

Technology of Titanium Ferroalloys

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Chapter Outline

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15.1 PROPERTIES OF TITANIUM AND ITS COMPOUNDS

Titanium (atomic number 22) belongs to the transition metals of the first period of the periodic table. Its atomic mass is 47.88, the external electron shell configuration is $3d^24s^2$, its melting temperature is 1671°C, and its boiling temperature is 3260°C. The density of titanium is 4.5 g/cm³, and its typical valencies are 2, 3, and 4. Titanium exists in two allotropic modifications: α -Ti with a hexagonal close-packed (HCP) lattice ($a = 0.2951$ nm, $c = 0.4697$ nm) and β -Ti with a body-centered cubic (BCC) lattice (A2 type), $a = 0.3269$ nm. Titanium's phase transition temperature is 883°C. In some titanium alloys (such as Ti-Al), the high-temperature BCC phase may undergo ordering into BCC (B2) type (Gasik et al., 2009).

The high affinity of titanium for oxygen, carbon, nitrogen, and sulfur is utilized in steelmaking to bind these elements and to decrease their harmful effects (Demos and Kremin, 1981). Titanium also acts as a grain refiner in many steels and alloys, much like niobium. In stainless steels, titanium is an important addition to control carbide and nitride precipitates (e.g., at mass ratio

Ti/C ~5, it prevents the precipitation of chromium carbides on grain boundaries, which greatly improves the corrosion resistance of stainless steels). In low-alloyed steels, titanium with excess carbon and nitrogen forms carbonitride (TiCN), which is known to remain in the structure during welding and thereby helps to retard austenite grain growth.

In the liquid state, titanium and iron form solutions with unlimited mutual solubility, but in the solid state they form intermetallic compounds such as TiFe_2 (Laves phase) and TiFe (Fig. 15.1). The system has two eutectics, one is iron-rich and the other titanium-rich. From the point of view of iron-based alloys, titanium belongs to a ferrite-forming group of elements and thus greatly reduces the austenitic γ -region.

With carbon, titanium forms thermodynamically strong titanium carbide (TiC) (density of 4.4 g/cm³). Carbide has a cubic structure and a wide-ranging stoichiometry (Fig. 15.2). The formation of carbide is preferential over the metallic phase when titanium oxides are reduced by carbon.

Titanium forms several compounds with silicon (Fig. 15.3). Silicides TiSi_2 and Ti_5Si_3 melt congruently, whereas monosilicide TiSi melts incongruently. Silicide Ti_3Si is known to require a rather long equilibration time to form, so in many cases its existence in solid Ti-Si alloys is kinetically suppressed.

The system Ti-Al is very complex and has been a subject of many investigations. One of the most recent versions is shown in Figure 15.4 (Witusiewicz et al., 2008). Titanium and aluminum form solid solutions and a number of

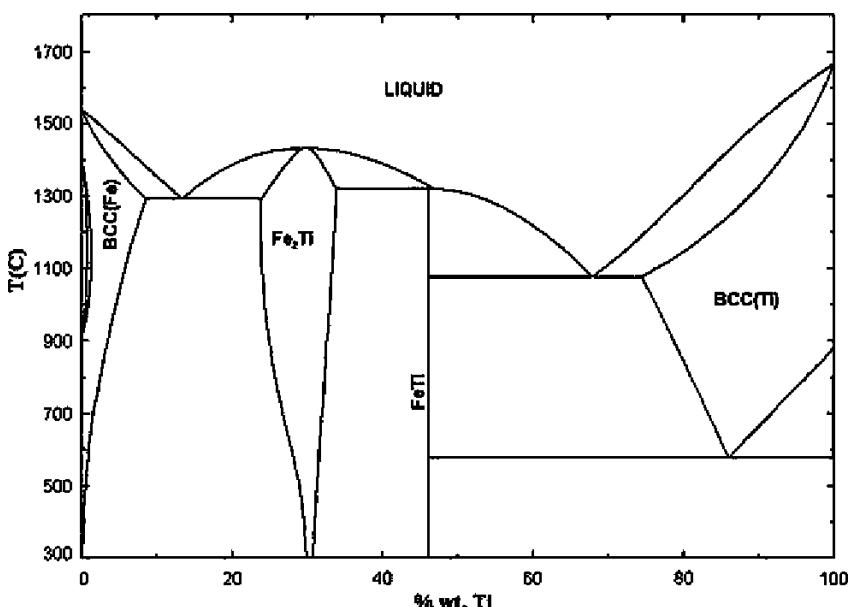


FIGURE 15.1 Diagram of the equilibrium state of the system Ti-Fe.

