for the determination of carbon. One for low levels of carbon, the other primarily for carbon in tungsten carbides.

A. Low Levels of Carbon

This method covers the determination of carbon in tungsten metal with an instrument range of 5–2000 ppm based on a 1-g sample.
A metal sample is heated in an induction furnace. The released carbon is oxidized to carbon dioxide and carried by an oxygen stream to a molecular sieve trap in the analyzer. The trap is heated and the carbon dioxide is swept by a stream of helium through a silica gel column and thermal conductivity cell. The change in conductance is processed by a computer section, and the amount of carbon present is indicated on a digital readout. The recommended instrument for this procedure is a LECO 521 induction furnace combined with a LECO 589-600 gas analyzer available from Laboratory Equipment Corporation, St. Joseph, Michigan.

For preparation of crucibles, add approximately 1 g of iron chip accelerator to each crucible and preheat in a muffle furnace at 900–1000°C for at least 1 hr. Allow the crucibles to cool in a covered container and use within 3 hr.

Setting up the instrument and calibrating procedures can be found in the instrument manual.

Wash metal samples (turnings only) in fresh trichlorethylene to remove oil contamination. Decant solvent and dry on low heat of a hot plate. Weigh normally 1.00 g (other sample weights may be used) of sample into the prepared crucible, add accelerator as with standards, and analyze. To calculate the results, divide the sample weight into the DVM (digital voltmeter) reading to get parts per million of carbon.

B. For Carbon in Tungsten Carbide

This method is good for the determination of carbon from 2 to 20% in tungsten carbide.

The sample is heated in an oxygen atmosphere in an induction furnace. The carbon is oxidized to carbon dioxide and is carried by the oxygen sweep to the gasometric analyzer. The carbon dioxide and oxygen mixture is collected in a burette, the mixture replacing a red leveling solution. The mixture of carbon dioxide and oxygen is then passed from the burette into a solution of potassium hydroxide in another vessel. Here all the carbon dioxide is absorbed and only the oxygen remains. The oxygen (less the CO₂) is then brought back to the original burette. The red leveling solution is then adjusted to provide atmospheric pressure in the burette, under which circumstance there is a column of red liquid above the zero point. The height of this red liquid column above zero is equal to the volume of the absorbed carbon dioxide. Instrument used is a LECO 521 induction furnace coupled with a LECO 572-200 gasometric analyzer, manufactured by Laboratory Equipment Corporation, St. Joseph, Michigan.

Prepare the crucibles in the same manner as for low-carbon determinations as outlined in the preceding procedure. Refer to the LECO instruction manual for operation of LECO gasometric analyzers. The answers are read directly off the burette.

II.3.2.2. Determination of Hydrogen

This method covers the determination of hydrogen in tungsten and tungsten alloys in the range of 1 to 1000 ppm.

In summary, a metal sample held by a single-use graphite crucible is fused in an argon atmosphere by an impulse-type fusion furnace. The high fusion temperature releases the gases, which are then swept through Schutze reagent, where the oxygen as carbon monoxide is converted to carbon dioxide and absorbed in Ascarite. Nitrogen is chromatographically separated on a molecular sieve column. Hydrogen measurement is by a thermistor bridge detector, the output of which is integrated and displayed on an electronic digital voltmeter. The recommended instrument is a model RH-1, manufactured by Laboratory Equipment Corporation, St. Joseph, Michigan.

Procedure for setting up the instrument and calibrating it can be found in the instrument
manual. Normally, a 0.25-g sample is used, with freshly cut surfaces free of contamination. Powder samples are either pelletized or weighed into a suitable metal capsule before analyzing.

**II.3.2.3. Determination of Nitrogen**

This method is good for 5 ppm to 2.5% nitrogen based on a 1-g sample.

The sample is dissolved in acids, and the resulting solution is made basic with strong sodium hydroxide solution. Nitrogen is separated as ammonia by steam distillation. Ammonia is determined volumetrically in the distillate by titration with hydrochloric acid. A modification of an apparatus available from the American Instrument Company, Silver Spring, Maryland, is shown schematically in Fig. II.1.

Weigh approximately 1.0 g of powder or fine turning samples into a clean 200-ml Teflon bottle. Add 3 ml phosphoric acid, 10 ml hydrofluoric acid, and 4 g potassium dichromate. Heat on a hot plate to maintain a moderate boiling rate. If necessary, add hydrofluoric acid to replace that lost in boiling. When the sample is completely dissolved, remove from heat and add approximately 25 ml deionized water.

