Technology of Tungsten Ferroalloys

Michael Gasik

Aalto University Foundation, Espoo, Finland

11.1 PROPERTIES OF TUNGSTEN AND ITS COMPOUNDS

Tungsten is one of the heaviest stable metals used commercially. It is located in the VIb subgroup of the periodic table, together with chromium and molybdenum. The atomic weight of tungsten is 183.85, and the external electronic configuration is $4f^{14}5d^{4}6s^{2}$. Tungsten has one stable phase with a body-centered cubic (BCC) structure of a = 0.3165 nm and a density of 19.3 to 19.9 g/cm^3. The melting point of tungsten is 3410°C and a boiling point is 5930°C, making it also one of the most refractory metals.

In metallurgy, tungsten is known for its tendency to form extremely hard and stable carbides, which is the reason for using tungsten as a component of high-speed and tool steels as well as many hard metal alloys (Durrer and Volkert, 1972). Tungsten finds a lot of applications as a pure metal and as a master alloy in special steels, superalloys, filaments, radiation shields, refractory applications, and so on. About half of the world's known tungsten reserves are estimated to be located in China, but important deposits also exist in Canada, the United States, South America (Bolivia, Peru), other parts of Asia

(Thailand, Myanmar, Kazakhstan, Uzbekistan, and Korea), and other places throughout the world (Australia, Russia).

The system W-Fe (Fig. 11.1) forms the basis of the industrial ferrotungsten alloy. Iron and tungsten react to form several intermetallic compounds, of which the most stable are the Laves phase (Fe_2W) and the μ-phase Fe_7W_6. At the content of tungsten of >60% wt. in the industrial FeW alloy, the melting temperature exceeds 2200°C. Tungsten stabilizes the BCC lattice of iron, which might thus dissolve up to 30% to 34% wt. tungsten at subsolidus temperatures (see Fig. 11.1).

In the system W-C (Fig. 11.2), two stable carbides are known: W_2C (3.07% C, density 17.5 g/cm^3) and WC (6.12% C, density 15.5 g/cm^3). Both carbides have high melting temperatures and high hardness, which is exploited in tool steels and hard metals. Additionally in ternary Me-W-C systems, η-carbide (Me_3W_3C) might form in the case of deficit of carbon. This phase is usually brittle and has to be avoided in tools applications by correlating the ratios of carbon, tungsten, and other metals.

In the system W-Si, two stable silicides form (Fig. 11.3): W_3Si_2 (9.21% Si) and WSi (23.3% Si). Like similar molybdenum silicides, they have high melting temperatures. Mutual solubility of silicon and tungsten is low.

With oxygen, tungsten forms several oxides, of which the most stable are WO_2 (dark brown color), W_4O_{11} (dark blue color), and WO_3 (lemon yellow
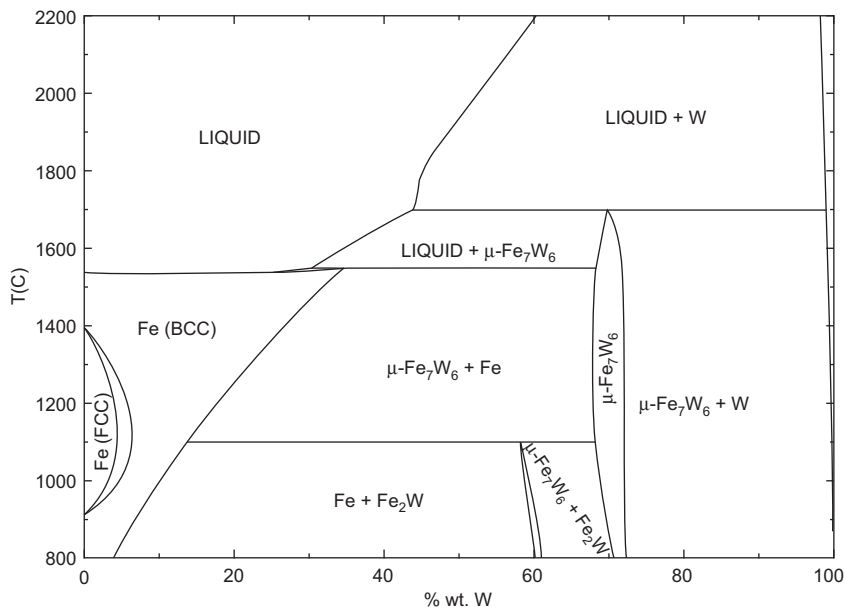