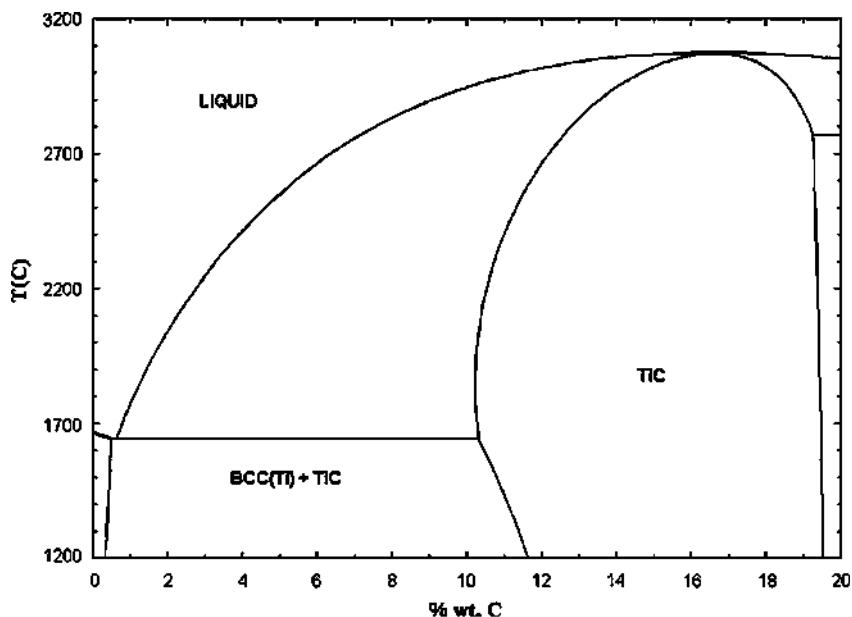


FIGURE 15.2 Diagram of the equilibrium state of the Ti-C system.

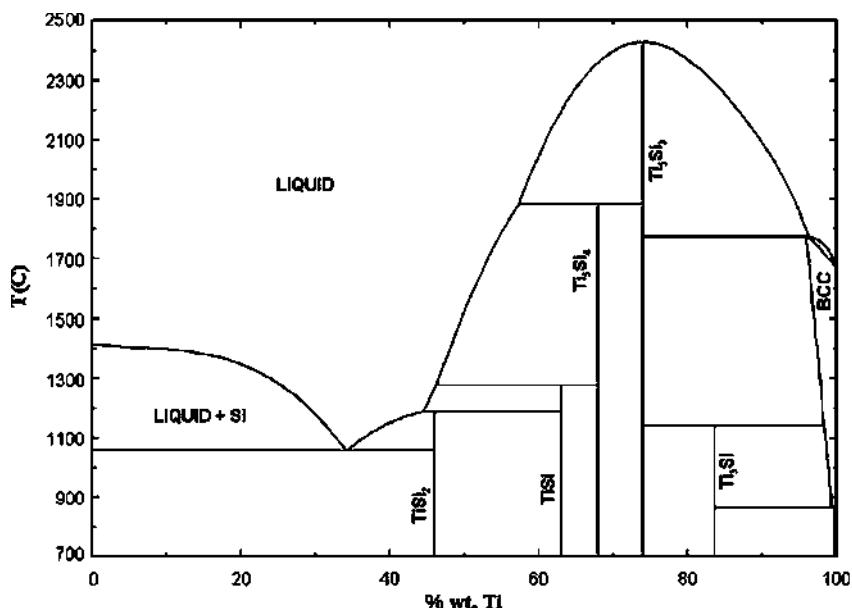


FIGURE 15.3 Diagram of the equilibrium state of the system Ti-Si.