![Steam Still](image)

![Condenser](image)

![Vacuum-jacketed flask](image)

Fig. II.1. Semimicro Kjeldahl steam distillation unit, modified.
Prepare a reagent blank in the same manner and include with each group of samples. Be sure to heat the blanks to boiling.

A 250-ml Erlenmeyer flask is prepared by rinsing with deionized water and adding 10 ml 0.5% boric acid solution and 2 drops of mixed indicator (0.1 g bromoresol green in 50 ml ethanol, 0.07 g methyl red in 70 ml ethanol and mix). Place the flask under the condenser delivery tube.

Transfer the sample quantitatively to the distillation apparatus and add excess 50% sodium hydroxide solution (30 ml) through the funnel. Steam distill until 50 ml of distillate has been collected. Titrate the distillate to a pink end point with 0.00357 N hydrochloric acid. Compare the end point of sample to the end point of the blank. 1 ml 0.00357 N hydrochloric acid is equivalent to 50 μg of nitrogen.

II.3.2.4. Determination of Nitrogen and Oxygen

Both of these gases can be determined together, using a LECO TC-30 Simultaneous Nitrogen–Oxygen Determinator, available from Laboratory Equipment Corp., St. Joseph, Michigan. The analytical range of the instrument is about 5 ppm to 5000 ppm for tungsten metal.

Briefly, a metal sample held by a single-use graphite crucible is fused in a helium atmosphere by an impulse-type fusion furnace. The high fusion temperature along with the use of platinum as a flux releases the gases, which are then swept through copper oxide, where the carbon monoxide is converted to carbon dioxide. Hydrogen gas, after conversion to water, is trapped, and the remaining nitrogen and carbon dioxide are separated chromatographically. Measurement is by a thermistor bridge detector. Bridge output is integrated, and nitrogen and oxygen results are displayed on separate electronic digital voltmeters. To set up the instrument and to calibrate it, refer to the instrument manual.

Sample preparation for solid material consists of cleaning by filing, cutting, or etching. Weigh about 100–200 mg sample, then degrease in trichloroethylene and rinse in acetone. Allow to dry. A powder sample of a size to contain nitrogen and oxygen quantities within the instrument range is weighed into a suitable metal capsule. Carefully wrap the sample in a sheet of degreased platinum foil weighing eight times as much as the sample. Blanks must be run on the platinum and subtracted from the gross readings.

II.3.3. Atomic Absorption Spectroscopy

The analysis of impurities in tungsten by atomic absorption is not as widespread as emission spectroscopy, but it is still a good technique for the determination of many elements. Neuman (1971a, b, 1972a, b) has authored several papers about the analysis of tungsten for impurities, including calcium, aluminum and calcium, potassium and sodium, and rhenium. The analytical range was approximately 1–20 ppm, except for rhenium, which had a lower limit of 250 ppm in the metal. General information along with specific determinations such as nickel and copper in tungsten metals is available (Perkin-Elmer, 1973). Iron and cobalt have been successfully determined by atomic absorption techniques by making up matrix standards in the ranges expected and setting up the parameters suggested by the instrument manual as provided by Perkin-Elmer. An example of a typical procedure is outlined below.

Sodium in Tungsten Metal

The sample is dissolved in hydrofluoric and nitric acids and diluted and aspirated
Table II.5. Operating Parameters for Perkin-Elmer Model 303 Atomic Absorption Apparatus

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>295 nm</td>
</tr>
<tr>
<td>Slit</td>
<td>4</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>1</td>
</tr>
<tr>
<td>Burner height</td>
<td>0.75</td>
</tr>
<tr>
<td>Range</td>
<td>Visible</td>
</tr>
<tr>
<td>Air</td>
<td>9</td>
</tr>
<tr>
<td>Fuel ((C_2H_2))</td>
<td>9</td>
</tr>
</tbody>
</table>

directly into an atomic absorption apparatus. The analytical range is from 10 ppm to 50 ppm.

Accurately weigh a 1-g sample into a 150-ml Teflon beaker prerinsed with distilled deionized water. Dissolve the sample with 5 ml hydrofluoric acid and dropwise addition of nitric acid. When sample is in solution, transfer to a 100-ml polyethylene volumetric flask and dilute to volume. Carry a reagent blank through the procedure.