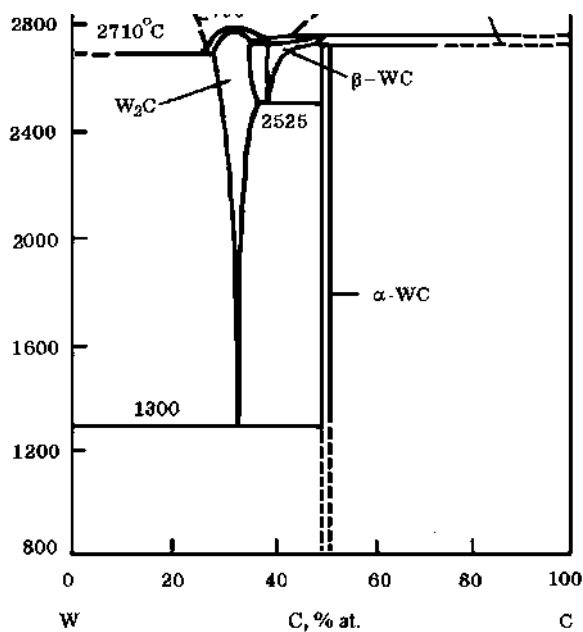**FIGURE 11.1** Phase diagram of the W-Fe system.

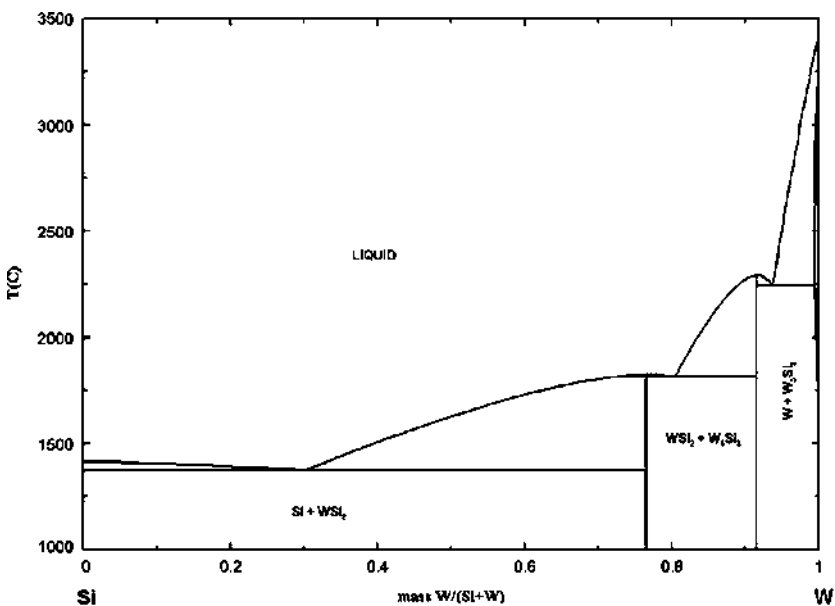**FIGURE 11.2**   Phase diagram of the W-C system.

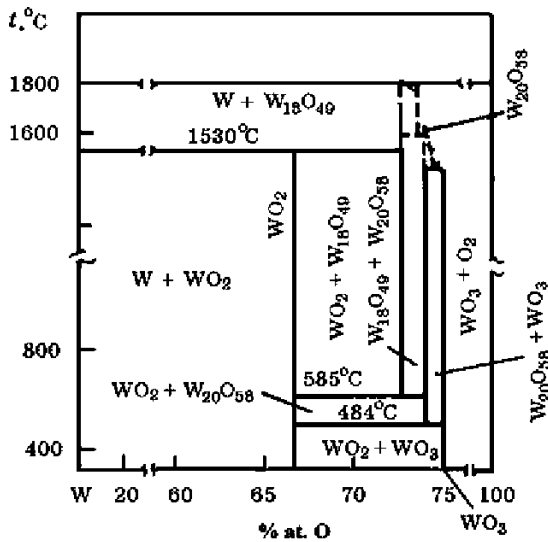**FIGURE 11.3**   Equilibrium diagram of the W-Si system.