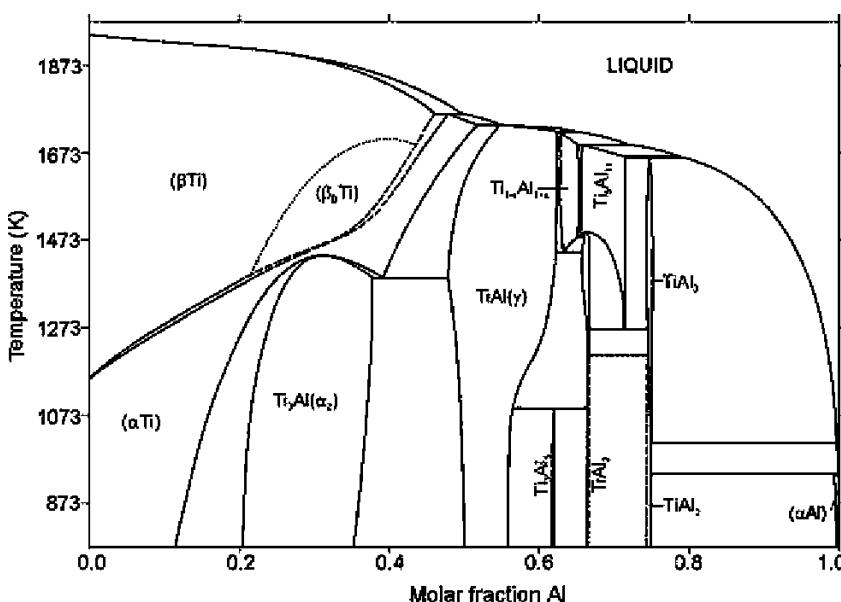


FIGURE 15.4 Diagram of the equilibrium state of the system Ti-Al.

aluminides: $\alpha_2\text{-Ti}_3\text{Al}$ (hexagonal DO_{19} structure), $\gamma\text{-TiAl}$ ($\text{L}1_0$ tetragonal structure), TiAl_2 , and TiAl_3 . Aluminides Ti_3Al and TiAl have a wide homogeneity range.

Titanium is a highly active element, which oxidizes at room temperature, forming a stable protective oxide coating on its surface. With oxygen, titanium forms several stable oxides (Fig. 15.5): TiO_2 , Ti_3O_5 , Ti_2O_3 , and TiO_x , but also a number of intermediate oxides, known as oxygen-deficit Magneli phases $\text{Ti}_n\text{O}_{2n-1}$ (Ti_2O_5 , Ti_4O_7 , etc.). As HCP $\alpha\text{-Ti}$ dissolves significant amounts of oxygen at all temperatures, this phase sometimes is referred to as $\alpha\text{-}(\text{TiO})$ or $\alpha\text{-TiO}_{0+x}$ (to show that the homogeneity range extends toward pure HCP titanium). Titania (TiO_2) exists in three modifications, of which rutile is the most stable; anatase and brookite are less stable (Gasik et al., 2009).

For the practice of ferrotitanium processing, oxide systems with iron, aluminum, and silicon, and calcium oxides, are important. In the system $\text{FeO}\text{-TiO}_2$, three compounds are known: ulvöspinel ($2\text{FeO}\cdot\text{TiO}_2$), ilmenite ($\text{FeO}\cdot\text{TiO}_2$), and pseudobrookite ($\text{FeO}\cdot 2\text{TiO}_2$) (Fig. 15.6).

Oxide TiO_2 has acidic properties, so basic oxides such as CaO readily form the corresponding compounds (Fig. 15.7), but acidic oxides (SiO_2) do not form compounds with TiO_2 (Fig. 15.8). In the system $\text{TiO}_2\text{-Al}_2\text{O}_3$, two compounds are known (Fig. 15.9).

In the ternary system $\text{CaO-SiO}_2\text{-TiO}_2$ (Fig. 15.10) sphene CaTiSiO_4 is the only ternary compound, but there are wide ranges of solid solutions (based on sphene, perovskite, rutile, and silica).