The recommended parameters using a Perkin-Elmer model 303, are given in Table II.5. Set zero on the null meter while aspirating water. Read the blank and then a 0.1-µg/ml sodium standard and a 0.5-µg/ml sodium standard solution, aspirating water between each. If the 0.5-µg/ml standard reading is not approximately five times that of the 0.1-µg/ml standard, contamination is present and the standards should be made over. Record all readings for the blank and standards. Aspirate the samples, checking the blank and low standard at least once, and record all readings. Calculate the amount of sodium present by comparing the sample absorbance with the absorbance of the standards.

II.3.4. Wet Chemical Procedures

While a great many of the impurities in tungsten metal and tungsten alloys can be determined by spectroscopy. There is still a need for wet chemical procedures, especially in ores and tungsten concentrates. Elwell and Wood (1966) describe procedures for boron, carbon, hydrogen, iron, molybdenum, nickel, nitrogen, oxygen, phosphorous, titanium, zirconium, and hafnium determination in tungsten metal and alloys. Peterson et al. (1962) have written methods for the determination of tin, copper, arsenic, antimony, phosphorous, sulfur, manganese, lead, and SiO in tungsten ores and concentrates. Szuc and Klug (1969) used a diethylidithiocarbamate extraction as a step in determining bismuth, cadmium, copper, lead, zinc, iron, nickel, and cobalt, at trace levels in tungsten and tungstates. Following are some methods available for the determination of impurities in various types of tungsten samples.

II.3.4.1. Nonvolatile Residue in Tungsten Powder

First oxidize the tungsten powder to tungstic oxide by ignition of a 5–10 g sample at 700°C for one hour. Cool and transfer one gram of the sample that has been oxidized, into a weighed boat. Introduce the boats in the combustion tube of an electric furnace maintained at 600°C, and volatilize the tungstic oxide by passing a slow stream of dry HCl gas through the tube (Figure II.2) (Li and Wang, 1955). The volatilization is complete when the yellow color of
the oxide has disappeared. Let the boats cool in a desiccator and weigh the remaining residue as the total nonvolatile residue.

**II.3.4.2. Antimony in Ores**

Weigh 2 g finely ground sample into an iron crucible and fuse with about 10 g sodium peroxide. Cool, and place the crucible into a 400-ml beaker and leach with about 200 ml of water. When the melt has completely disintegrated, rinse the crucible thoroughly with water. Add 20 g tartaric acid and acidify with approximately 40 ml HCl. Heat and filter to obtain a clear solution (Li and Wang, 1955).

Pass hydrogen sulfide through the solution for about 30 min, then filter and wash with 1:99 HCl saturated with H₂S. Wash the precipitate back into the original beaker and add 30 ml potassium hydrogen sulfide (KHS) solution. (Dissolve 35 g of KOH per liter. Saturate 400 ml of the solution with H₂S and mix well with the other 600 ml.) Boil gently to dissolve all the antimony sulfide and refilter through the original filter paper. Wash with a dilute solution of KHS. Acidify the solution with 50 ml HCl and add KClO₃ a little at a time, to oxidize the sulfur. Boil the solution to expel chlorine and evaporate to 50 ml.

After cooling, reduce the volume of the solution by adding 60 ml H₂SO₄ and boil down to 50 ml. Then add 40 ml HCl and evaporate to 50 ml. Finally, add 50 ml 40% HCl and evaporate to 50 ml. Add 100 ml boiling water and titrate hot with 0.05 N KBrO₃ solution, using methyl orange as indicator.

In the presence of tin, treat as follows: After the oxidation with HCl–KClO₃ and evaporation to 50 ml, add 10 g oxalic acid, 10 g ammonium oxalate, and heat to a boil. Add 250 ml hot water and saturate the solution with H₂S. Filter off the tin sulfide and then continue the oxidation and reduction.

**II.3.4.3. Arsenic in Tungsten Matrix Materials**

This colorimetric method is good for a range of 5–400 ppm, based on a 0.5-g sample. A sample is converted to a soluble form by sodium carbonate–potassium carbonate fusion. The arsenic is separated by distillation and then determined as a heteropolyarsenomolybdo complex. Hydrazine sulfate is used for reduction of the complex to the molybdenum blue color.
Appendix II

A. Special Reagents

Hydrazine sulfate–ammonium molybdate: Dissolve 5 g ammonium molybdate in 500 ml 5 N sulfuric acid. Dissolve 0.25 g of hydrazine sulfate in 100 ml water. Dilute 50 ml of the ammonium molybdate solution, mix with 5 ml hydrazine sulfate solution and dilute to 500 ml. The mixed solution should be prepared fresh daily.