FIGURE 11.4   Equilibrium phase diagram of the W-O system.

color) (Fig. 11.4). Additionally, like molybdenum, it has a set of intermediate oxides like $W_{18}O_{49}$, $W_{20}O_{58}$, and so on, generally expressed by formula WO_{3-x} and sometime referred as "blue oxide," which is an intermediate product of some hydrometallurgical and chemical processes of WO_3 extraction from ores and recycled materials.

Tungsten oxides can be reduced by hydrogen to tungsten metal or by carbon either to metal or to carbide phases. Figure 11.5 shows the example of the phase dominance diagram of the W-C-O system at 1500°C. The figure shows that it is thermodynamically possible to obtain metallic tungsten at this temperature using equilibrium with gas of 1% to 15% CO_2. A higher CO_2 fraction moves equilibrium toward the oxide's stability, whereas CO-rich gas will favor the formation of tungsten carbide.

11.2 MINERALS, ORES, AND CONCENTRATES OF TUNGSTEN

Several tungsten minerals have practical industrial importance, particularly ferberite $FeWO_4$, hubnerite $MnWO_4$, wolframite $(Fe, Mn)WO_4$, and scheelite $CaWO_4$. The first two have rare separate occurrences, as they usually form an isomorphic mixture—wolframite, in which manganese and iron can substitute for each other in the crystal lattice (Gasik et al., 2009). Wolframite has 76.5% WO_3 and has a density of 7.1 to 7.5 g/cm^3. Scheelite has 80.6% WO_3 and has a density of 5.8 to 6.2 g/cm^3.

Tungsten ores contain an average of 0.2% to 0.5% WO_3, rarely exceeding 1% wt. Tungsten ores often include other minerals with molybdenum, tin,
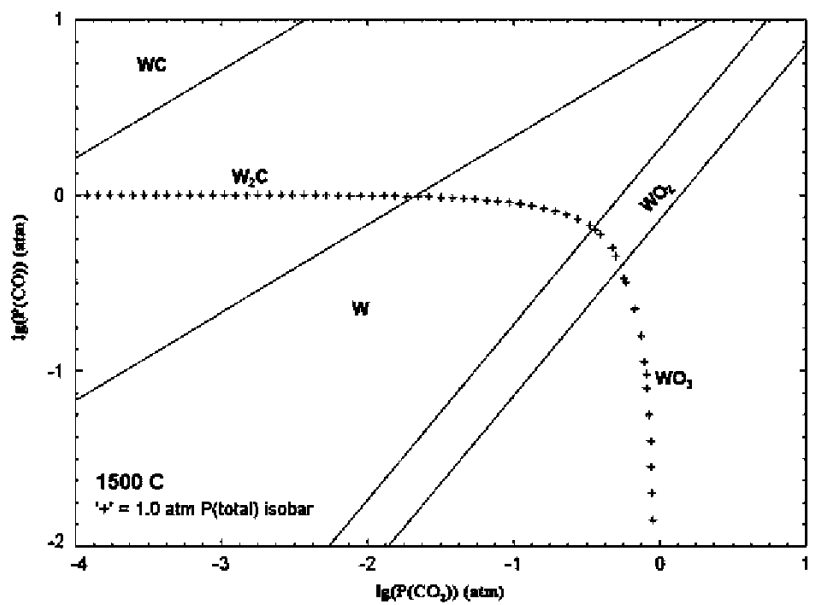
FIGURE 11.5   Phase dominance map of the W-C-O system at 1500°C. Cross marks indicate 1 bar total pressure isobar.

copper, arsenic, and so on. Dressed tungsten ores could be roughly divided into two classes depending on the leading mineral (either wolframite (hubnerite and ferberite) or scheelite type) (Table 11.1). Tungsten concentrates with high sulfur content (1% to 7%) are subjected to oxidizing roasting to decrease sulfur content below 0.1% to 0.5% S.