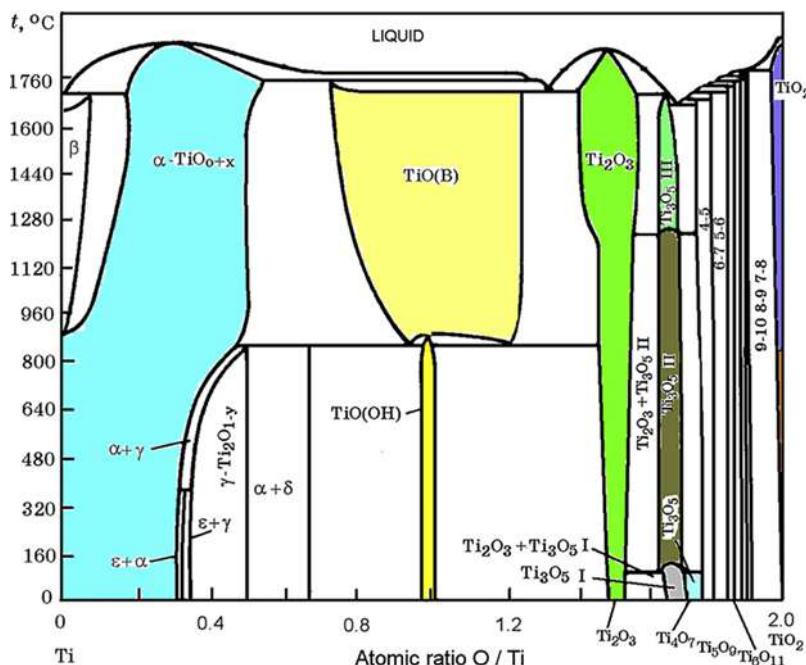


FIGURE 15.5 The phase diagram of the system Ti-O, built on aggregated data (α - TiO_{0+x} , solid solution of oxygen in titanium; TiO , high- and low-temperature modification of titanium monoxide; Ti_3O_5 , different phase modifications (I, II, III), and Magneli phases Ti_nO_{2n-1} ($n = 4$, Ti_4O_7 ; $n = 5$, Ti_5O_9 ; $n = 6$, Ti_6O_{11} ; etc.).

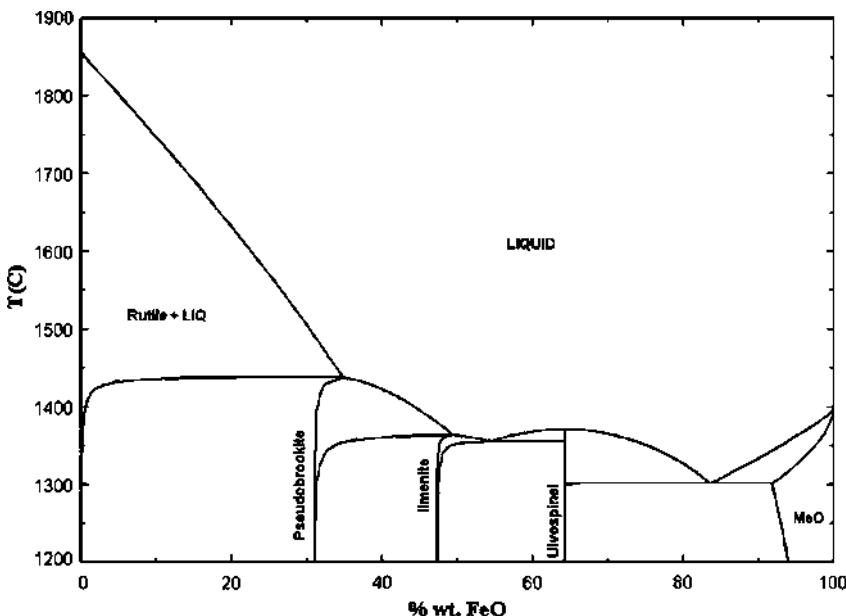


FIGURE 15.6 Diagram of the equilibrium state of the system FeO-TiO₂.