Standard arsenic solution (100 g/ml): Dissolve 0.132 g of arsenic trioxide in 2 ml 1 N sodium hydroxide solution; dilute with water to 1 liter.

HCl–HBr solution: 2 ml HBr to 20 ml HCl.

Hydrazine sulfate–HCl mixture: Prepare a slurry by mixing 15 g hydrazine sulfate in 500 ml concentrated HCl.

B. Procedure

Weigh accurately from 0.25 to 0.5 g of sample into a platinum dish that contains about 2 g sodium carbonate and 1 g potassium carbonate and mix well. Cover with about another 2 g of carbonate mixture. Fuse in a muffle furnace at 1000°C for about 5 min. Remove and cool. Add a small amount of water to extract the melt; warm if necessary.

Transfer the sample to a 250-ml Teflon beaker, then decant the liquid into a distilling flask (Fig. II.3). Add 5–10 ml of concentrated HCl to the beaker, making a slurry of the insoluble portion of the sample, and transfer it also into the distilling flask. Keep the water to a minimum, but quantitatively transfer all sample.

Add 2 ml HBr and two 10-ml portions of hydrazine sulfate–HCl slurry. Wash the salt into the flask with concentrated HCl. Assemble the apparatus, adding a drop of concentrated H₂SO₄ at the joint as lubricant, and prepare a clean 250-ml beaker containing 50 ml water to receive the distillate. Pass a slow stream of dried nitrogen through the solution. Slide the heating mantle upward until the hemispherical pad just touches the bottom of the flask. Insert a thermometer in the well and distill for 15 min. Add 20 ml HCl–HBr solution through the

![Image](https://example.com/image.png)

Fig. II.3. Scherrer distillation apparatus.
funnel and distill for an additional 15 min. Remove the heating mantle, then rinse the
condenser thoroughly with water. Add 20 ml HNO₃ to the distillate and evaporate to dryness
over low heat. (Loss of arsenic will occur over 130°C.) Bake in an oven at 110°C for 15 min,
then add about 40 ml hydrazine sulfate–ammonium molybdate solution and rinse the sides of
the beaker down with the same solution and cover the beaker with a watch glass.

Place the sample in a hot water bath at 80–90°C for 15 min, allow to cool a little, then
transfer the solution to a 50-ml volumetric flask. Dilute to volume with hydrazine sulfate–
ammonium molybdate solution and shake thoroughly. Measure the absorbance of the
sample at 840 nm using water as a reference. Calculate results by comparing readings to a
standard curve of 20–100 μg as per 50 ml.

II.3.4.4. Calcium in Scheelite Ore Concentrates

This gravimetric method is for easily dissolved scheelite ores. Calcium
determination in wolframite, huebnerite, and other ores low in calcium can more
easily be done by atomic absorption techniques, which are more sensitive and
interference free.

Transfer a 0.5-g sample into a 400-ml beaker. Add 100 ml HCl and digest on a hot plate at
90°C for at least 1 hr. Stir and evaporate to 40 ml. Police the bottom of the beaker thoroughly
and add 40 ml HCl and 15 ml HNO₃. Warm gently until reaction subsides and then evaporate
to 15 ml. Add 100 ml of water and boil gently for a few minutes. Allow it to stand for 1 hr or
longer.

Filter into a 600-ml beaker and wash with 1:9 HCl. To the filtrate, add 5 g NH₄Cl and
dilute to about 300 ml. Add two drops of methyl red indicator and 35 ml saturated solution of
ammonium oxalate. Bring to a boil and add NH₄OH until alkaline, then add 3 ml in excess.
Boil for an additional 10 min and cool to room temperature. Filter and wash with small
portions of hot water several times. Place the precipitate in a platinum crucible and ignite to a
constant weight. Weigh as CaO.

II.3.4.5. Niobium, Tantalum, Titanium, and Zirconium in Tungsten Alloys and Ores

In order to determine the above elements accurately, it is best to separate them
from each other first. Previously described methods involve precipitation,
separation (Furman, 1962; Li and Wang, 1955), and ion exchange techniques
(Sugawara, 1964; Kallman, 1961) with either colormetric or gravimetric finishes.
The following procedure utilizes all these techniques.

