Kirk-Othmer Encyclopedia of Chemical Technology.

TUNGSTEN AND TUNGSTEN ALLOYS

Tungsten (wolfram) [7440-33-7] is a silver-gray metallic element with atomic number 74 and appearing in Group VIB of the periodic table below chromium and molybdenum. Its atomic weight is 183.05, and there are 31 isotopes ranging from 160 to 190; the abundance of the five stable isotopes is given in Table 1 (1). Tungsten has the highest melting point of any metal (3695 K), a very low vapor pressure, and the highest tensile strength of any metal above 1650°C.

The term *tungsten*, meaning heavy (tung) stone (sten) in Swedish, was first applied to a tungsten-containing mineral in 1755. The mineral was subsequently identified by Scheele in 1781 as containing lime and a then-unknown acid that he called *tungstic acid*. The mineral was then referred to as *scheelite*. Metallic tungsten was first produced by the carbon reduction of tungstic acid in 1783 in Spain and termed *wolfram*. This designation become common usage in German. In 1957, the IUPAC (International Union of Pure and Applied Chemistry) chose the English term *tungsten* and the French term *tungstene* with *wolfram* as an alternative. However, W is still used as the chemical symbol.

During the nineteenth century, tungsten remained a laboratory material. The latter half of the century saw the development of high-speed tool steels containing tungsten, which became the prime use for the metal in the first half of the twentieth century. The pure metal itself was first used as a filament for electric lamps at the beginning of the twentieth century. After some limited success with paste-extruded tungsten powder, the Coolidge process was developed in 1908, by which a pressed and sintered tungsten ingot could be worked at high temperatures by swaging and drawing to form a fine-wire filament. This was a landmark in the development of the incandescent-lamp industry and, later, in the use of tungsten as a welding electrode. In the 1920s, the search for an alternative to expensive diamond dies required for the drawing of the tungsten wire led first to cast tungsten carbides and then to the manufacture of cemented carbides, now accounting for over half of the tungsten consumption in the world.

Tungsten is the eighteenth most abundant metal, having an estimated concentration in the earth's crust of 1–1.3 ppm. Of the more than 20 tungsten-bearing minerals known, Table 2 lists the most significant ones, but only four are of commercial importance: ferberite (iron tungstate), huebnerite (manganese tungstate), wolframite (iron–manganese tungstate containing ~20–80% of each of the pure components), and scheelite (calcium tungstate). Typical concentration in ores is ~0.5% and only rarely exceeds 2%.

The WO_3 content of wolframite minerals varies from 76.3% in $FeWO_4$ to 76.6% in $MnWO_4$. These minerals, are commonly called *black ores*, as their colors range from black to brown. They occur as well-defined crystals to irregular masses of bladed crystals. They have a Mohs hardness of 5.0–5.5 and a specific gravity of 7.0–7.5 and tend to be very brittle. They are also weakly magnetic. Scheelite contains 80.6% WO_3, is white to brown, and is strongly fluorescent in short-wave ultraviolet radiation. Scheelite occurs as massive crystals and as small grains. It has a Mohs hardness of 4.5–5.0 and a specific gravity 5.6–6.1 and is very brittle.

Table 1. Isotopes of Stable Tungsten[a]

Isotope	CAS Registry no.	Abundance, %
^{180}W	[14265-79-3]	0.13
^{182}W	[14265-80-6]	26.30
^{183}W	[14265-81-7]	14.30
^{184}W	[14265-82-8]	30.67
^{186}W	[14265-83-9]	28.60

[a] Ref. 1.

Table 2. Minerals of Tungsten

Anthonite	$Al(WO_4)(OH)\cdot H_2O$	Cuprotungstite	$Cu_2(WO_4)(OH)_2$
Ferritungstite	$Ca_2Fe_2{}^{2+}Fe_2{}^{3+}(WO_4)_7\cdot 9H_2O$	Raspite	$PbWO_4$
Russellite	Bi_2WO_6	Sanmartinite	$ZnWO_4$
Scheelite	$CaWO_4$	Stolzite	$PbWO_4$
Tungstenite	WS_2	Tungstite	$WO_3\cdot H_2O$
Ferberite	$FeWO_4 + <20\%\ MnWO_4$	Huebnerite	$MnWO_4 + <20\%\ FeWO_4$
Wolframite	$(Fe, Mn)WO_4$		

1. Occurrence

Tungsten is found in mountainous areas of the world in magma–thermal intrusions in hard rock formations, During the cooling process of the earth's crust magma bodies may have intruded into a higher-level formation where crystallization began. As basic rocks of gabbro, diorite, granodiorite, monzonite, and granite formed, tungsten and other elements that are associated with magma-thermal residual formations such as tin, molybdenum, and copper were concentrated and are commonly found in the same ore bodies. Tungsten occurs only in combined form with other elements, principally, manganese, iron, copper, and sulfur.

Tables 3 and 4, show respectively the estimated reserves (2) by country and output capabilities for larger mines, revealing that more than half the world reserves are in China, followed by Canada, the former Russian territories now CIS (Commonwealth of Independent States) and Kazakstan, the United States, Korea, and Austria.

2. Physical Properties

Some of the physical properties of tungsten (3–12) are given in Table 5. Although these data are in general reliable, the original references should be consulted if precise values are required. For further property data, see Refs. 14–16. For thermodynamic values, Refs. 13–15 should be consulted. Two values are given for the melting point. The value of 3660 K was selected as a secondary reference for the 1968 International Practical Temperature Scale. However, since 1961, the four values that have been reported ranged from 3680 to 3695 and averaged 3688 K.

3. Chemical Properties

The oxidation states of tungsten range from $+2$ to $+6$, and some compounds with zero oxidation state also exist. Above 400°C, tungsten is very susceptible to oxidation. At 800°C, sublimation of the oxide becomes significant and the oxidation is destructive. Very fine powders are pyrophoric. Above 600°C, the metal reacts vigorously

Table 3. World Tungsten Resources, 10^3 t[a]

Country	Reserves	Other[b]	Total
North America			
United States	125	325	450
Canada	270	320	590
Mexico	20	5	25
Other	1	2	3
Total[c]	*420*	*650*	*1070*
South America			
Bolivia	39	86	125
Brazil	18	40	58
Other	2	2	4
Total[c]	*60*	*130*	*190*
Europe			
Austria	18	55	73
France	16	2	18
Portugal	24	30	54
U.S.S.R.	210	320	530
U.K.	0.5	65	65
Other	30	9	39
Total[c]	*300*	*480*	*780*
Africa			
Zimbabwe	5	5	10
Other	5	14	19
Total[c]	*10*	*18*	*28*
Asia			
Burma	30	75	105
People's Republic of China	1400	2300	3700
Democratic People's Republic of Korea	110	140	250
Republic of Korea	80	80	160
Malaysia	15	30	45
Thailand	20	20	40
Turkey	75	14	89
Other	5	5	10
Total[c]	*1700*	*2620*	*4320*
Oceania			
Australia	110	260	370
Other	0.5	2	3
Total[c]	*110*	*260*	*370*
World total	*2600*	*4200*	*6800*

[a] Ref. 2.
[b] Derived in collaboration with the U.S. Geological Survey.
[c] Data may not add to totals shown because of independent rounding.

with water to form oxides. In lamps, in the presence of water vapor, a phenomenon called the *water cycle* occurs in which the tungsten is oxidized in the hottest part of the filament and then reduced and deposited on the cooler portion of the filament. Tungsten is stable in nitrogen to over 2300°C. In ammonia, nitrides form at 700°C. Carbon monoxide and hydrocarbons react with tungsten to give tungsten carbide at 900°C. Carbon dioxide oxidizes tungsten at 1200°C. Fluorine is the most reactive halogen gas and attacks tungsten at room temperature. Chlorine reacts at 250°C, whereas bromine and iodine require higher temperatures.

Table 4. Tungsten: World Concentrate Production, by Country[a, b, c]

	Metric tons of tungsten content				
Country	1992	1993	1994	1995	1996[d]
Australia	159	23	11	—[e]	—[f]
Austria	1,489	104	—[d]	188[e]	360[f]
Bolivia	851	287	462	655[e]	582[f]
Brazil	205	245	155	98	100
Burma[g]	531	524	548	531	328
China[d, h]	25,000	21,600	27,000	27,400[e]	24,000
India	2	1	2	2	2
Japan	347	66	—	—	—
Kazakstan[d]	200	200[e]	200	255[e]	220
Korea North[d]	1,000	1,000	900	900	900
Korea Republic of	247	200	—	—	—
Malaysia	3	2	—	—	—
Mexico[d]	162	—	—	228[e]	149
Mongolia[d]	260	250	150	200	200
Peru	543	388	259	728[e]	331[f]
Portugal[d]	1,126	768	100	1,511[e]	1,343[f]
Russia[d]	10,000	8,000	4,000	5,400	3,000
Rwanda[d]	175	175	30	—	—
Tajikastan[d]	200	150	100	75	50
Thailand	70	80	40[e]	60[d, e]	50
Uganda[d]	16[e]	5[e]	12[e]	17[e]	—[f]
United States	—[i]	—[i]	—[i]	—[i]	—[i]
Uzekistan[d]	300	300	300	300	300
Total	*42,900*[e]	*34,200*[e]	*34,300*[e]	*38,500*[e]	*31,500*

[a] Reference 16.