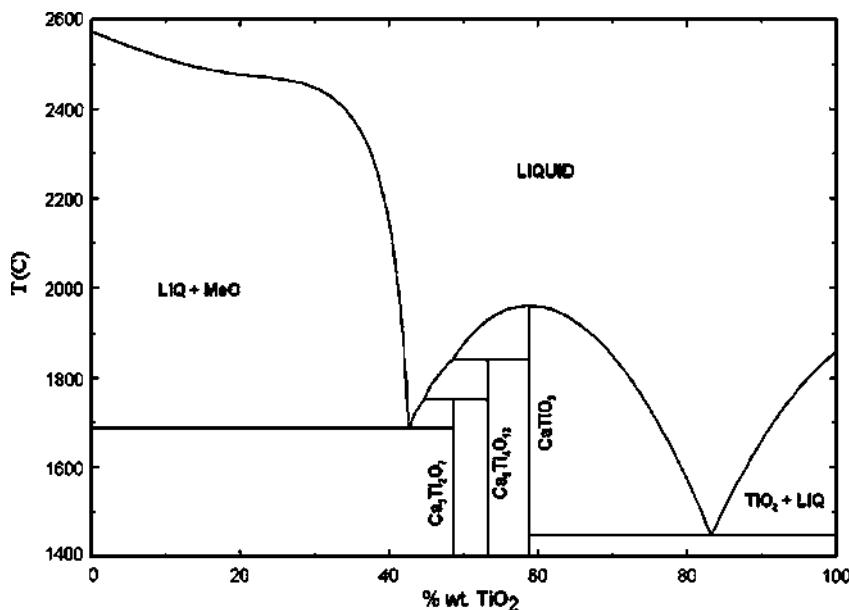


FIGURE 15.7 Diagram of the equilibrium state of the system CaO-TiO₂.

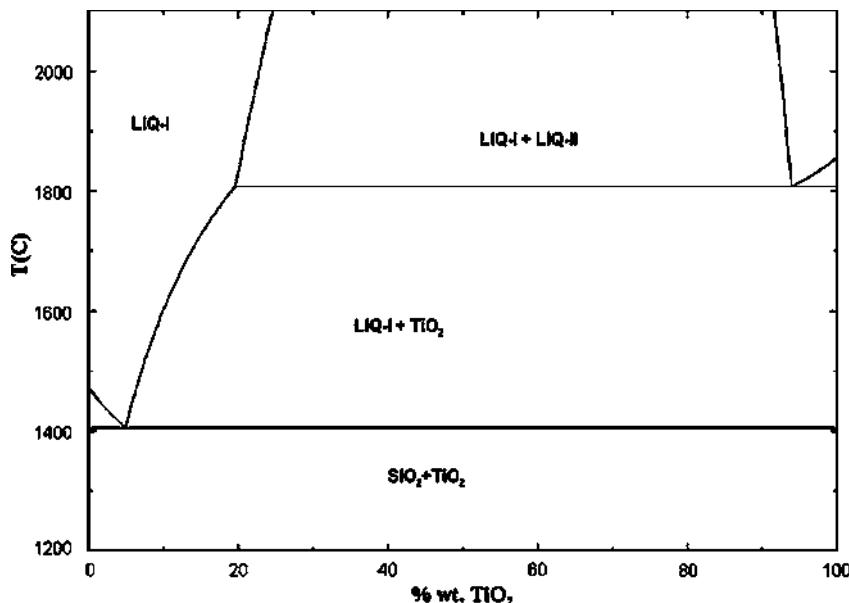


FIGURE 15.8 Diagram of the equilibrium state of the system SiO₂-TiO₂.

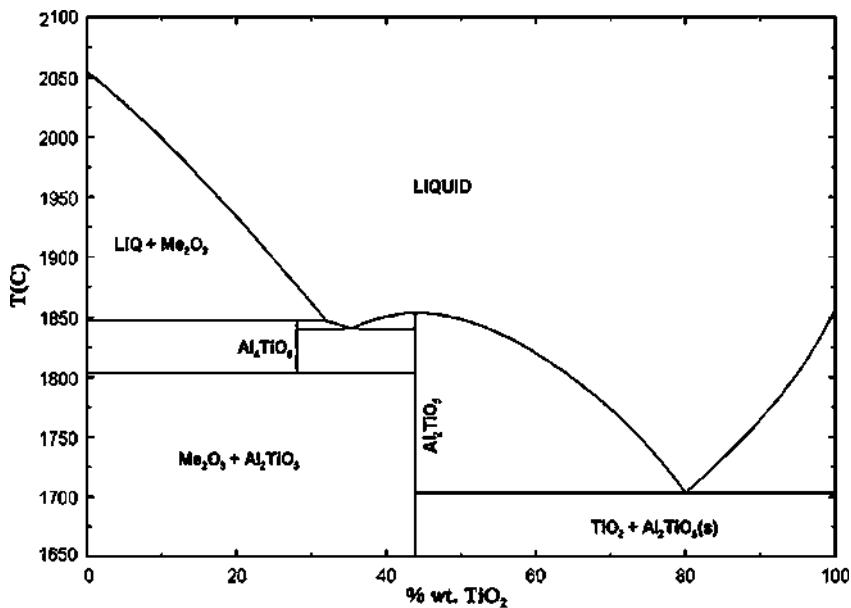


FIGURE 15.9 Diagram of the equilibrium state of the system $\text{Al}_2\text{O}_3\text{-TiO}_2$.