To prepare ion exchange columns for the separation, use columns of polyethylene tubing
0.5 in. in diameter by 10 in. long. Attach a reservoir to the top by welding to the tubing an
inverted 4-oz polyethylene bottle with the bottom cut out. To the other end of the tubing,
insert the female portion of a Quick Disconnect (Nalgene brand), and weld in place. Attach a
short piece of small-diameter tubing so that the columns may be clamped off. Wash a portion
of 100–200 mesh Dowex 1 × 8 resin three times with 2 N HCl, each time decanting the fines.
Place a plug of carbon wool in the bottom of the column and transfer enough resin into the
column to give a resin bed height of 7–8 in. When the resin has settled to the prescribed height,
place some plastic turnings on top of the resin to prevent disturbing the resin as solutions are
poured onto the column.

To separate the elements of concern, take an aqueous sample solution containing no
more than 0.5 g of total metal and adjust to 1 N in HF and 0.1 N in HCl; the total volume
should not exceed 50 ml. Introduce the sample solution onto the column and let drain; flow
control is not necessary. Rinse the sides of the reservoir twice with 1 N HF–0.1 N HCl solution
and then add 100 ml of the same solvent and let drain. This will elute aluminum, iron, and
vanadium if present. Elute zirconium and titanium and some of the tungsten with 30 ml 1 : 6 : 3 (volume ratio) HF–HCl–water. Add an additional 30 ml of the 1 : 6 : 3 HF–HCl–water to elute the remaining tungsten. Very little molybdenum will elute with this second 30-ml elution. Elute niobium and the remaining molybdenum with 100 ml 14% NH₄Cl in 1 : 24 HF, and elute tantalum with 100 ml 14% NH₄Cl in 1 : 24 HF adjusted to pH 5.5 with NH₄OH. If needed, molybdenum can be removed selectively before niobium by elution with 100 ml of 4 : 5 : 11 HF–HCl–water.

The titanium can be determined colorimetrically with hydrogen peroxide (Snell and Snell, 1957; Sandell, 1959) on the first elution and the zirconium by taking a portion of the same solution and doing a mandelic acid precipitation on the zirconium (Snell and Ettere, 1971). The niobium and tantalum can be precipitated from their respective solutions with cupferron (Sandell, 1959) and determined gravimetrically.

II.3.4.6. Copper in Ores

The following procedure describes an iodometric titration for the determination of copper (Li and Wang, 1955).

Weigh 2 g finely ground samples into a 400-ml beaker, and add 40 ml HCl and 15 ml HNO₃. Heat gently for about 45 min, and then evaporate down to about 15 ml. After cooling, add 10 ml H₂SO₄ and heat to strong fumes. Cool, then add 100 ml water and boil enough to dissolve the soluble salts. Cool again, and filter and wash thoroughly with 5% H₂SO₄. Discard the residue and dilute to 250 ml and heat to boiling. Add 20 ml 50% Na₂S₂O₃, and boil for 5 min or until the precipitate settles. Filter immediately and wash with water. Transfer the paper and precipitate to a porcelain crucible. Ignite gently until the carbon is destroyed. After cooling the crucible, add 5–10 ml HNO₃ and heat gently for 30 min. Transfer the solution to a 250-ml beaker, rinsing the crucible with a little water. Evaporate the solution to about 5 ml and add 2 ml water. Add NH₄OH dropwise until the solution is alkaline to litmus. Boil off the excess ammonia, add 5 ml acetic acid and again boil for a minute. Cool the solution to room temperature, add 5 ml 50% aqueous solution of KI, stir well, and immediately titrate with a standard Na₂S₂O₃ solution. When the brown tint has nearly disappeared, add 5 ml of starch solution and continue the titration until one drop changes the color from blue to yellowish-white persisting for 15–20 sec.

II.3.4.7. Iron in Tungsten and Tungsten Alloys

This colorimetric method for iron is good to approximately 25 to 300 ppm iron based on a 1-g sample.

Dissolve 1 g metal in a 250-ml polyethylene beaker with 5 ml HF and a minimum of 1 : 1 HNO₃, controlling the addition of HNO₃ dropwise. When the sample is about all into solution, let it warm in a hot water bath for about 5 min to make sure every bit of the sample is in solution. Add more HNO₃ if necessary. Remove the sample from the hot water bath and dilute to about 75 ml with water. Transfer the solution into a clean polyethylene 100-ml volumetric flask. Let cool, bulk to the mark, and transfer a 25-ml portion of the solution into a clean 250-ml polyethylene beaker. Add exactly 1 g hydroxylamine hydrochloride to each sample and blank. Let warm in hot water bath for 5 min. To each sample, add 25 ml ammonium citrate solution (25% aqueous solution) and 6 g boric acid. Whirl gently to dissolve the boric acid. When the boric acid is in solution, remove the sample from the hot water bath, and adjust the solution to a pH of 5 with NH₄OH and 1 : 1 HCl. To each sample and blank, add 2 ml hydroxylamine and 5 ml 0.1% aqueous solution of o-phenanthroline. Transfer the solution into a 100-ml volumetric flask and bulk to the mark. Let warm in a hot water bath for 10 min, then let cool in a cold water bath to room temperature. Adjust volume to the mark and mix thoroughly. Measure the iron concentration at 515 nm on a
spectrophotometer, compared with standards prepared in the same manner. A reagent blank is carried through the procedure.