[b] World totals and estimated data are rounded to three significant digits, may not add to totals shown.

[c] Table includes data through June 9, 1997.

[d] Estimated.

[e] Revised.

[f] Reported figure.

[g] Includes content of tin–tungsten concentrate.

[h] Based on data published in the *Yearbook of Nonferrous Metals Industry of China*, 1993–1996.

[i] Withheld to avoid disclosing company propietary data, not included in total.

Tungsten is resistant to many chemicals. At room temperature, it is only rapidly attacked by a mixture of hydrofluoric and nitric acids. Attack by aqua regia is slow. Hot sulfuric, nitric, and phosphoric acids also react slowly. Sodium, potassium, and ammonium hydroxide solutions slowly attack tungsten at room temperature in the presence of an oxidizing agent such as potassium ferricyanide or hydrogen peroxide. Molten sodium and potassium hydroxide attack tungsten only moderately. The attack is accelerated by the addition of an oxidizer. Tungsten resists attack by many molten metals. The maximum temperature of stability for various metals is as follows:

Metal	Mg	Hg	Al	Zn	Na	Bi	Li
Temperature, °C	600	600	680	750	900	980	1620

In contact with various refractory materials, tungsten is stable in vacuum as shown below:

Refractory	Al_2O_3	BeO	MgO	ThO_2	ZrO_2
Temperature, °C	1900	1500	2000	2200	1600

In reducing atmospheres, however, the temperatures are lower.

4. Sources and Supplies

For tungsten, the normal supply–demand relationship has been distorted by other considerations. At the time of the Korean war the U.S. government decided that tungsten should be classified as a strategic metal and ordered that a stockpile equal in amount to 10 years of estimated consumption be built up. A bountry was paid for any domestic ore concentrate produced. This decision led to the operation of some 300 mines in the country and a price of $200 per short-ton unit (STU) of tungsten.[1] The material produced was placed in a stockpile under the control of the General Services Administration (GSA). Since the late 1950s Congress has from time to time authorized reductions in the amount of material in the stockpile in ways that would not disrupt the marketplace. It can be noted that tungsten was the highest–dollar-value item in the GSA stockpile and therefore was a source of cash other than taxes. In April 1997, Congress voted to eliminate the tungsten stockpile completely by the year 2005. The order to dispose of this item was however rescinded in August 1997.

Both the CIS and Ukraine countries (formerly Russia) and China have also had stockpiles of tungsten and have released substantial amounts in recent years.

Until the early 1970s China marketed the bulk of its tungsten as ore concentrates. The extent of these sales seemed to relate to the need for hard currency rather than market demand, and this led to extreme volatility in the price of tungsten in world markets. It can also be noted that each autonomous region of China competed separately for sales volume. In the 1980s China acquired Western technology to process tungsten to intermediate products such as (ammonium para tungstate) (APT), tungstic oxide, blue oxide, tungsten metal, and tungsten carbide powders. Intermediate materials such as APT or “yellow oxide” and tungsten metal powder were sold at about the same price at one point. The resultant low prices and market disruption caused the U.S. industry to seek protection under antidumping laws, and as a result increased import duties were levied on these intermediate products. Prices had reached levels that were below operating costs for U.S. mines. This led to closure or reduction of activity to a care and maintenance basis of all North American mines where tungsten in the primary metal mined. This situation continues at the present time. It was noted earlier that tungsten mines are located in mountainous areas, and this results in high costs and long lead times to reopen old mines. An important consideration other than competitive operating costs is that selling prices must be predictable and stable long enough to enable recovery of start-up costs.

China has both state-owned and privately owned mines and has introduced some controls over their mines by requiring them to be licensed, setting their production levels and withdrawing subsidies. This may lead to closure of some older mines where the deposits with economic tungsten concentration levels are exhausted.

Following the collapse of the Soviet Union, the demand for tungsten in the Soviet economy fell from 5000 metric tons of tungsten (MTW) to 2000 MTW per year, but the subsidized mines continued operating at their earlier levels until 1996. It can be conjectured that such a dramatic drop in consumption may have been caused by reduced production of ordnance, such as tungsten penetrators. Whatever the cause, this resulted in a substantial inventory buildup of ore concentrate. This material has been drawn down for export to and use in the strong Western economies over the last three years. The statistics of the U.S. Geological Survey Reports (16) in Table 6 indicate a marked drop in mine production on a worldwide basis from 1992 to 1996. Part of the shortfall in mine output has been met by the drawdown of the Russian inventories noted above.

Table 5. Physical Properties of Tungsten

Property	Description or value	Reference
crystal structure	Body-centered cubic	
Lattice constant at 298 K, nm	0.316524	
Shortest interatomic distance at 298 K, nm	0.2741	
density[a] at 298 K, g/cm^3	19.254	
melting point, K	3660	3
	3695 ± 15	4
boiling point, K	5936	5
linear expansion, K^{-1}		6
At 293–1395 K	$4.226 \times 10^{-6}(T-293) + 8.479 \times 10^{-6}(T-293)^2\ 1.974 \times 10^{-13}(T-293)^3$	
At 1395–2495 K	$0.00548 + 5.146 \times 10^{-6}(T-1395) + 1.952 \times 10^{-10}(T-1395)^2 + 4.422 \times 10^{-13}(T-1395)^3$	
At 2495–3600 K	$0.01226 + 7.451 \times 10^{-6}(T-2495) + 1.654 \times 15^{-9}(T-2495) + 7.568 \times 10^{-14}(T-2495)^3$	
specific heat at 273–3300 K, C_p, J/(mol·K)[b]	$24.94\,[(1-4805)/T^2] + 1.674 \times 10^{-3}\,T + 4.25 \times 10^{-10}\,T^3$	6
enthalpy, $H_T - H_{298}$, J/mol[b]	$24.94\,[(T+4805)/T] + 8.372 \times 10^{-4}\,T^2 + 1.062 \times 10^{-10}\,T - 7917.8$	6
entropy at 298 K, J/mol[b]	32.66	5
heat of fusion, kJ/mol[b]	46.0	7
heat of sublimation at 298.13 K, kJ/mol[b]	859.8	8
vapor pressure at 2600–3100 K, Pa[c]	$\log P_{\mathrm{pa}} = (45395/T) + 12.8767$[d]	9
thermal conductivity W/(cm·K)		
at 0 K	0.0	
at 10 K	97.1	
at 50 K	4.28	
at 100 K	2.08	
at 500 K	1.46	
at 1000 K	1.18	
at 2000 K	1.00	
at 3400 K	0.90	
electrical resistivity ρ, at 4–3000 K, nΩ·m	$\dfrac{0.04535\,T^{1.2472} - 2.90 \times 10^{-9}\,T^3}{1 + \frac{(3.442 \times 10^5)}{T^{2.98}}} + \rho_0$	10
total emissivity ϵ_H at 1600–2800 K	$-2.685790 \times 10^{-2} + 1.819696 \times 10^{-4}\,T^4$	11

[a] Determined by x-ray.

[b] To convert J to cal, divide by 4.184.

[c] To convert Pa to mm Hg, multiply by 0.0075.

[d] To convert $\log P_{\mathrm{pa}}$ to $\log P_{\mathrm{mmHg}}$, subtract 2.1225.

Table 6. Salient Tungsten Statistics (Metric Tons of Tungsten Content Unless Otherwise Specified)[a, b]

	1992	1993	1994	1995	1996
United States					
Concentrate					
mine production	—[c]	—[c]	—[c]	—[c]	—[c]
mine shipments	—[c]	—[c]	—[c]	—[c]	—[c]
value (thousands $)	—[c]	—[c]	—[c]	—[c]	—[c]
consumption	4,310[d]	2,870[d]	3,630[d]	6,320	5,420
excluding government stocks	—	—	—	—	—
exports	38	63	44	20[e]	72
imports (for consumption) stocks,	2,480	1,720	2,960	4,660[e]	4,190
Dec. 31					
producer	44	44	44	44	44
consumer	702	592	756	631	569
APT					
production	5,760	4,730[d]	536[f]	2,580[g]	4,450[h]
consumption	7,010	6,970	7,080	7,920[e]	7,800
stocks (consumer and producer)	333	420	82	727[e]	558
Primary products					
net production	8,450	9,410	7,410	8,410[e]	7,810
consumption	6,910	7,580	8,110	8,800[e]	7,530
stocks Dec. 31 producer[i]	1,510	1,480	1,160	1,300[e]	1,400
consumer	601	716	849	547	399
World concentrate					
production	42,900[e]	34,400[e]	34,300[e]	38,500[e]	31,900
consumption[j]	36,500	31,900[e]	31,600	31,000[k]	—[l]

[a] Reference 16.

[b] Data are rounded to three significant digits.

[c] Withheld to avoid disclosing company propietary data.

[d] Excludes 2 months of "withheld" data.

[e] Revised.

[f] Excludes 11 months of "withheld" data.

[g] Excludes 7 months of "withheld" data.