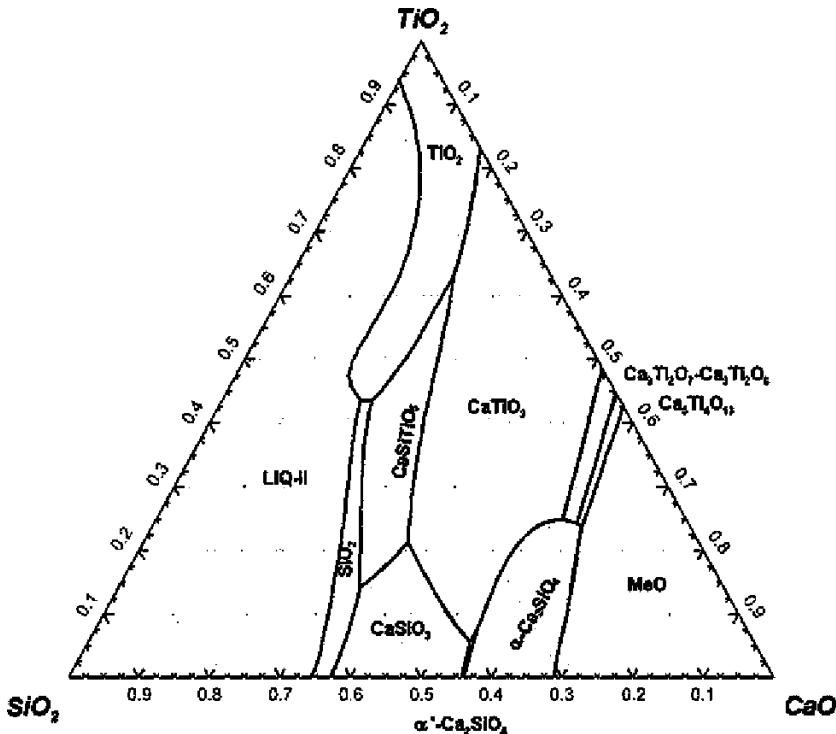


FIGURE 15.10 Diagram of the equilibrium state (liquidus projection, composition in weight fractions) of the system $\text{CaO}\text{-TiO}_2\text{-SiO}_2$.

15.2 SOURCES OF TITANIUM AND METHODS OF ITS REDUCTION

15.2.1 Titanium Raw Materials

There are many known titanium minerals, which might be combined into five groups: rutile (TiO_2), ilmenite ($\text{FeO} \cdot \text{TiO}_2$), perovskite ($\text{CaO} \cdot \text{TiO}_2$), pyrochlore ($\text{Na,Ca,..}(Nb,\text{Ti})_2\text{O}_6(\text{F},\text{OH})$), and sphene $\text{CaTiSiO}_4 \cdot (\text{O},\text{OH},\text{F})$. The rutile-type minerals in the first group (anatase TiO_2 , brookite TiO_2 , leukocene $\text{TiO}_2 \cdot \text{nH}_2\text{O}$, etc.) are often observed together due to the proximity of the titanium ionic radii making it possible to substitute isomorphically with other metals. The most important and most common titanium mineral is, however, ilmenite, which forms continuous solid solutions with geikilit (MgO· TiO_2) and hematite (Fe_2O_3). Ilmenite, titanomagnetite, and titanium-zirconium ore are of great importance to the ferrotitanium industry (Gasik et al., 2009). They are usually subjected to gravitational enrichment (separation), and magnetic and flotation methods. The chemical composition of titanium concentrates used for the smelting of ferrotitanium is given in Table 15.1.

Ilmenite concentrates normally have 96% to 98% ilmenite (corresponding to 50% to 65% TiO_2) and up to 0.20% to 0.25% S. This is too much for making standard ferrotitanium, so concentrates are roasted in a rotary kiln at 600° to 800°C. The roasting process leads also to the oxidation of FeO and the formation of Fe_2O_3 . This breaks down the ilmenite structure and improves the recovery of titanium. In some cases, titanium oxide lean materials are also used (e.g., “red mud” containing <20% TiO_2) (Puri et al., 2004).