For processing of pure tungsten and its alloys, pure oxide WO_3 is extracted by a series of sophisticated chemical and hydrometallurgical operations on these concentrates. The side rocks here are represented by mostly quartz, calcite, and fluorite (Gasik et al., 2009).

TABLE 11.1 Typical Chemical Composition, % wt., of Tungsten Ore Concentrates

Ore Type	WO_3	MnO_2	SiO_2	P	S	As	Sn	Cu	Mo
Wolframite	60−65	15−18	<5	<0.05	<0.8	<0.05	<0.15	<0.1	<0.2
Scheelite	60−65	<1	<6	<0.03	<0.3	<0.02	<0.05	<0.1	<3

11.3 TECHNOLOGY FOR PRODUCING FERROTUNGSTEN

Standard ferrotungsten is available in several grades (Table 11.2). The major difference is defined by the alloy production method, which is reduction by either aluminum or carbon and silicon. This also determines the amount and distribution of impurities. The density of ferrotungsten is high (14 to 15.5 g/cm^3), as is its melting temperature (~2700°C), so it dissolves in the steel-making furnace slowly and tends to sink at the bottom (Voronov et al., 2000).

The reduction of tungsten by carbon and silicon usually involves being preformed in small furnaces (3.5 to 5 MVA), and the liquid alloy is scooped out of the furnace with a specially designed spoon if the liquidus temperature is too high (this would prevent normal tapping, as the alloy would be solidified during this process). Higher-grade FeW alloy is usually made by aluminum reduction. Thermodynamically, tungsten has a low affinity for oxygen and from its oxides can be reduced with silicon, carbon, and aluminum.

11.3.1 Reduction by Carbon and Silicon

The smelting furnaces are lined with magnesite bricks, which are partially destroyed during the melting and replaced by ferrotungsten metal skull. The raw materials used in the process are tungsten concentrate (see Table 11.1), coke, granulated ferrosilicon (65% to 75% Si), steel chips, and recycled tungsten-containing slag. The composition of the charge is calculated taking into account that impurities would be transferred into the alloy in the following ratios, % wt.: Mo, 100; Cu, 100; As, 15; S, 15; and Sn, 30% of the amount in the smelting charge (Gasik et al., 2009).

By the nature of occurring physical and chemical processes, the smelting operations used are divided into three periods. After the third period, the bath in the furnace contains ferrotungsten melt (from the previous smelting) with 3%

TABLE 11.2 Typical Chemical Composition of Ferrotungsten Alloys, wt. %, Depending on the Production Method: A—Reduction by Aluminum, CS—Reduction by Carbon and Silicon

Method	W Content	Mo	Mn	Si	C	Al
A, high purity	85−90	<0.2	<0.1	<0.1	<0.05	<0.1
A, high grade	75−80	<0.4	<0.1	<0.5	<0.1	<3
A, low grade	70−75	<6−7	<0.3	<2	<0.7	<3−6
CS, high grade	70−75	<2	<0.3	<0.5	<0.3	<0.04
CS, low grade	65−70	<6	<0.6	<1	<0.6	<0.10

to 8% Si, 1.7% to 4.5% Mn, <2% C, and 50% to 55% W. At the beginning of the first period, this melt is refined from Si, Mn, and C by loading into the furnace tungsten concentrate, recycled tungsten slags, and dust (from the gas cleaning). Silicon, manganese, and carbon all reduce WO_3 to tungsten, which dissolves in the melt. Iron oxides reduce simultaneously. To reduce the viscosity of the melt, iron (steel) chips are proportionally added before filling the concentrate. The slag formed in the furnace at this stage has 16% to 23% WO_3, 15% to 20% FeO, 28% to 32% SiO_2, 10% to 15% MnO, 8% to 10% CaO, 1% to 3% MgO, and 2% to 4% Al_2O_3. To improve the refining rate and increase metal temperature, the furnace is run on maximum power.