[h] Excludes 4 months of "withheld" data.

[i] Excludes cast and crystalline tungsten carbide powder.

[j] Based on data received from United Nations Conference on Trade and Development, Jan. 1996.

[k] Estimated.

[l] The United Nations is no longer collecting and publishing this information.

A growing factor in determining whether there will be a future shortfall will be the increased use of recycled materials in the industry. It has been reported (16) that in 1996, 2500 tons of tungsten-containing materials, such as used tungsten carbide cutting inserts and mining inserts were recovered for use in the United States equal to 33% of a total year's production of 7500 tons. Worldwide the production of tungsten is estimated at 35,000 tonnes and consumption at 40,000 metric tonnes, recycling 15% of these world amounts would help correct the apparent imbalance. Industry recirculates its own waste or "yield loss" materials from each process step. In addition, from time to time quantities of obsolete armor-piercing ammunition which contain tungsten are released for recovery of the tungsten to industry. The volumes of these materials may be included in statistics for truly recycled material from end users because of intercompany transactions and this too may impact the margin between production and consumption. (see also Section on recycling).

There are two significant processes for recycling tungsten products. The highest-volume process in use is the *zinc process*, in which scrap tools are heated in an argon gas atmosphere together with an amount of high-purity zinc (see also Zinc and zinc alloys). The zinc alloys with the cobalt with a resulting increase in volume that disintegrates the material. The zinc is removed by vacuum distillation leaving the tungsten carbide, cobalt metal, and other cubic carbides in the composition such as tantalum, niobium, and titanium carbides after crushing as a fine powder. This powder can be utilized directly into grade powders for production of cutting inserts. Tools that contain only tungsten carbide and cobalt, such as mining tools, must be separated from tools that contain cubic carbides; this can be done by hand sorting prior to processing. Cubic carbides are typically limited to $\sim$0.2 wt% of the composition for straight WC–Co-grade applications. Tool shape is a factor in sorting; for instance, a mining tool cannot be mistaken for a cutting tool. Initially some material separation was done by mercury flotation where tools containing titanium and tantalum carbides that have a lower density will float. The dangers of mercury poisoning essentially prohibit using this method.

In the second process, which is used commercially for recovery of machined chips of *heavy-metal alloys* containing tungsten, nickel, and iron the “chips” are first oxidized in air and then reduced in a hydrogen atmosphere. Here again the recovered material is a micrometer sized powder that can be incorporated directly into new production.

An alternate process route for both of these classes of material is to oxidize the used or scrap materials and then digest them by fusion in sodium carbonate for recovery through the wet chemical processes used for recovery from ores.

5. Manufacturing and Processing

The complexities of mining tungsten ore are examined in detail by Yih and Wang in their book on tungsten (17). An idea of what is involved can be gathered by a short discussion about two particular mines; the Bishop mine located in the Sierra Nevada mountains in California and the Mittersill mine near Kitzbuhl in Austria.

The Bishop tungsten mine was found in a search for gold in the late eighteenth century. It was developed to support ordnance requirements during World War 1. The mine is at an elevation of 8000 ft (2440 m) and is tunneled for 2 m (3.2 km) into the mountain and has been worked upward to an elevation of 12,000 ft (3660 m). Beneficiation and conversion to APT is at the mine site. The main ore mineral is scheelite embedded in tactite. Mining is mostly by *sublevel stoping* using vertical blast holes and ore removal at the bottom or haulage level. In 1990 the mine was closed on a care–maintenance basis caused by low market prices for ore. The APT plant has a modern liquid ion–exchange (LIX) facility and operates on ores from other Avocet mines located in Portugal, Peru, and Russia or purchased in the open market.

The Mittersill mine ore body was discovered in 1967 by tracing tungsten found in river silt in Germany to its source, where an outcrop of scheelite was found at an elevation of 6900 ft (2100 m) near Kitzbuhl, a ski area in Austria. For the first 6 years after mining began in 1976, open-pit mining was used during spring and summer. The workforce began development for deep mining during the winter snow season; now the ore is only deep-mined. The Austrian government decided that the ore should be processed in country, in areas of low employment. Thus the chemical plant, tungsten reduction, and carburizing operations are at Bergla, about 100 km from the mine. It is interesting to note that this mine is in operation at the present time, whereas there is no mine operating in North America.

At typical concentration levels of 0.3–0.8 wt% the ore must be crushed and milled to a size that exposes the scheelite crystals. Overmilling reduces the efficiency of separation and allows slime containing tungsten to build up and be deposited in the tailings pond. Undermilling leaves small embedded crystals of scheelite in the waste rock.

Beneficiation to reach the international trade practice of requiring concentrates to contain a minimum of 65 wt% of WO_3 is necessary. This is achieved by a combination of stage crushing; gravity concentration, typically by using shaker tables and supplemented by flotation separation for fines; and magnetic separation, where appropriate. (Ferberite and wolframite are feebly magnetic.) Recovery should approach 90%; occasionally tailings can be reworked with alternate technology for further recovery.

The options for treating concentrates to an intermediate tungsten compound, typically ammonium paratungstate, differ for the principal minerals wolframite and scheelite, for their concentration levels, and for the main impurities present. These options are discussed later in this article in the section on chemical processing.

APT can be processed to tungsten metal powder by alternate routes: (*1*) By calcining APT to the yellow oxide WO_3 and then by reduction in hydrogen; (*2*) by calcining to blue oxide $WO_{2.93}$ followed by reduction in hydrogen.

In each case ammonia is removed in the calcining step. This avoids a buildup of nitrogen in the reduction furnace where economics and grain size of the metal required dictate that hydrogen be recirculated. The reaction of hydrogen with tungsten oxide produces water, thus increasing the dew point of the hydrogen. This has a significant influence on the grain size of tungsten produced; a low dew point allows fine grain sizes to be made, whereas wet hydrogen assists in production of coarser tungsten powder. Accordingly, the hydrogen is scrubbed, dried by refrigeration, and then dried by absorption over an activated alumina column so that the dew point can be kept low enough to make fine grain size powder.

Yellow oxide WO_3 is a fine (1–5-μm) powder whereas blue oxide $WO_{2.93}$ (a mixture of $W_{18}O_{49}$ and $W_{20}O_{58}$) retains the coarser structure of the APT crystals typically in the 30–100-μm range. The porosity in a bed of powder between the coarser material is greater than that between a finer powder. In a bed of oxide to be reduced, the lower-diffusion-path cross section in fine oxide leads to a wider grain size distribution than that obtained in the diffusion paths of greater cross section found in a bed of blue oxide. The control of grain size distribution is normally made by changing the depth of the powder in the boat. This translates to a lower-weight throughput when using yellow oxide; thus there is a cost advantage in using the blue oxide.

The reduction process is carried out mostly in multiple-tube, three-zone, gas-fired furnaces. A recirculating hydrogen gas atmosphere with controlled dew point is normal. The tubes and work boats are typically cast high-temperature alloys. Automated arrangements for charging controlled weights of oxide to the boats, loading, unloading, and discharging boats are preferred for good quality control and low operating costs. A 14-tube furnace can produce about 1.5 tons of tungsten per day. This varies with the grain size required; output is lower for fine grain sizes. An alternative is to use a large-diameter rotary furnace, which can be useful for finer grain sizes, although there may be some carryover of fine powder into the recirculating system with this design. This requires the equipment to be shut down periodically to recover material carried into the recirculating system.

Since the bulk of tungsten is used in hard metals as carbides, the additional process steps to accomplish this at the powder stage are outlined. Tungsten powder is mixed with carbon powder produced by burning, in a low-oxygen atmosphere, natural gas or other hydrocarbons available at oil refineries. The mixture of tungsten and carbon powders may be lightly consolidated or compacted into bars, which are then placed in graphite boats. The mixture is heated typically in a stoker-type electric muffle furnace using molybdenum or graphite heating elements in a hydrogen atmosphere. The hydrogen, which enhances the carburizing reaction, is burned on exit from the furnace. It is not recirculated since it carries impurities. This reaction is strongly exothermic, and temperatures of up to 1750°C can be reached briefly in furnaces set at 200°C below that. The product is controlled closely for combined and free-carbon content, average grain size, and grain size distribution in both the “as received” condition and “as lab-milled” condition. Lab milling breaks down aggregates but does not change the particle size. In production, a milling or vibratory sieving operation is normal to break up aggregates.

Wear applications for carbides are best serviced with carbide powders below 1 μm, and this is a rapidly growing market segment. Existing technology has limitations for these nanometer-sized carbides. Carburizing in a fluidized bed with its shorter dwell time is promising. At the time of writing, the Dow Chemical Company is expected to have a new facility on stream in 1998 with 500 t/yr capacity using new technology.