15.2.2 Reduction of Titanium from Oxides

Reduction of titanium from ilmenite and rutile by carbon proceeds first with the reduction of iron oxides and later with the reduction of titanium, which partially dissolves in ion melt and partially transforms into carbide (TiC). Smelting of ilmenite with carbon usually leads to the formation of Fe-Ti-C alloy with a high

TABLE 15.1 Chemical Composition of Major Titanium Concentrates, % wt.

Ore		TiO_2	Fe_2O_3	Fe_{tot}	SiO_2	Al_2O_3	MgO	MnO	V_2O_5	S
Concentrate										
Ilmenite										
		52–63	~26.5	~33.5	1–3	1.5–3	0.6–1.6	0.5–1	0.1–0.3	0.04–0.05
Ilmenite from										
titanomagnetite		44.3	—	36.5	2.16	2.55	2.52	0.68	0.22	0.4
Iron-titanate		59.8	—	20.4	2.6	6.12	0.6	0.77	0.2	—

carbon content (35% to 40% Ti; 5% to 8% C; 1% to 3% Si). Such alloys with high carbon content may be used for deoxidation and alloying of carbon steels.

Using silicon as a reductant for titanium is more problematic, as silicon has a lower affinity for oxygen than does titanium, and thus recovery of TiO_2 is only possible with a high content of silicon in the ferroalloy. Also, the presence of iron is needed as it decreases titanium activity and promotes reduction. The resulting Fe-Si-Ti alloy has a composition of 20% to 25% Ti, 20% to 25% Si, and ~ 1% C, which has limited application in steelmaking.

The aluminothermic method for ferrotitanium processing is the most common (Gous, 2006). Reduction of titanium by aluminum from ilmenite and rutile proceeds via the formation of intermediate monoxide TiO (TiO_x), which, as basic oxide, is able to form titanium aluminate. This decreases the activity of TiO and makes titanium recovery more difficult. To suppress the process of binding TiO with alumina, lime is injected to the charge: CaO replaces TiO , forming $\text{CaO} \cdot \text{Al}_2\text{O}_3$. However, the balance must be kept, as an excess of CaO in the charge is not desirable: it decreases the activity of titanium dioxide by forming perovskite $\text{CaO} \cdot \text{TiO}_2$. Lime also has a great influence on the viscosity and fluidity of the slag. The optimum amount of it in the charge is about 20% by weight of aluminum (Gasik et al., 2009). This method has been greatly improved and applied in several ways, both by using a conventional furnace and by using an electric furnace with preheating of the charge and the use of iron-thermal (exothermic) mixtures (Kotzé et al., 2006). Slag of ferrotitanium is then postprocessed in an electric furnace to recover the rest of titanium and to produce high-alumina (68% to 78% Al_2O_3 , 14% to 17% CaO) slag, which is used as a high-alumina cement addition (Pourabdoli et al., 2007). Although different alternative methods of ferrotitanium processing are being studied (e.g., by electrolysis in molten salts as shown by Shi et al., 2011), these methods still mostly take place in the laboratory.

15.3 TECHNOLOGY OF TITANIUM FERROALLOYS

The composition of standard ferrotitanium is shown in Table 15.2 (Gasik et al., 2009). Depending on its composition, it may also have <0.8% Mn, <0.8% Cr, 0.2% to 1.5% Zr, and 0.05% to 0.3% Sn. Different alloy manufacturers also produce other compositions on demand.

For titanium reduction by aluminum, the main critical parameter is the specific exothermal heat release of the process, referred to 1 kg or mole of smelting products (metal and slag). Assuming some heat losses (~11%), it provides the required temperature of the melt after the end of the process:

$$\Delta H_{req} = \frac{T_{process} + C}{K \cdot 0.89}$$

where for ferrotitanium smelting $K = 32.6$ and $C = 170$ (Gasik et al., 2009). To provide the necessary conditions for the smelting process, the temperature

TABLE 15.2 Composition of Ferrotitanium, % wt.

