CHAPTER 12.40

Tungsten

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PROPERTIES

Tungsten (atomic number 74) is a high-density metal with an extremely high melting point. It was first noted during the 16th century in the tin mines of Germany and later in the tin mines in Cornwall, England. At first, it was said to consume the tin like a wolf and was given the German name *wolfram*. Hence, this is why the atomic symbol is W versus T or Tu.

In the late 1700s, Swedish chemist Carl Scheele identified a compound with calcium and an unknown acid. The acid-forming element was named *tungsten* by Axel Fredik Cronstedt. In Swedish, *tung* means "heavy" and *sten* means "stone." A short time later, the brothers Juan José and Fausto de Elhujar discovered wolframite. Because iron and manganese mainly occur together, and because wolframite contains both iron and manganese ($FeMnWO_4$), it is thus named. The mineral is called ferberite ($FeWO_4$) if it contains only iron. If it contains only manganese, the mineral is called huebnerite ($MnWO_4$). The calcium tungstate that Scheele identified was eventually named after him as *scheelite* ($CaWO_4$). These two minerals—wolframite and scheelite—are the two economically important ores of tungsten and both are mined around the world.

In the mid-1800s, Robert Oxland developed a process to produce pure tungsten metal and iron–tungsten alloys. It would not be until the early 1900s that a practical use for tungsten would be found in filaments for incandescent lightbulbs. About this same time, it was discovered that tungsten could be alloyed with iron to form tool steel. This first became important during World War I when it was misconstrued that Germany would quickly use its supply of ammunition. Germany's use of tungsten–iron alloy as tool steels and cutters produced much more ammunition than thought possible. After the war, it was learned that much of the tungsten had come from the tin mines in Cornwall, England.

Although tungsten carbide had been known since the 1890s, it only became practical to use in 1927 when the Krupp Company in Germany developed a process to cement the carbide together with a binder. Once again, Germany used this new technology to help arm itself for World War II, even with limited natural resources. After the war, tungsten carbide development outpaced tungsten, although both products are extremely important in today's manufacturing.

ORES

Tungsten ores are located around the world including the United States, Russia, Southeast Asia, Portugal, Bolivia, Brazil, Canada, Africa, Korea, and China. China holds about 70% of the world reserves and is the largest producer. Tungsten deposits are all formed from igneous activity, mostly following a magmatic-hydrothermal model. Although the commercial ores are scheelite and wolframite, tungsten does form several other minerals, including the following (Yih and Wang 1979):

- Tungstite or meymacite ($WO_3 \cdot H_2O$)
- Ferritungstite [$Ca_2Fe_2^{2+}Fe_2^{3+}(WO_4)_7 \cdot 9H_2O$]
- Raspite (tetragonal) and stolzite (monoclinic) ($PbWO_4$)
- Russelite (Bi_2WO_6)
- Tungstenite (WS_2)
- Sanmartinite ($ZnWO_4$)
- Cuprotungstite [$Cu_2(WO_4)(OH)_2$]
- Anthoinite [$Al(WO_4)(OH) \cdot H_2O$]
- Powellite [$Ca(MoW)O_4$]

The main ore deposits are classified as pegmatite, greisen, and contact metasomatic. Several minor deposits include hot springs, replacement, pnuematolytic, secondary enrichment, and placer. The mining of these deposits follow three traditional methods depending on the type: underground, open pit, and placer. Underground is the most common.

Ore Valuation and Trends

The ore price is based on tungsten content and the market value of ammonium paratungstate (APT). The unit of measurement is the metric ton unit (MTU), which is equal to 10 kg. During the 1980s and 1990s, the price was between US$25 and US$30/MTU. This was mostly because of the large amounts of Chinese ore that were available. Because of this low-cost ore, most Western producers were not profitable, and many mines closed, including all the mines in the United States and Canada. At the turn of the century, the Chinese

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stopped all ore exports, and the price gradually increased to nearly US$500/MTU in 2008. With the economic downturn, the price slowly dropped to US$150/MTU and has currently rebounded to US$282/MTU. The first new and only mine in the United States is scheduled to open on the Utah–Nevada border, south of Wendover, Nevada, when the price of tungsten rebounds.

MINERAL PROCESSING

Once the material is removed from the ground, the beneficiation steps required are crushing, grinding, sizing, and concentrating; the steps are supplemented with leaching, roasting, or magnetic separation if needed. The crushing and grinding is typically accomplished with cone crushers, roll crushers, jaw crushers, ball mills, and rod mills. Sizing is mainly done with screens and classifying. The typical size of finished ore is 1–4 mm (sand or finer). Wolframite is usually coarser than scheelite. Concentrating is typically performed with gravity tables and/or spirals or flotation. Flotation is most often used when treating scheelite, as scheelite produces more fines during crushing. This concentrating purity of tungsten oxide (WO) is around 60%–70%, with some processes requiring at least 65% tungsten trioxide (WO_3) content.