Cemented carbides (see also Carbides) are prepared from micrometer-sized mixtures of WC and cobalt plus, in some compositions, cubic carbides of titanium, tantalum, and niobium. These mixtures are wet-milled in a liquid that is environmentally acceptable, such as a higher alcohol, heptane, or water. A temporary lubricant/binder (eg, in paraffm wax at 1.5–2 wt%) is conveniently added during the milling operation, to facilitate the next process step of compacting the powders. After drying these slurries, the powder mixture does not readily flow in feed shutes for the automatic compacting presses. This is overcome by granulating the powder into 30–70-μm granules. One way to do this is to prepress the powder mixture in the pressure range 35–50 MPa [5000–7250 psi (lb/in.^{2})] and crush the material in a Stokes granulator followed by sieving a 35/50-mesh fraction. Expect an 80% yield, and recirculate the fines. A more elegant method of producing granules with a good flow rate is to spray-dry the wet slurry directly from the milling operation in a Niro spray drier. A nitrogen atmosphere is necessary for use of all organic liquids, but water-based emulsions may be sprayed in air. The spray-dried spherical granules have Hall flow rates of ~20–30 seconds when the liquid/lubricant combination results in an emulsion but if the lubricant is soluble in the liquid, 25–35 s is more likely, caused by solvent retention at solidification. A time of ~37 s is borderline for a no-flow condition. The importance of this flow rate is that the compacting press used for production has tooling set up to put powder into a die cavity on a volume basis, whereas the real need is to achieve a constant weight of powder in the die cavity. Consistent and free-flowing powders are critical for continuous operation of automatic compacting presses and for maintaining good dimensional control of the sintered product. Sintered dimensions relate to the "shrink factor" characteristic of the powder, the weight charged to the die cavity controlled by the height of the "fill" in the die cavity. The compacting pressure is set to give the correct height for the pressed compact.

5.1. Wrought Tungsten

Because of its high melting point, tungsten is usually processed by powder metallurgy techniques (see Powder metallurgy). Small quantities of rod are produced by arc or electron-beam melting.

For rod and wire production, ingots ranging in sizes from 12 to 25 mm square by 600–900 mm are mechanically pressed at ~300 MPa (45,000 psi). The bars are very fragile and are presintered at 1200°C in hydrogen to increase their strength. Sintering is done by electric resistance heating. The ingot is mounted between two water-cooled contacts inside a water-jacketed vessel containing a hydrogen atmosphere. A current is passed through the ingot, heating it to about 2900°C. This not only sinters the bar to a density of 17.9–18.2 g/cm^3, but also results in considerable purification by volatilization of impurities. Larger billets for forging or rolling are isostatically pressed. The powder is placed in a plastisol bag, sealed tightly, and placed in a fluid in a high-pressure chamber at 200–300 MPa (30,000–45,000 psi). Sintering takes place in an electric-resistance or induction-heated furnace at 2200°C in a hydrogen atmosphere. Densities after sintering are 17.8–18.1 g/cm^3. Small parts are made by mechanically pressing powder to which a lubricant has been added, followed by sintering at 1800–2100°C. For some applications, the sintering temperature can be lowered to 1500°C by the addition of small amounts of nickel or palladium, which do, however, embrittle the tungsten.

5.2. Metalworking

Tungsten is unusual in that its ductility increases with working. As-sintered or after a full recrystallization anneal, it is as brittle as glass at room temperature. For this reason, it is initially worked at very high temperatures, and large reductions are required to achieve ductility. Furthermore, the low specific heat of tungsten causes it to cool very rapidly, and any working operation requires rapid transfer from furnace to working equipment and frequent reheating during the working operation.

Swaging, is historically the oldest process used for the metalworking of tungsten and is the method used first for the manufacture of lamp wire (Coolidge process). Swaging temperatures start at 1500–1600°C and decrease to ~1200°C as the bar is worked. These temperatures are just below the recrystallization temperature and the working is, therefore, technically "cold working." Reductions per pass start as low as 5% but then increase to as high as 30% as the size decreases. Total reductions of ~60–80% between anneals are possible.

For rod and wire production, rod rolling—or, more recently, Kocks mill rolling—is applied, at least in the initial breakdown stages. For rod rolling, oval-to-square sequences are used with reductions of 15–25% per pass. A Kocks mill consists of 8–12 roll stands in sequence, with each stand consisting of three rolls at 120° to each other, producing a hexagonal cross section. The material is rolled through the stands at very high speeds to avoid cooling problems. Wire drawing starts at ∼4 mm ϕ (diameter) and at temperatures as high as 800°C, decreasing to 500°C for fine wire. The graphite lubricant required must be replaced after each draw pass. Reduction per pass is 30–35% at the start of drawing and drops to 7–10% in fine wire. For drawing dies, tungsten carbide is used to a diameter of 0.25 mm; for smaller wire diameters, diamonds dies are used.

For larger-diameter rods or plates, rolling is also employed, with temperatures starting at 1600°C. However, for rolling large cross sections, very sturdy and powerful equipment is needed to handle large reductions; otherwise large center-to-edge variations develop. These variations lead to center bursting or nonuniform structures after annealing. Large total size reductions overcome this effect to some extent. As the material is worked to larger reductions, the temperature is gradually lowered to avoid recrystallization during reheating. Once total reductions in area of >95&*percnt*; are achieved, temperatures can be as low as 300°C.

Forging is also used on tungsten. Hammer forging is generally preferred to press forging because the temperature is better maintained with the higher rate of deformation. Temperature control is also critical here and even more critical with extrusion. Conventional extrusion of glass-coated billets is employed. A rather delicate balance between heat loss in the billet and heat generation in the die is required for good results.

5.3. Chemical Processing

5.3.1. Mining and Beneficiation

Tungsten mines are generally small, producing less than 200 tonnes of raw ore per day. Worldwide, there are only about 20 mines producing over 300 t/d. Many small mines are inactive at times, depending on the market price of tungsten. They are limited primarily by the nature of the ore body, and mining is now performed almost exclusively by underground methods. Where open-pit mining has been employed, underground methods are used as the deposit diminishes. Ore deposits usually range from 0.3 to 1.5% WO_3 with exceptional cases can be as high as 4% WO_3. Because of the low tungsten content of the deposits, all mines have beneficiation facilities that produce a concentrate containing 65–75% WO_3.

Since scheelite and wolframite are both friable, care must be taken to avoid overgrinding, which can lead to *sliming* problems. The ores are crushed and ground in stages, and the fines are removed after each stage. Jaw crushers are employed for the first stage because the tonnages are low. Either jaw- or cone-type crushers are used for the second stage. In some cases, sizes are further reduced by rod milling. After each stage, the fines are removed and the coarse fraction is recirculated. Screening is the preferred method for fairly large particle sizes. Mechanical and hydraulic classifiers can also be used.

Since tungsten minerals have a high specific gravity, they can be beneficiated by gravity separation, usually by tabling. Flotation is used for many scheelites with a fine liberation size but not for wolframite ores. Magnetic separators can be used for concentrating wolframite ores or cleaning scheelites.

5.3.2. Extractive Metallurgy

In extractive metallurgy, a relatively impure ore concentrate is converted into a high-purity tungsten compound that can subsequently be reduced to metal powder. This is a particularly important step since high purity is required for all uses of tungsten except as a steel-alloying additive. The two most common intermediate tungsten compounds are tungstic acid, H_2WO_4 and ammonium paratungstate (APT), $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (see Fig. 1). Most commercial processes today use APT. Depending on their source, the impurities in ore concentrates vary considerably, but those of most concern are sulfur, phosphorus, arsenic, silicon, tin, lead, boron, and molybdenum compounds.

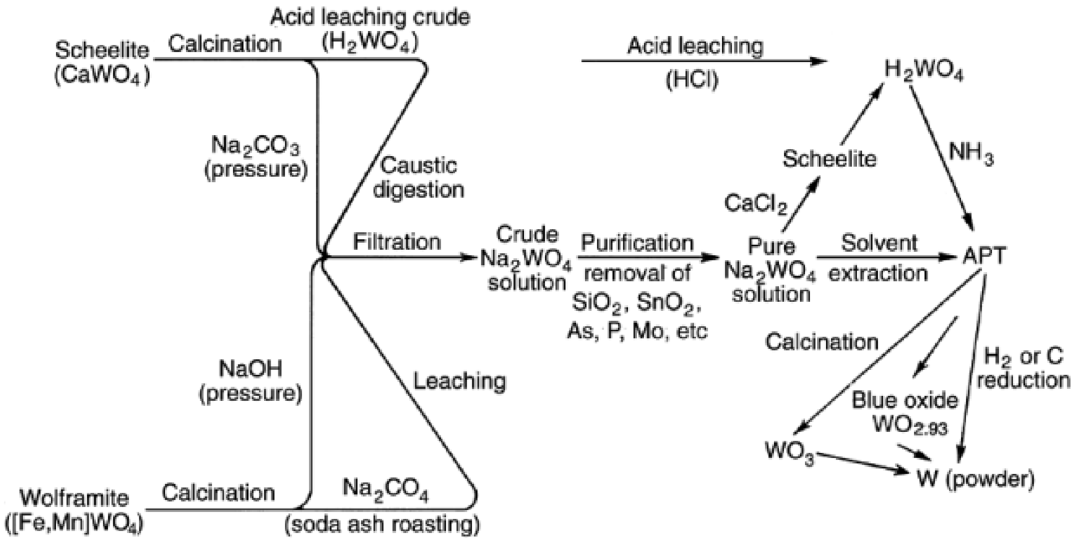

Fig. 1. Production of tungsten materials from ores.