II.3.4.8. Iron in Ores

This procedure describes a redox titration of iron using potassium dichromate as the titrant and diphenylamine as the indicator.

Weigh a 0.5 g sample into a zirconium crucible containing about 6 g sodium peroxide. Mix and fuse over a Meeker burner until cherry red. Hold at that temperature for a few minutes, then cool. Knock the melt into a plastic beaker containing 50 ml water. Make acid with concentrated HCl, then make basic with ammonia, adding 10 ml excess. Heat on a boiling water bath for 5 min, then filter hot through a fairly coarse filter paper. Wash three or four times with a dilute NH4Cl solution. Wash precipitate back into the original beaker, and wash any remaining hydroxides through the paper into the beaker using hot dilute HCl.

Add 20 ml HCl and heat on the hot water bath until the iron is in solution. The tungsten will probably be hydrolyzed. Add 2–3 drops HF, and this will clear the solution. Add 10% stannous chloride dropwise until the yellow color of iron disappears, then add 2–3 drops in excess.

Cool in a water bath, then add 10 ml saturated mercuric chloride. Let set several minutes. A white silky precipitate will appear. Add 10 ml 1:1 H2SO4, 10 ml concentrated H3PO4, 3–4 drops diphenylamine indicator, and titrate to a blue-purple color with potassium dichromate. One milliliter of K2Cr2O7 solution (4.391 g/liter) is equal to 0.005 g iron.

II.3.4.9. Fluoride Ion in Tungsten Metal

This procedure describes the determination of fluoride using a fluoride-ion-specific ion electrode, with no prior separation. It is good down to 5 ppm, based on a 0.5-g sample.

Weigh 0.5000 g finely divided (<325 mesh desirable) sample into a plastic bottle. Add 5 ml 30% hydrogen peroxide in 1-ml portions, waiting for the reaction to subside between each addition. Swirl the sample occasionally during the addition of the hydrogen peroxide. After 5 ml hydrogen peroxide have been added, place the sample in an ultrasonic bath for 15 min. Cover loosely. At the end of 15 min remove the sample from the sonic bath and decant the liquid into a second plastic bottle. Add 3 ml hydrogen peroxide to the residue in the first bottle in 1-ml portions, waiting for the reaction to subside between each addition. After 3 ml hydrogen peroxide have been added, place the sample in the sonic bath again and vibrate until solution is complete. After dissolution is complete, combine the two portions. Rinse the empty bottle sparingly with water. Add 15 ml 20% ammonium citrate solution to the sample. Using a microburette, add 1.00 ml 10 μg/ml fluoride standard (0.0221 g/ml NaF aqueous solution) to one bottle and 2.00 ml of the same standard to the other bottle. Dilute to 40 ml plus or minus 0.5 ml with water and cap.

The measurement of fluoride ion is made by means of a specific-ion electrode with the appropriate reference electrode and a specific-ion meter with a fluoride mode. Initially rinse the electrodes with water, then insert the electrodes in the 10-μg fluoride standard. Set a magnetic stirrer to a slow speed, maintaining this same speed throughout the entire analysis. Set the meter to 100 with the calibration knob. Allow the meter to come to equilibrium. Repeat the procedure with the 20-μg standard, except that the meter is set to 200 with the temperature control knob.

Repeat this procedure until the 10-μg standard reads 100 and the 20-μg standard reads 200 without further adjustment. Add Teflon-coated stir bars to the samples, set each sample on the magnetic stirrer, insert the electrodes, and obtain a reading for each sample. Estimate
the amount fluoride present by subtracting the amount of the spike from the reading and dividing by the sample weight.

II.3.4.10. Lead in Ores

A procedure using dithizone as a colorimetric reagent is described as follows (Peterson et al., 1962).