Extraction Processes

At this point, some of the ores need to be processed further to be used. Many of the ores (scheelite and wolframite) are roasted to remove sulfur. These ores are then further treated with chemicals. The main process is to add hydrochloric acid (HCl) and carbon to form tungstic acid. The tungstic acid is then processed into APT by digesting the tungstic acid with ammonia. To help purify the APT, additives such as magnesium oxide and carbon (to help remove phosphorus, arsenic, iron, and silica) are added before filtration. The purified APT solution next goes through an evaporation process to produce APT crystals. These APT crystals are converted to oxides. The three main oxides produced are WO_3 (yellow), tungsten dioxide WO_2 (brown), and an intermediate oxide W_4O_{11} (blue). These oxides are produced by heating the APT crystals in purified air. The blue oxide is done with a slightly reducing atmosphere. Both of these can be done with either stationary or rotary furnaces.

The oxides now need to be further reduced with hydrogen. The same types of furnaces as before can be used. This is accomplished by using hydrogen and a temperature of ~850°C. The end product is pure tungsten metal powder, which can now be further processed into a variety of useful products.

Tungsten and Ferrotungsten Powder Production

Although there are several other methods (reduction with carbon, aluminothermic reduction, silicothermic reduction, reduction with calcium, and reduction with other metals such as zinc) of producing tungsten and ferrotungsten, the major method is to use powder metallurgy. The tungsten metal powder can be made at different micrometer levels. Mainly, these range from 1 to 15 µm but can be made as large as 500 µm with doping agents added. These tungsten metal powders can be mixed with iron at a 35:65 ratio to form ferrotungsten. The same tungsten particles can be milled with lube or wax for green strength and then pressed into shapes. The two main ways of pressing are mechanical and isostatic.

With mechanical pressing, a die cavity is filled with the powder. Two rams compress the powder at high pressure (typically, mechanical presses range from 50 to 500 t). The isostatic pressing occurs in a chamber filled with a liquid, usually water. The powder is placed in a tube or boot made from rubber or plastic. The tube is sealed and placed in the chamber then pressed with an average of 172 kPa. The boot is withdrawn from the chamber and dried. The slug or billet is removed from the boot. This slug has green strength from the wax or binder and can either be sintered as is or green machined into shapes, then sintered.

Tungsten Production

The billets or parts can be sintered at high temperatures. This process solidifies and produces a dense metallurgical bond. These large billets can be sintered using induction. The smaller parts can use more conventional furnaces. Temperatures of 2,300°–2,400°C are needed during the final cycle to sinter the product. This process is also done in a reducing environment, most commonly using hydrogen.

The sintered parts can be finished machined, ground, or polished. The billets are usually extruded, forged, rolled, or swaged. The process used is dependent on the end product desired and the crystal structure of the grains. The majority are extruded to form bars or rods. The rods are further processed to form wire that will be used in lamp filaments, heater filaments, and heat elements. Other products include sheets, bars, and tubes. These materials will become rocket nozzles, electrodes, supports, seals and contacts, to name a few. For most of its history, filaments for lamps and furnaces were the major use of pure tungsten.

Other Tungsten Products and Applications

Another industrial application uses the same milling process to mix the tungsten with nickel, iron, and/or copper to produce what is known as *heavy* metal. This material is mainly used as radiation shielding, heat sinks, and counterweights. These products are used in electronics, medical equipment, and aerospace industries. Powder metallurgy is used to blend powders of tungsten and the alloying ingredients. Then they are milled, pressed, or extruded and sintered. These parts can be machined or ground to finish quality. Medical equipment that performs radiography, magnetic resonance imaging, and computed tomography would not be available without these alloys.

The original use of tungsten was to make steels, especially tool steels. The high-strength steels produced by adding tungsten began the modern machining era during the first quarter of the 20th century. Later, high-temperature and wear-resistant steels were developed. The wear-resistant steels mixed with cobalt and chrome are trademarked as Stellite alloys, which are used in high-temperature applications that also require wear and corrosion resistance.

Some magnetic steels, stainless steels, and specialty steels are also made with tungsten. Again, many of these are used in specific applications. Pumps, turbines, nozzles, tubing, food industry knives, as well as space vehicles, all use these types of steels.

Tungsten Carbide

Tungsten carbide (WC) became important before World War II, critical during the war, and since has become the major use of tungsten. Tungsten forms two carbide phases: The stable completely carburized WC and W_2C. Macrocrystalline carbide, cast carbide, and conventionally carburized tungsten carbide are the three main types of tungsten carbide. Macrocrystalline

WC is produced directly from the ores through an aluminothermic process. Macrocrystalline WC is single-crystal WC that has a stoichiometric carbon content of 6.13%. This material is used in hard-facing welding rods; plasma tungsten arc welding powders; hot-press powders; cemented carbide powders and parts; and matrix powders, which are infiltrated with copper alloys to produce polycrystalline diamond (PCD) oil and gas drill bits.