The concentrate may first be pretreated by leaching or roasting. In scheelite concentrates, hydrochloric acid leaching reduces phosphorus, arsenic, and sulfur contents. Roasting of either scheelite or wolframites eliminates sulfur, arsenic, and organic residues left from the flotation process.

Next, the concentrate is digested to extract the tungsten. For lower-grade scheelites, the high-pressure soda process is commonly employed. The concentrate is first ground to $<100\ \mu m$ (-150 mesh) size, and then digested in an autoclave with sodium carbonate at ~200°C at a pressure of >1.2 MPa (~ 11.9 atm).

$$NaCO_3 + CaWO_4 \longrightarrow Na_2WO_4 + CaCO_3$$

The sodium tungstate solution is filtered from the resulting slurry. Similarly, in the alkali roasting process, the concentrate, either scheelite or wolframite, is heated with sodium carbonate in a rotary kiln at 800°C and then leached with hot water to remove the sodium tungstate. Wolframite ores are also decomposed by reaction with a sodium hydroxide solution at 100°C.

$$(Fe, Mn)\,WO_4 + 2NaOH \longrightarrow (Fe, Mn)\,(OH)_2 + Na_2WO_4$$

The insoluble hydroxides are removed by filtration. In another process, scheelite is leached with hydrochloric acid:

$$CaWO_4 + 2HCl \longrightarrow CaCl_2 + H_2WO_4$$

In this case, the tungstic acid is insoluble and is removed by filtration and washed. For purification, it is digested in aqueous ammonia to give an ammonium tungstate solution. Magnesium oxide is added to precipitate magnesium ammonium phosphorus and arsenates. Addition of activated carbon removes colloidal hydroxides and silica, which are then filtered. Evaporation of the ammonium tungstate solution gives APT. The evaporation is not carried to completion, so most of the impurities still present remain in the mother liquor and are removed.

The sodium tungstate from the soda and caustic processes is purified by first adding aluminum and magnesium sulfates to remove silicon, phosphorous, and arsenic, whereas sodium hydrogen sulfide removes molybdenum and other heavy metals. The pH is controlled and the impurities are removed by filtration. Then the sodium tungstate is converted to ammonium tungstate by means of a liquid ion-exchange process. Since this involves the exchange of anions, most of the impurities that are present as cations are left behind. The ammonium tungstate solution is then evaporated to a fixed specific gravity under constant agitation to produce APT.

5.4. Reduction to Metal Powder

The metal powder is obtained from APT by stepwise reduction with carbon or hydrogen. The intermediate products are the yellow oxide, WO_3; blue oxide, W_4O_{11} (which is actually a mixture of two oxides, $W_{18}O_{49}$ and $W_{20}O_{58}$); and brown oxide, WO_2 (see Tungsten compounds). Because carbon introduces impurities, hydrogen is preferred. The reduction is carried out in either tube furnaces or rotary furnaces, heated by gas or electricity and having three separately controlled heat zones. A tube furnace consists of multiple tubes 7–9-m long 80–150 mm diameter. The boats containing the oxide have rectangular or semicircular cross sections and are 375–450-mm long. Both tubes and boats are made of Inconel or a similar heat-resistant alloy (see High temperature alloys). The boats are either manually or automatically stoked through the furnaces. Hydrogen is fed through each tube countercurrent to material flow. The hydrogen is recirculated and is scrubbed, purified, and dried, and new hydrogen is added in each cycle. To avoid a buildup of nitrogen in the recirculating system, the ammonia present in the APT must be removed. This is achieved in the calcining to WO_3 and also in the preparation of the blue oxide; however, for environmental and economic reasons, however, it is easier to collect the ammonia from the closed blue oxide furnace. Today the bulk of tungsten is produced via the blue oxide process. A rotary furnace consists of a large tube 3–10-m long. It is partitioned into three sections to restrict powder movement down the tube and has longitudinal vanes to carry the powder. The tube is tilted at a small angle and rotated to provide continuous flow of powder through the furnace.

Ammonium paratungstate is decomposed to yellow oxide by heating in air at 800–900°C. The blue oxide is obtained by heating APT to about 900°C in a self-generated atmosphere in the absence of air. Metal powder can be made directly from APT, but particle size is better controlled with a two-stage reduction by controlling temperature, bed depth, and hydrogen flow. Since rotary furnaces have effectively a shallow bed, they tend to be used to produce fine powders. Tube furnaces are generally preferred for the final reduction. Temperatures of 600–900°C are used to produce particle sizes of 1–8 μm.

For the production of lamp-filament wire, potassium, and potassium aluminum silicate dopants are added to the blue oxide. Some dopants are trapped in the tungsten particles on reduction. Excess dopants are then removed by washing the powder in hydroflouric acid. For welding electrodes and some other applications, thorium nitrate is added to the blue oxide. After reduction, the thorium is present as a finely dispersed thorium oxide.

6. Economic Aspects

The worldwide value of the tungsten industry is estimated to be about 1.6 billion dollars and in the United States to be about $450 million. The mining and beneficiation to a minimum 65% level has as its share a value of approximately $145 million worldwide and essentially zero in the United States, where no tungsten has been mined since 1989. The added value for recovery of tungsten from concentrate to the intermediate salt APT is about $30 million, of this amount, roughly $6 million is for conversion in the United States. The additional added value for production of tungsten metal powder and tungsten carbide is about $26 million in the United

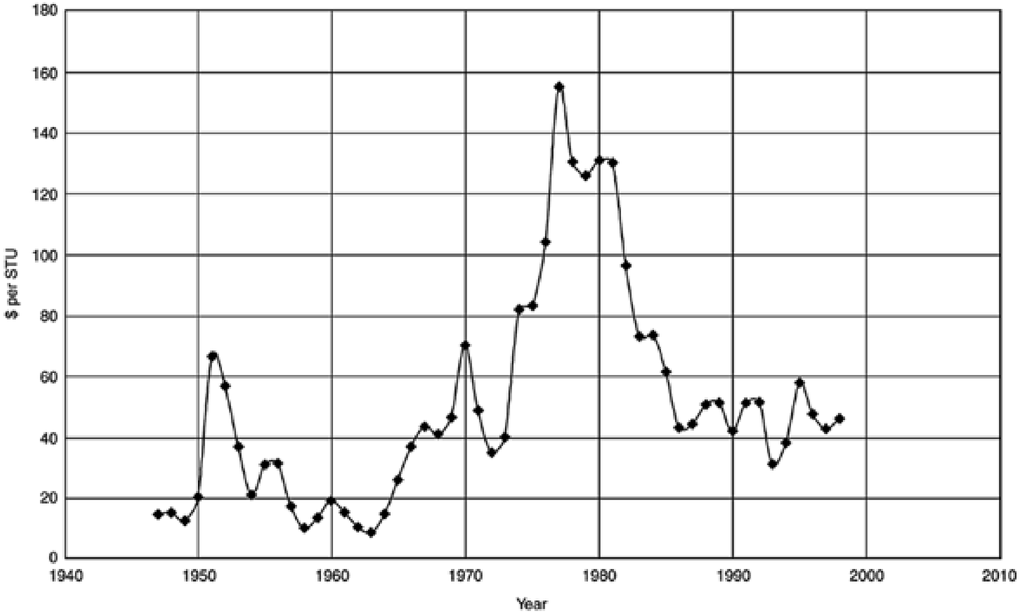

Fig. 2. Mean *London Metal Bulletin* price for tungsten ore concentrate.

States. Final product manufacture accounts for an additional added value of about $315 million in the U.S. market.

The price of tungsten metal is very volatile (see Table 7 and Fig. 2). There are a number of external factors affecting this, besides the normal influence of supply and demand.

- The former Russian government, the Chinese government, and the U.S. government all have had stockpiles of tungsten in various forms but principally as ore concentrates for many years. The objectives for these stockpiles differed in emphasis, but a common factor has been to reduce the amounts of material held. Indications are that both the former Russian and Chinese stocks are largely depleted. Whereas Congress had set a target date to dispose of the U.S. GSA stockpile by the year 2005, this has been put on hold, at least temporarily.
- Since tungsten ores are found in mountainous areas at high altitudes and in relatively small pockets, new mines take a long time to become productive and cannot immediately influence the supply side.
- Low prices for Chinese concentrates (about $50 per unit) and other intermediate products since the late 1980s has caused all North American mines to cease production. While most are on a care-maintenance basis, prices of the order of $90 per unit will need to be sustained to reverse this situation.
- The market is further distorted by nonuniform import duties, between ore, intermediates, tungsten and tungsten carbide powders, and scrap materials (see Table 8). An antidumping tariff of 150% on intermediates is in effect for Chinese source materials.
- Statistics show in general that consumption exceeds production. There may be some distortion in the statistics caused by recovery of scrap materials from production and recycling of used products, which may be on an intercompany basis. However, there is an underlying trend showing an increased gap between consumption and production.