At the end of the first period, tungsten concentrate and coke are loaded with the purpose of obtaining the working slag with 10% to 12% WO_3. Here reduction of wolframite and scheelite proceeds via carbon, but silicon and manganese remaining in the melt also take part in reduction reactions. By the end of the first period, the melt has a standard content of tungsten and impurities.

In the second period, which lasts 1 to 1.5 hours, the operating voltage is reduced in an attempt to preserve the heated metal and to keep it in a solid–liquid state. Also during the second period, the alloy is dredged using special machine constructions on site (see, for example, Fig. 11.6). The alloy from the furnace is taken with a spoon made of carbon steel, containing 50 kg of metal at each turn. The metal spoon is dipped into a water tank, cooled, and knocked to extract the ingot. To ensure even alloy pickup, the bath of the furnace is rotated.

The purpose of the third period is to reach the final reduction of WO_3 from the slag by silicon (ferrosilicon) to levels <0.25% WO_3. The metal is enriched with silicon and manganese, reducing the tungsten concentration in the alloy from 65–75% to 52–55% W. When the tungsten oxide content in the slag reaches 0.25% (typically 0.05% to 0.15%), the furnace is held for 10 to 15 minutes; after that the slag is tapped. The final slag contains (by weight) 0.05% to 0.20% WO_3, 0.3% to 2% FeO, 45% to 50% SiO_2, 15% to 20% MnO, and 25% to 30% CaO. The metal left in the furnace after the third period and slag tapping typically has (by weight) 66% to 70% W, 5% to 7% Si, 0.7% to 2.5% Mn, 0.03% to 0.14% S, and 0.1% to 0.2% C. After the third period, the process is repeated.

If carbon, silicon, and manganese concentrations in the alloy are getting higher, the amount of the tungsten ore concentrate in the charge is increased. If WO_3 content in the slag is too high, more coke is added to increase metal and slag temperature—slag foams better; electrodes slip down; and the rate of C, Si, and Mn oxidation improves (Gasik et al., 2009).

To produce 1 ton of ferrotungsten by this method, ~1530 kg of tungsten concentrate (60% WO_3) is required. Additionally, ~108 kg of ferrosilicon (75% Si), 87 kg of coke, and 40 kg of electrode paste are consumed. The extraction degree of tungsten is high, typically >99%. The main cost share of the ferro-tungsten process is the cost of the tungsten oxide concentrate (96% to 98% of
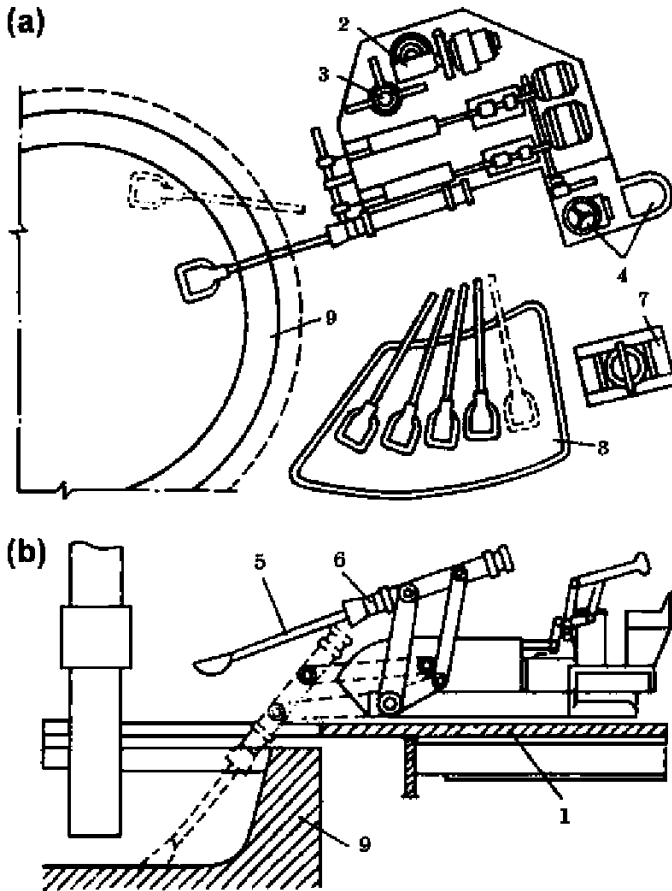
FIGURE 11.6   The machine for scooping of ferrotungsten (a, top view; b, side view): 1, working level; 2, turning mechanism; 3, axis of rotation; 4, remote control; 5, spoon; 6, holder; 7, device for ingot extraction; 8, stand; 9, electric furnace.