Dissolve a 0.5-g sample by fusing with sodium carbonate in a platinum crucible using roughly 5 g Na₂CO₃ mixed with the sample and heated in a muffle furnace for about 15 min at a temperature of 900–1000°C. Dissolve the melt after cooling by leaching the crucible and sample in a 400-ml beaker with water. Remove and completely rinse the crucible, then boil down the sample solution to about 50 ml. With HCl, adjust the pH to just neutral. Add 5 ml hydroxylamine hydrochloride solution and boil to liberate any CO₂ present. Cool the solution and transfer to a 100-ml volumetric flask and dilute to the mark.

Transfer a portion containing 1–20 µg lead to a 60-ml separatory funnel, and dilute to about 10 ml with water. Add 5 ml lead buffer solution and 5 ml dithizone solution and shake for 4 min. Allow the carbon tetrachloride to separate, and transfer a portion to a 1-cm absorption cell. Read the absorbance of the sample against a distilled water blank at a wavelength of 520 nm. Calculate the lead present from a curve generated from standards of 0–20 µg lead prepared in the same manner.

Reagents Needed:

Dithizone solution: Dissolve 0.007 g purified dithizone in 250 ml pure carbon tetrachloride.

Hydroxylamine hydrochloride solution: Dissolve 75 g NH₂OH·HCl in water and dilute to 500 ml.

Lead buffer solution: A combination of the following reagents: hydroxylamine hydrochloride, 20 g; ammonium citrate, 75 g; potassium cyanide, 30 g; potassium fluoride, 20 g; ammonium hydroxide, 100 ml; water, dilute to 500 ml.

Adjust the pH of the buffer solution to 10 with citric acid or ammonium hydroxide as necessary. Traces of metals are removed from the buffer by shaking with 0.5% dithizone solution in chloroform. The dissolved dithizone then is removed with successive shakings of clear chloroform. The dissolved chloroform is removed by shaking once with carbon tetrachloride. The buffer as prepared is usable for 3–4 weeks before it decomposes and yields erratic results.

II.3.4.11. Manganese in Ores

A colorimetric procedure measuring the permanganate ion is described as follows

Weigh a 1-g ore sample into a platinum crucible, mixing thoroughly with 7 g sodium carbonate, then cover the mixture with an additional 3 g Na₂CO₃. Cover the crucible with a platinum lid and heat in a muffle furnace for 30 min at a temperature of 950°C.

Cool, then dissolve the melt by digesting in a 400-ml beaker with about 125 ml of water acified with a few drops of HCl. Rinse the crucible and lid well with water, and digest the sample until the melt is completely disintegrated. If the solution shows any sign of permanganate ion color, add a few drops of sodium sulfite or sodium nitrite to reduce the permanganate to manganese dioxide. Boil the solution for about 5 min, then filter and wash the precipitate three or four times with a 5% sodium carbonate solution.

Wet-ash the sample and filter paper by digesting with 10 ml concentrated HNO₃ and 7–10 ml concentrated perchloric acid. Evaporate the solution to about 2 ml, cool, and redissolve
any salts with 50 ml water. Add 10 ml 1:1 H₂SO₄, 5 ml HNO₃, and 5 ml H₃PO₄. Filter any insoluble calcium sulfate from the solution, and oxidize the manganese to permanganate ion using potassium periodate. Cool, and transfer to a 100-ml volumetric flask. Dilute to the mark, and measure the absorbance with a spectrophotometer at a wavelength of 526 nm. Determine the amount of manganese present by comparing to a standard curve previously prepared. Carry a reagent blank through the procedure.

II.3.4.12. Molybdenum in Tungsten Metal

A colorimetric procedure using the thiocyanate–molybdenum complex is as follows (ASTM, 1971b):

Weigh a 1.0-g sample into a 200-ml platinum beaker and dissolve by just covering with HF and adding HNO₃ dropwise until sample is dissolved. Add 1–2 ml HNO₃ in excess and heat gently. Add 10 ml 1:1 H₂SO₄ and let stand until strong fumes of SO₃ appear.

Dilute the sample, after cooling, to about 20 ml with water, then add 4 g/ml NaOH solution until the sample solution clears, then add 2 or 3 ml in excess. Cool, and add 3 drops of phenolphthalein indicator, acidifying with 1:1 HCl.

After transferring the sample solution to a 100-ml volumetric flask and diluting to volume, take a portion not exceeding 15 ml and containing not more than 3 mg molybdenum and place in a 50-ml volumetric flask.