In the late 1970s the industry had a few large vertically integrated companies and many smaller companies covering the later process steps only. The large companies have grown in good part by increased

Table 7. Tungsten Prices \$/kg[a, b]

Year	WO_3	W
Late 1950s	2.42	3.05
1962	0.88	1.10
1977	17.80	22.19
1982	10.63	13.40
1994	4.54	5.65
1996	6.62	8.34

[a] Reference 16.
[b] To convert \$/kg to \$/STU (short-ton unit), multiply by 9.07. The STU contains 9.07 kg WO_3 or 7.19 kg W.

Table 8. U.S. Import Duties for Tungsten, May 1998

Product form		Duty[a]
Ore and concentrate	(2611.00)	\$0.375/kg tungsten
Ammonium paratungstate	(2841.80)	6.4% advalorum
Tungsten oxides	(2825.90)	6.4%,
Tungsten carbides	(2849.90.30)	8.5%,
Tungsten powder	(8101)	7.7%,
Tungsten wire		6.5%,
Cemented tungsten carbide	(8113)	41.%,
Tungsten scrap		0.0%,

[a] Duty drawback is allowed for exported material.

international activity. The smaller companies have been consolidated into larger and more efficient units. The driving forces for this are twofold: (*1*) owners and managers of private companies have wanted to retire, and (*2*) financiers have seen an opportunity to build larger units that could be offered on a stock exchange.

Only the major companies operating in each country are listed in alphabetic order in Table 9 with notes regarding their range of activity. Some of these companies are units of conglomerates so that financial data are not generally available relative to their tungsten operations.

These companies constituting the greater part of the industry have formed an active international association, ITA (International Tungsten Association), headquartered in London, to promote the use of tungsten and to analyze factors such as those affecting future supplies, health, safety, and environmental questions and governmental actions on tariffs.

The high-temperature processes for tungsten require substantial amounts of energy. Plant location for the high-demand process steps is important. In states such as Tennessee and Alabama, where the Tennessee Valley Authority operates, 1 kWh of electricity costs 6 cents, whereas in the Northeast it costs 12.1 cents. Initially the industry sintered materials in a hydrogen atmosphere and the hydrogen was generated locally by electrolysis of water. Today sinter processes are almost universally carried out in vacuum furnaces that combine removal of the lubricant (typically paraffin wax used in compacting the powder) and the high-temperature sinter or consolidation process. Development of a process using microwave heating decade for sintering ceramic materials has been under way since the late 1980s, and has recently been used to heat-press compacts for dewaxing and sintering of cemented carbides. Patents have been granted in Germany. It is expected that this process, which sinters at somewhat reduced temperatures and uses only a fraction of the power consumed in existing furnaces, will initially be used for processing micrograin materials, a rapidly growing market segment. Hydrogen is still needed for the reduction and carburizing process steps, but today the source for hydrogen is the lower-cost natural-gas industry. Where applicable, such as in the heating of tungsten reduction furnaces, natural gas is the preferred low-cost energy source. The distribution of the direct costs in the reduction and carburizing processes for tungsten is as follows: hydrogen 5%, natural gas 3%, electricity 6%, carbon 10%, and labor 76%.

Table 9. Major Tungsten-Producing Companies in Operation in Market Economy Countries in 1998, by Country

Country/Company	Remarks
Austria	
Plansee Metall AG:	a leading producer of wrought tungsten; produces tungsten carbide powders and sintered tungsten carbides for cutting and metal forming tools; holds many patents; is vertically integrated and markets its products internationally
Wolfram Bergbau und Hutten GmbH:	owned by Inmet of Toronto, Canada; operates the Mittersill mine; converts ore to intermediate products; produces tungsten and tungsten carbide powders in Bergla; annual production ~3000 tonnes; annual capacity, ~3500 tonnes
Brazil	
Brassinter SA:	a vertically integrated company starting from intermediates; produces tungsten carbide cutting and metal forming tools; recycles materials by both the “zinc process” and chemical routes; markets in South American and European countries
Canada	
North American Tungsten:	purchased assets of Canada Tungsten, which includes the Can Tung mine in the Northwest Territories, the Mac Tung property and the Hemerdon mine in England; has part ownership of APT equipment at Bishop mine in California.
Sweden	
Sandvic Coromant A.B.:	a large international producer of tungsten carbide cutting tools; the company grew rapidly in 1960s by acquisition of existing producers domestically and abroad, and is now the major producer or supplier in each European country
Seco	operating as “Seco Rock,” has always been a major supplier of tungsten carbides for mining applications, in part because of their close association with Atlas Copco, mining machines manufacturer; is an international operator; after a period of retrenchment, “Seco Tool” acquired the “Carboloy” division of the General Electric Co. in the United States and transferred much of the processing to Sweden; the company is a vertically integrated producer
United States	
Avocet Tungsten Inc.:	a wholly owned subsidiary of Avocet Mining PLC in the United Kingdom; largest mine operator in Market Economy Countries (MEC); mines in Portugal (Beralt), two mines in Peru 2, U.S. Bishop joint venture with U.S. Tungsten; Russia, 10% interest in Lermontov mine; APT conversion capacity 4100 tonnes/yr; AMT 800 tonnes/yr
Kennametal Inc.:	a leading producer of tungsten carbide and other metal cutting and forming products; operates internationally, is a vertically integrated producer from ore to finished products; operates a unique “menstruum” process for production of coarse tungsten carbide powders
Osram Sylvania Inc.:	formerly GTE Sylvania; is a leading producer in the tungsten “lightbulb” and tungsten chemical compounds fields; converts from ores to APT and AMT; produces tungsten, tungsten
Germany	
Hermann C. Starck:	produces tungsten and tungsten carbide powders from ore concentrates and by recycling of tungsten containing materials
Krupp Widia GmbH:	owned by Cincinnati Milacron USA; a vertically integrated producer of metal cutting and forming tools; has patents in some new technologies, including “microwave sintering” of tungsten carbide alloys; operates internationally
Walter Hartmetall GmbH:	a joint venture of Walter and the U.S. company Ingersoll Inc.; makes metal cutting inserts from grade powders; specializing in tools for milling of metals
Japan	

Table 9. *Continued*

Country/Company	Remarks
Mitsubishi	a vertically integrated producer of cemented carbides for metal cutting and forming tools; operates internationally
Tokyo Tungsten:	a producer of cemented carbide cutting tools
South Africa	
Boart Longyear Ltd.:	a producer of cemented carbides for mining tools, Morgan mill rolls and anvils used in diamond synthesis used in diamond synthesis at high temperatures and pressures; has recycling capabilities
South Korea	
Korean Tungsten Mining Company:	owns mines, but currently produces tungsten intermediates, tungsten, and tungsten carbides from ore concentrates for international markets carbide, and hard-metal-grade powders; operates chemical recovery processes for tungsten-bearing materials
Teledyne Metal Working Products	owned by Allegheny Teledyne Inc.; is the major producer of tungsten, tungsten carbide, and grade powders in the United States; operates internationally in both powders and in its Stellram division for finished products; is the largest operator of the “zinc reclaim” process for recycling used cemented tungsten carbide products; operates a chemical recovery unit also for recovering used tungsten bearing-materials; is a producer of wrought tungsten wire, welding electrodes, and sheet products; manufactures high-density tungsten alloy components

From the initial mining of the ore body, where the mining plan and its execution determine what percentage of the tungsten present in the lode is recovered, through every process step thereafter the question is always “What is the yield.” Good yields are the key to low cost and on-time deliveries in this industry. In some cases “yield” is a tradeoff against quality, such as between impurity levels and recovery in crystallizing APT. Another factor requiring close attention is that a problem in one process step may not be detected until two or three process steps later. Five sequential process steps, each with a 98% yield, give an overall yield of only 88%. One mitigating factor is that the tungsten is not lost and is typically only about 20% of the overall product cost. A significant factor in this area is the move to using statistical quality control and ISO (International Standards Organization) 9000 quality-control certification programs.

The industry is structured in a pyramid fashion with only a few companies operating from APT through manufacture of grade powder with increasing numbers of sintering material and more still in finishing operations. This is now driven by economics, whereas in earlier times it was considered necessary to carry out every process as an “acknowledgment” of a company’s “technical prowess.” Economy of scale and the large investments needed in the earlier stages for automation and lower labor costs are another factor in this trend. Cutting inserts are sized to international standards; the product identification may differ, but except for the “marking,” the same product can be marketed anywhere in the world.

7. Grades, Specifications, and Quality Control

There is a *World Directory of Companies* that lists companies and their products operating in the tungsten carbide industry (19) and showing the grade designations and their applications. There are two principal systems for grade designation. Under the ISO system the grade designation indicates the application field for the grade; for instance, K20 would indicate a tool for general-purpose machining of cast iron, and P10 would indicate a grade for finish machining of steel. Under the U.S. industry system the grade designation defines the characteristics of the cutting tool itself; for example, C1 would indicate a high-hardness, low-cobalt, fine-grain straight WC cobalt grade for light machining of cast iron whereas C2 would denote lower hardness, increased cobalt, and coarser grain size, indicating increased toughness for heavier-duty cutting. For the "straight" tungsten carbide cobalt grades, cobalt content and hardness on the Rockwell A scale essentially designate the grade. In grades containing cubic carbides, there were categories identifying the application, but these were still overridden by companies who wanted to identify their particular products. Today the performance of cutting tools depends more on the multilayer coatings of titanium carbides, nitrides or carbonitrides, and aluminum oxides that do the actual cutting work, the structure of the transition zone between the substrate and the coating, than the substrate itself, which was previously used as the tool. Today the identification relates more to the coating than the substrate.