the total), so all possible measures are taken to reduce the loss of tungsten from the slag, waste gas, and dust. The vapors (mainly in the form of WO_3 and WO_2) are captured using a series of equipped cyclones and electrostatic precipitators. The collected dust is smelted separately, resulting in alloy (40% to 50% Pb, 45% to 50% Bi, and 5% to 8% Sn) and slag with 35% to 40% WO_3. This recycled slag is fed into the FeW smelting furnace together with other furnace charges.

Some plants use a two-stage technology for FeW smelting. Here two furnaces are engaged: the first (1 to 3 MVA) melts tungsten and iron ore concentrates with carbon, leading to alloy with >80% W, 1.5% C, 1.5% Mn, 0.1% Si, and slag <0.15% WO_3. The second furnace refines this alloy by

adding extra tungsten and iron ore concentrates, leading to the oxidation of carbon (decreases <0.4% C) and manganese (decreases <0.4% Mn) from the metal and to the formation of slag with 10% to 15% WO_3, which is fed back into the first furnace. Tungsten losses with gas and dust in this process are about 3% to 4% (Gasik et al., 2009).

11.3.2 Reduction by Aluminum

Reduction by aluminum is used when the tungsten content in the alloy should be higher and other impurities (especially carbon) content should be lower. During reduction, oxides of tungsten, molybdenum, iron, and silicon are reduced into metal melt.

Despite the high exothermic effect of reduction reactions, the heat released is not enough to ensure formation of the metal melt and its separation from the slag because of the high melting point of ferrotungsten. Additional heat is provided from the furnace transformer of ~1 MVA power. The furnace lining is made of magnesite.

Scheelite concentrate (see Table 11.1) is the main component of the charge. On every 100 kg of scheelite charge, the following components are added: primary aluminum powder 23 kg, iron chips 3 kg, steel slag 4 to 5 kg, and lime 1 kg. Also to improve the recovery of tungsten, recycled scrap, slag residuals, and collected dust are added. Depending on the volume of the furnace, 2500 to 5000 kg of concentrate is smelted per one batch (Gasik et al., 2009).

For the aluminum reduction process, 1 ton of ferrotungsten requires ~1555 kg of scheelite concentrate, 345 kg of primary aluminum powder, 20 kg lime, and ~80 kg iron chips. The extraction of tungsten in this process is high (>99%).

Ferrotungsten mixed alloy (with increased molybdenum content) is also produced by remelting W and Mo metallic and oxide scrap with the addition of lime, iron chips, and FeSiAl as a reductant (Voronov et al., 2000). This mixed alloy (nonstandard) has ~20% to 25% Mo and 20% to 25% W, with <10% to 15% Si used for alloying high-speed steels where both tungsten and molybdenum are required. Similar technology is used for making Cr-30%W and Ni-30%W master alloys.

REFERENCES

Durrer, R., Volkert, F., 1972. Metallurgie der Ferrolegierungen. (Metallurgy of Ferroalloys), Springer, Berlin, 506 pp.

Gasik, M.I., Lyakishev, N.P., Gasik, M.M., 2009. Physical chemistry and technology of ferroalloys [in Ukrainian]. Dnipropetrovsk: Sistemnye Tehnologii, 494 pp.

Voronov, Yu.I., Zaiko, V.P., Zhuchkov, V.I., 2000. Technology of ferroalloys with molybdenum. Ekaterinburg: IMET UrO RAS, 276 pp.