Cast carbide is the near eutectic of the two phases of tungsten carbide (WC/W_2C). The carbon content varies between 3.8% and 4.2%. It is produced by arc melting tungsten and carbon and pouring it into chilled molds. The quicker the material cools, the better the microstructure. The material is then crushed into various screen sizes. The best microstructure is a finely layered or feathery structure of the WC and W_2C phases.

Over the last decade, a spherical cast carbide has been produced by melting normal cast carbide through a plasma torch and cooling immediately with an inert atmosphere. This material is even harder and more erosion resistant. Spherical cast carbide is expensive to produce and therefore used in only specific high-wear applications. Cast carbide is used in most of the same areas as macrocrystalline WC.

Conventionally carburized WC is the most abundantly used tungsten carbide. This WC is made by adding tungsten and carbon into boats. They are then placed through a furnace to cause a diffusion of the carbon into the tungsten. The carbon level has to be controlled to produce a near stoichiometric product. Most of the WC is from submicrometer to 30 µm in size, but with special treatment, it can be made to 60 mesh. This process produces a low-impurity carbide with specific micrometer sizes. It is used to make cemented carbide powders and sintered parts.

Cemented Tungsten Carbide

Usually, cemented carbide is what most people mean when talking about tungsten carbide. Tungsten carbide is typically cemented together with a binder of cobalt. Nickel and iron can be used with other smaller fractions of materials such as titanium carbide, tantalum carbide, niobium carbide, vanadium carbide, or chromium carbide. The amount of cobalt varies from 6% to 30%, depending on the properties desired. The lower the cobalt content, the more wear resistant. The higher the cobalt content, the tougher the grade.

Another factor that becomes important is that the size of the carbide used has an effect on the toughness. Similar to producing tungsten powders, cemented carbides are milled with a wax or lubricant and a milling liquid. The powders are then either spray dried or tumble dried. These powders are then pressed into green parts. Like tungsten, they can be mechanically pressed, cold isostatically pressed (CIP), or extruded. Most parts are mechanically pressed using single- or dual-axial presses. The cavity of the press is filled with powder and then loaded from the top, the top and bottom, or even with a floating die. The pressed parts are placed on trays, which are loaded into furnaces for sintering.

The CIP method is used for bigger parts that are usually green machined before sintering. The sintering process is similar to tungsten with vacuum furnaces being cycled through a ramp, de-lube, ramp, and then held at sintering temperature before entering a slow cooling section.

Many tungsten cemented carbide parts are processed using sinter-HIP (hot isostatic pressure). This is the same as sintering, except once the sintering temperature is reached, the furnace is filled with an inert gas to produce a high pressure. Using sinter-HIP helps eliminate very fine porosity for maximum density. Depending on the type of parts, after sintering, they can be machined, ground, polished, etched, or finished using electrical discharge machining (EDM). They can also be coated by chemical vapor deposition or physical vapor deposition for enhanced properties. These cemented carbide parts are used for multiple applications.

Applications. Most cemented carbide parts are produced for metalworking, including cutting tool inserts, bores, drills, end mills, taps, and milling tools. In the oil and gas industry, carbide is found in compacts, bit nozzles, stabilizers, mud motor bearings, balls and seats, shafts, substrates for PCD cutters, anvils for the cubic presses to produce PCD cutters and synthetic diamonds, fracking nozzles, flow control parts, and disk stacks. Mining and construction applications include inserts for mining bits, picks for road planning and coal mining, roof bits, trenching tools, snowplow blades, skid plates, and ground-engagement tools. In general, industry carbide is supplied for rollers, pumps, centrifuge nozzles, slurry nozzles, mixer paddles, crusher teeth, seals, hammers, EDM blanks, and saw teeth.

Hard-facing applications. Hard-facing, thermal spray, and cladding are also major uses of tungsten carbide. As discussed earlier, plasma tungsten arc powders use WC mixed with nickel chrome alloys and are applied to all kinds of wear parts. Cladding is used for extrusion barrels and screws for plastics and pet foods, pump parts, turbines, fan blades, boiler tubes, screens, shafts, and bearings.

Thermal spray powders are made from sintered spherical spray dried or sintered crushed cemented carbides. These are used in plasma and spray guns to spray jet engine turbines, shafts, molds, downhole, and other parts needing a thin uniform coating.

Hard-facing wires, stick electrodes, and tube-filled rods are made containing macrocrystalline WC, cast carbide, cemented carbide pellets, and crushed recycled cemented carbide. These are deposited with oxyacetylene gas, arc, tungsten inert gas or metal inert gas welding. Hard-faced items include everything from tri-cone mill tooth drill bits, drums, agriculture and mining wear parts to flour mill hammers. Because of the extensive industrial applications, tungsten is one of the most critical strategic metals.

REFERENCE

Yih, S.W.H., and Wang, C.T. 1979. *Tungsten: Sources, Metallurgy, Properties, and Applications*. New York: Plenum Press.