The ISO has developed a formal program, ISO 9000 for requirements in a quality-control system, and a system of accreditation that audits facilities for compliance initially, and at regular intervals. Large, accredited manufacturing companies in the United States and abroad require their suppliers to be accredited in this program. This requirement has resulted in an upgrade of quality control in the tungsten industry, in particular by the increased use of statistical process control techniques.

The carbide industry in the United States initially controlled its final product by Rockwell hardness testing on the A scale. Organized by the Cemented Carbides Producers Association (CCPA), the principal carbide manufacturers operating in the United States periodically check by means of a round-robin method that they are all in agreement. A more appropriate hardness test would have been the Vickers pyramid diamond measurement commonly used in Europe. Today the hardness test is supplemented by measurement of magnetic properties for *magnetic saturation*, which gives an indication of the magnetic cobalt in the material, which varies from the total cobalt present according to the carbon level. A second magnetic property, coercive force, varies according to the grain size in sintered material. There is normally some grain growth during sintering. Knowing the starting grain size a comparison with the coercive force value gives an indication of acceptable sinter parameters. Graded powders are traded today with close specification limits on magnetic properties that can be achieved in the sinter process.

8. Analytical Methods

The presence of tungsten is usually identified by atomic spectroscopy. With optical emission spectroscopy, tungsten in ores can be detected at concentrations of 0.05–0.1%, whereas X-ray spectroscopy detects 0.5–1.0%. Scheelite in rock formations can be identified by its luminescence under ultraviolet radiation. In a wet method, the ore is fired with sodium carbonate and then treated with hydrochloric acid; addition of zinc, aluminum, or tin produces a brilliant blue color if tungsten is present.

In the convention method for the quantitative analysis of tungsten in ore concentrates, the ore is digested with acid, and the tungsten is complexed with cinchonine, purified, ignited, and weighed. More commonly today, X-ray fluorescence spectrometry is used and its accuracy is enhanced with a known addition of tantalum as an internal standard. Assays for ores for calculation of price differentials from the nominal 65% level of WO_3 are usually made at independent laboratories. X-ray fluorescence is an important tool for bulk chemical analysis in the presence of tungsten, and of cobalt, tantalum, and niobium in both grade powder and recycled products. The material to be assayed is calcined to the oxide, then fused with lithium tetraborate and cast into discks about 30 mm in diameter. The disk is irradiated with X rays from a rhodium target, and the secondary X rays generated are analyzed for wavelength and intensity by element.

Analysis of *trace elements*, including aluminum, calcium, copper, nickel, molybdenum, sodiumm, silicon, and potassium, is done by *atomic absorption* (AA) on a solution (using HF/nitric acids) that is aspirated into a flame burning a nitrous oxide, acetylene mixture (see Trace and residue analysis). Routinely AA instruments use absorption tubes that measure only one or two elements at a time. A technique that uses either a *direct-coupled plasma* (DCP) or an *inductively coupled plasma* (ICP), rather than a flame to excite the sample, allows determination of multiple elements simultaneously.

Carbon and sulfur contents are determined by ignition in a flow of oxygen, in which the carbon dioxide released is detected by absorption of infrared light; and sulfur dioxide content is determined by instruments manufactured by the Laboratory Equipment Company of St. Joseph, Minnesota (Leco).

Oxygen content of materials in the ppm range is measured by vacuum fusion in a pure metal additive in the presence of carbon, any CO evolved is converted to CO_2. Heating of the sample is by high-frequency induction, and the carbon dioxide evolved is measured by infrared absorption.

9. Environmental Concerns

The fact that tungsten is found in relatively small ore bodies, at higher altitudes in mountainous country, together with rather low concentration levels, makes it imperative to concentrate the ore at the mine site. Two factors are of concern in this situation: (*1*) beneficiation of the ore, which is in part a wet process, and leading to the need for a storage and settling pond, thus posing a risk of leakage into waterways at lower altitudes; and (*2*) spoilation of the area, in which crushed rock is discarded, unless it can in part be returned to worked-out areas of the mine.

Similar risks are found at the sites of chemical processes to refine and convert tungsten to intermediates such as ammonium paratungstate. Again the effluents discharged to a *holding pond* are a controlled risk to the environment. Permissible concentration levels will be set at the planning stage for such holding ponds as well as limits for discharge and or disposal.

Overall, residues and effluents from tungsten recovery and processing are readily handled and are not considered to be high risk.

10. Recycling

In recent years, processes that can convert used carbide cutting tools and used tungsten alloy penetrators back into powdered form that can be used directly new products have been developed. At the time of writing it is estimated that in 1998 ∼30–35% of cutting inserts used in the United States will be recycled in this way.

Trent at Powder Alloys Limited (UK) proposed recovery of used carbide tools by immersing them in molten zinc (20). Cobalt and zinc are mutually soluble, and by penetration of the zinc into cemented carbides, there is an increase in volume and on cooling the carbides are left dispersed in the Co/Zn alloy. The carbides were recovered by acid leaching the Co/Zn. The U.S. Bureau of mines demonstrated an improvement on this process by removing the zinc by vacuum distillation (21). This allows recovery of both carbides and cobalt as fine powders. Initially the driving incentive for this process was recovery of high-tantalum-content materials, however, cobalt and tungsten prices later increased such that they were of equal importance. Residual traces of zinc are released during vacuum sintering of cemented carbides made with recovered powders; this can be troublesome when a buildup of zinc occurs in the furnace. Teledyne Wah Chang further developed this process on a commercial basis by achieving zinc levels in the low ppm range (∼20 ppm). The fact that the materials were vacuum-sintered in their original form where certain impurities are removed leads to lower impurity levels in the recovered powders. There is a slight oxidation or loss of carbon that must be compensated; otherwise the recycled powder is not in any way inferior.

High-density tungsten alloy machine chips are recovered by oxidation at about 850°C followed by reduction in hydrogen at 700–900°C. Typically the resultant powders are about 3 μm in grain size and resinter readily. There can be some pickup of refractory materials used in furnace construction, which must be controlled. This process is important commercially. For materials that may be contaminated with other metals or impurities, the preferred recovery process is chemical conversion as for ores and process wastes. Materials can always be considered for use as additions in alloy steel melting.

11. Health and Safety Factors

There are no documented cases of tungsten poisoning in humans. However, numerous cases of pneumoconiosis have been reported in the cemented-carbide industry, but whether its cause is WC or cobalt has not been definitely determined. It has been stated that the principal health hazards from tungsten arise from inhalation of aerosols during mining and milling operations. The principal compounds of tungsten to which workers are exposed are ammonium paratungstate, oxides of tungsten (WO_3, W_2O_5, WO_2), metallic tungsten, and tungsten carbide. In the production and use of tungsten carbide tools for machining, exposure to the cobalt used as a binder or cementing substance may be the most important hazard to the health of the employees. Since the cemented tungsten carbide industry uses such other metals as tantalum, titanium, niobium, nickel, chromium, and vanadium in the manufacturing process, the occupational exposures are generally to mixed dust.

Potential occupational exposures to sodium tungstate are found in the textile industry, where the compound is used as a mordant and fireproofing agent, and in the production of tungsten from some of its ores, where sodium tungstate is an intermediate product. Potential exposures to tungsten and its compounds are also found in the ceramics, lubricants, printing inks, paint, and photographic industries.

11.1. Permissible Exposure Limits in Air

Occupational exposure to insoluble tungsten shall be controlled so that employees are not exposed to insoluble tungsten at a concentration greater than 5 mg/m^3 of air, measured as tungsten, determined as a time-weighted average (TWA) concentration for up to a 10-h workshift in a 40-h workweek.

Occupational exposure to soluble tungsten shall be controlled so that employees are not exposed to soluble tungsten at a concentration greater than 1 mg/m^3 of air, measured as tungsten determined as a TWA concentration for up to a 10-h workshift in a 40-h workweek. A short-term exposure limit (STEL) value of 5 mg/m^3 was set by the American Conference of Governmental Industrial Hygienists (ACGIH) in (22).

Occupational exposure to dust of cemented carbide containing more than 2% cobalt shall be controlled so that employees are not exposed at a concentration greater than 0.1 mg/m^3 of air, measured as cobalt, determined as a TWA concentration for up to a 10-h workshift in a 40-h workweek.

Occupational exposure to dust of cemented carbide that contains more than 0.3% nickel shall be controlled so that employees are not exposed at a concentration greater than 15 μg $nickel/m^3$ of air determined as a TWA concentration for up to a 10-h workshift in a 40-h workweek.

Hazards encountered with tungsten may be caused by substances associated with the production and use of tungsten, including As, Sb, Pb, and other impurities in tungsten ores; Co aerosols and dust in the carbide industry; and thoria used in welding electrodes. Lanthanum is being promoted as a substitute for thoria in this application.