Add 2–3 g ammonium citrate and swirl until dissolved. Using a pipette and swirling after each addition, add 5 ml ammonium thiocyanate (100 g/liter), 20 ml acetone, and 7 ml SnCl₂ solution. (Dissolve 20 g stannous chloride dihydrate in 150 ml 1:1 HCl with gentle heating. Cool and dilute to 200 ml with 1:1 HCl. Prepare daily.) Measure the absorbance of the solutions within 15 min at a wavelength of 460 nm. Compare to a calibration curve prepared from standards of 10–300 μg molybdenum. Carry a reagent blank through the procedure.

II.3.4.13. Molybdenum in Ores

The same procedure as outlined in Sec. II.2.2.

II.3.4.14. Phosphorus in Ores

The following describes a colorimetric procedure for determination of phosphorus at 40–600 ppm range.

Weigh a 0.5-g sample into a zirconium crucible and fuse with sodium peroxide. After cooling dissolve the melt in a 400-ml beaker with water, warming if necessary. Rinse thoroughly and remove the crucible. Dilute to about 100 ml with water. Acidify with HCl and warm on a low heat. Make sure the pH is < 5; the tungsten should be precipitated by this time.

Make the sample basic with NH₄OH. Swirl and warm the solution to coagulate the precipitate. Filter the sample, using plastic filter funnels, discarding the filtrate. Wash the precipitate three times with hot 1:9 NH₄OH, and finally once with water.

Dissolve the precipitate through the filter paper with 48% HF into a 400-ml high-temperature-resistant Teflon beaker. Add the HF to the filter dropwise. Wash the filter paper thoroughly with HF, as ZrP₂O₇ is difficult to dissolve. Wash the filter paper once with water.

Heat the sample solution on a hot plate until SO₃ fumes appear and heat for an additional 5 min and allow to cool. Add 50 ml 2.4% HF, mix, and after covering with a plastic lid, heat until the solution is clear. Allow the solution to cool to room temperature. If at this point the solution has a blue tint (reduced molybdenum), add 0.004 M KMnO₄ dropwise until the color disappears.

Add 10 ml 0.25% NH₄VO₃, followed immediately by 65 ml 15% ammonium molybdate solution. Stir and allow to stand for at least 15 min. Dilute the sample to about 150 ml with water and transfer to a 250-ml separatory funnel. Add 40 ml MIBK (methyl isobutyl ketone)
and shake for 1 min. Sample should be approximately room temperature for the extraction. Allow the layers to separate, and discard the aqueous phase.

Transfer the organic phase to a 50-ml volumetric flask and dilute it to 50 ml with MIBK. Mix thoroughly, and measure the absorbance at 400 nm using a spectrophotometer. Compare with standards of 20–300 µg phosphorus levels.

II.3.4.15. Rhenium in Tungsten–Rhenium Alloys

The following is a colorimetric procedure using thiocyanate as a coloring reagent.

Weigh a 0.5-g sample into a plastic or platinum 250-ml beaker. Take into solution with HF and HNO₃. Add 10 or 20 drops of 10% NaOH, and dilute to 500 ml in a volumetric flask.

For samples containing 25% rhenium, transfer a 5-ml portion into a 100-ml volumetric flask and dilute to approximately 50 ml. For other concentrations of rhenium, take appropriate portions.

Add 10 ml special tartaric acid solution (dissolve 500 g tartaric acid and 90 g sodium tungstate in 1 liter water), 5 ml 10% sodium thiocyanate, 5 ml 10% SnCl₂. Let the color develop for 30 min, and read the absorbance at 385 nm. Carry a reagent blank through analysis and compare to standards run in a similar manner.

II.3.4.16. Tin in Ores

Described in the following is a redox titration procedure for determination of tin using iodine as a titrant (Li and Wang, 1955).

Dissolve and precipitate a 1-g sample as previously outlined in the cinchonine procedure, Sec. II.2.1. Filter off the cinchonine precipitate, catching the filtrate in a 125-ml Erlenmeyer flask, washing thoroughly with cinchonine wash solution. Add 50 ml concentrated HCl and about 10 g test lead. Using a rubber stopper with a bent glass tube, stopper the flask and start reducing the tin by boiling it gently. When the solution is colorless, boil for 35 min longer. Remove the flask to a cold water bath with the lower end of the stopper tube in a saturated solution of sodium bicarbonate. As soon as the solution is cold, titrate immediately with 0.1 N iodine solution, using starch as indicator. With each batch of titrations, run a standard using 0.3 g pure tin metal in the same manner, starting with the addition of 50 ml HCl after dissolving with 15 ml H₂SO₄.
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