A considerable difference in the toxicity of soluble and insoluble compounds of tungsten has been reported (18). For soluble sodium tungstate, $Na_2WO_4{\cdot}2H_2O$, injected subcutaneously in adult rats, LD_{50} is 140–160 mg W/kg. Death is due to generalized cellular asphyxiation. Guinea pigs treated orally or intravenously with $Na_2WO_4{\cdot}2H_2O$ suffered anorexia, colic, incoordination of movement, trembling, and dyspnea.

Orally in rats, the toxicity of sodium tungstate was highest, tungsten trioxide was intermediate, and ammonium tungstate [15855-70-6], least. In view of the degree of systemic toxicity of soluble compounds of tungsten, a threshold limit of 1 mg of tungsten per cubic meter of air is recommended. A threshold limit of 5 mg of tungsten per cubic meter of air is recommended for insoluble compounds.

The market share by application should be evident from the U.S. Geological Survey data shown in Table 10. However, the withholding of data for nondisclosure of proprietary company data does not allow an accurate breakdown by product segment.

The largest usage of tungsten is in the form of tungsten carbide, as the major constituent in *hard metals*, where—bonded with cobalt and in some cases with cubic carbides—properties can be suited to the cutting,

Table 10. Reported Consumption (Metric Tons of Tungsten Content) and Stocks of Tungsten Products in the United States in 1996, by End Use[a,b]

End use	Ferro tungsten	Tungsten metal powder	Tungsten carbide powder	Tungsten scrap[c]	Other tungsten materials[d]	Total
Steel						
stainless and heat-resistance	—[e]	—[e]	—[e]	—[e]	2	2
alloy	33	—	—	—	—	33
tool	434	—	—	—	—[e]	434
Superalloys	—[e]	—[e]	—[e]	—[e]	—[e]	—[e]
Alloys (excludes steels and superalloys)						
cutting and wear-resistant materials	—[e]	—[e]	—[e]	—[e]	—[e]	—[e]
other alloys[f]	—[e]	—[e]	—[e]	—[e]	—[e]	—[e]
Mill products (made from powder)	—	551	—	—	—	551
Chemical and ceramic uses	—	—	—	—	90	90
Miscellaneous and unspecified	55	158	5,760	415	32	6,420
Total	*522*	*709*	*5670*[g]	*415*	*123*	*7,530*
Consumer stocks Dec. 31, 1996	27	36	298[g,h]	24	14	399

[a] Ref. 16.

[b] Data are rounded to three significant digits and may not add to totals shown.

[c] Does not include that used in making primary tungsten products.

[d] Includes tungsten chemicals and others.

[e] Withheld to avoid disclosing company proprietary data; included in "Miscellaneous and unspecified."

[f] Includes "welding and hard facing rods" and "materials and nonferrous alloys."

[g] Based on reported consumption plus information from secondary sources on companies not canvased; includes estimates.

[h] Includes scheelite, natural and synthetic.

drilling, forming, or molding application. Tungsten carbide accounts for about 65% of all tungsten usage in the United States and 60% in world markets (see Tungsten compound). The particle size and size range distribution are critical for specific applications, and since control of these attributes is determined by process conditions at both tungsten reduction and the carburizing process steps, it is common for suppliers to carry out the complete conversion from tungsten oxide to tungsten carbide. It can be noted that tungsten carbide is only close to being stoichiometric even when an excess of carbon is present. Excess carbon, however, is determental to mechanical properties in sintered hard metals. In fact, substoichiometric or carbon-deficient materials result in some solution hardening of the cobalt binder with tungsten. Certainly the control of the "carbon balance" is one of the most important factors for the quality of hard metals, and this is dependent primarily on this process step. Cutting tools in the form of indexable inserts are the bulk of this market sector. Their performance in use is improved by a factor of >3 by application of thin (1–7-μm) *chemical vapor deposition* (CVD) coatings of titanium carbide, nitride, or carbonitrides and aluminum oxide. Inserts for mining tools are of importance in both mineral recovery and oil prospecting and production. Sintered carbide rools are important in *hot-rod rolling* of steel *rebar* for reinforcement in concrete. The stiffness or high modulus and hardness of sintered carbide is important in rolling of thin sheet metal in Zenzimmer mills. Wear-resistant applications have a significant share of this segment with application in dies for compacting, drawing, or stamping. Wear surfaces can be protected by applying thin tiles of carbide by brazing or cementing with epoxy cement.

About 12–16% of tungsten usage is as an alloy addition. Tungsten added to steels forms a dispersed carbide phase that imparts a finer grain structure and increases the high-temperature hardness. The finer grain size improves toughness and produces a more durable cutting edge. For this type of application, up to 3% of tungsten is used, usually with 1–4% of chromium. For hot-working tool steels, up to 18% tungsten is added. Such steel, when heat-treated at a high temperature, then quenched and tempered, retains its hardness up to "red heat." Tungsten is also used as an additive in nickel- and cobalt-based superalloys. Here again, tungsten imparts high-temperature strength and improved creep strength and wear resistance. (see High-temperature alloys). There is a proportionately higher consumption of tool steel alloys in developing economies and lower usage in advanced economies where tool steel are increasingly being displaced by tungsten carbide tools. European usage of tungsten in tool steels is proportionately higher than in the United States, where, as a result of domestic availability of molybdenum, less tungsten is used in tool steels. An alloy of iron with ~40% tungsten that can be atomized in a size range suitable for use as shotgun pellets has been developed to replace lead, which is no longer acceptable for ecological reasons. The process has been patented (23) and is being taken up commercially.

Metallic tungsten accounts for 12–16% of tungsten consumption. Frequently tungsten is used because of its unique high melting point and low vapor pressure. The best-known use in this field is the manufacture of lamp filaments, where potassium and potassium–aluminum silicate dopants are added to the oxide. After sintering, up to ~60 ppm of potassium is retained in small voids. During working these voids are stretched into long stringers. After heating, they form rows of tiny bubbles that control grain boundary movement, resulting in grains that are much longer than the wire diameter and whose boundaries are at a small angle to the wire axis. This structure is very creep-resistant and allows the lamp filament coil to maintain its shape throughout the life of the lamp. New lighting technology may reduce the amount of tungsten used in lighting in the future. Tungsten is widely used as an electron emitter because it can operate at very high temperatures. Thoria is added to reduce the work function during fabrication and to increase electron emission. It also improves arc stability in welding and increases electrode life. Thoria is a controlled radioactive material, and there is increasing pressure to discontinue its use in tungsten inert gas (TIG) welding electrodes. Lanthanum has been introduced as an alternate material and is showing good promise. The rare-earth metal cerium may be an alternate replacement. Tungsten is used as a target in high-intensity X-ray tubes. Other high-temperature applications include furnace heating elements, heat shields, vacuum metallizing coils and boats, glass melting equipment, and arc lamp electrodes. Tungsten is used in applications requiring high elastic modulus and good wear resistance. An example of this is its use in high-speed impact dot-matrix printers. Its low coefficient of thermal expansion makes it ideal for glass-to-metal seals and as a base for silicon semiconductors. There are few tungsten-based alloys. Tungsten rhenium alloys are used for thermocouple wires and for shock-resistant lamp filaments. Tantalum 10% tungsten alloys show promise for high-temperature corrosion-resistance applications. Partially sintered tungsten can be infiltrated with copper or silver to render materials suitable for electrical contacts, heat sinks, rocket nozzles, and guidance vanes. Composite materials with barium and strontium compounds are used in electron-emitting devices.

Heavy-metal or *high-density tungsten nickel iron alloys* are readily machineable metals with densities in the range 17.0–18.5 g/cm^3 that find application in counterweights for aircraft, (eg, ~750 kg is used on a Boeing 747), for radiation shielding, and for collimation in X-ray equipment. In ordnance applications it can account for 10–20% of the annual consumption for tungsten metal powder. In ordnance 95–97 wt% tungsten alloys are used as armor piercing penetrators in high-rate-of-fire cannons. The naval Phalanx close-in weapons system for defense against missiles is capable of using 400 kg/min of tungsten alloy. Consider a 30-mm cannon mounted on a ground attack aircraft. The weight of ammunition for one mission may weight 2 t of which ~40% will be tungsten alloy. Ammunition procurement is prone to budget cutting, so the demand pattern is cyclical.

Miscellaneous applications that account for about 5–10% of the market share include *hard facing*, where crushed sintered carbide scrap fragments are loaded in tubular steel electrodes for weld deposits on surfaces that need improved wear resistance on bulldozer blades, for example. Fused carbides prepared by decomposing the monocarbide WC to W_2C by arc melting at 2400°C are also used in crushed form inside weld electrodes used in hard surfacing, particularly in the oil-drilling industry. Very coarse tungsten powders in the 30–100-μm size range prepared by a menstruum process or by leaching the binder phase from scrap high-density alloys have high apparent densities to ~11 g/cm^3. They can be bonded or infiltrated to make high-density shaped pieces for balance weights or radiation shielding.

1. One STU is 1/100 of a ton or 20 lb of WO_3, which contains 15.86 lb of W. In the case of a metric ton unit (MTU), it is 10 kg of WO_3 equivalent to 7.93 kg of W.

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THOMAS W. PENRICE
Consultant