Alloy	Ti	AI	Si	C	P	S	V	Mo	Cu
		Max.							
FeTi70Si05	68–75	5	0.5	0.2	0.05	0.05	0.6	0.6	0.2
FeTi70Si08	68–75	4	0.8	0.3	0.03	0.03	1.8	2	0.3
FeTi70Si05V	65–75	5	0.5	0.3	0.03	0.03	2.5	2.5	0.3
FeTi70Si1	68–75	5	1	0.4	0.05	0.05	3	2.5	0.4
FeTi35Si5	28–40	8	5	0.2	0.04	0.04	0.4	0.2	2
FeTi35Si7	28–40	9	7	0.2	0.07	0.05	0.8	0.5	2
FeTi35Si8	28–40	14	8	0.2	0.07	0.07	1	1	3
FeTi30	28–37	8	4	0.12	0.04	0.03	0.8	0.4	0.4
FeTi20	20–30	5–25	5–30	1	0.08	0.03			—

should be at least 2260 K, so the equation leads to a required exothermic heat supply of 83.6 kJ/mol. The whole heat supply comes from reactions of the reduction of iron and titanium oxides by aluminum, and it is believed that the best conditions correspond to the ratio of $\text{Fe}_2\text{O}_3:\text{TiO}_2$ in ilmenite concentrates close to unity.

The most common technology of this process is realized as follows. The cast-iron hearth is mounted on a movable platform, lined with a refractory brick. The hearth walls are coated with a mixture of magnesite (95%), fired clay (4.3%), and sodium silicate (“liquid glass”) as a binder up to the thickness of the lining of 10 to 15 mm. The hearth is moved into the melting chamber space, equipped with feeding hoppers and ventilation hoods.

The composition of the charge for the smelting of ferrotitanium is shown in Table 15.3. About 200 kg of the charge is loaded into the hearth, and the ignition mixture is placed on top of it (sodium nitrate and magnesium turnings or chips). The mixture is initiated with a spark or magnesium, and the exothermic process starts. Upon the progress of the melting, small portions of charge are regularly added into the hearth. One typical heat consists of smelting of 4 to 4.5 tons of ilmenite concentrate in 15 to 20 min leading to an ingot that is 3 to 4.5 m in length (Gasik et al., 2009).

To produce 1 t of ferrotitanium, the requirement is about 940 kg ilmenite concentrate, 400 kg aluminum powder, 100 kg lime, 24 kg ferrosilicon FeSi75, and 130 kg iron ore. Up to 9 to 10 kg of titanium scrap might also be added. The phase composition the alloy depends on the content of titanium and impurities in

**TABLE 15.3 Charge Composition for Smelting of Ferrotitanium
(kg by 100 kg of ilmenite concentrate)**

	Ignition Mixture	Main Charge	Reducant Mix
Ilmenite concentrate		100	
Iron ore	100	15–30	100
Aluminum powder	30–40	45–60	35–40
FeSi	12–20	<6	
Lime	15–25	8–12	10–25
NaCl		<2	

ferrotitanium. In the microstructure of FeTi alloy eutectics and intermetallics, FeTi, Fe₂Ti are usually present. Excess phases in ferrotitanium are nitride (TiN), aluminide (AlTi), and sulfide (TiS). Oxide inclusions consist mainly of corundum (α -Al₂O₃), alumina with a mixture of TiO₂ and Cr₂O₃, mullite (3Al₂O₃·2SiO₂), gehlenite (2CaO·Al₂O₃·SiO₂), sphene (CaTi(SiO₄)(O,OH,F)), and the ilmenite (FeO·TiO₂).

The process could be carried out with either top or bottom primer (ignition). In the first case, all charge is loaded in the hearth and the ignition is started from the top, so the melting front and the liquid phase go down. The final liquid products' volume in the hearth is only 30% to 35% of the hearth's total volume, so the productivity of this method is not high. Additionally, it is not possible to control the melting rate once the process has been started. The benefit, however, is that the process is straightforward and easily executed. The bottom primer in general is more efficient, as additional charge might be loaded later and the hearth volume could be fully utilized.

Besides ilmenites, perovskite (CaO·TiO₂) is also a valuable raw material for smelting ferrotitanium. It may substitute for up to ~ 25% of the ilmenite concentrate in the charge, thus eliminating the need to add extra lime to the charge. However, the heat of exothermic reduction reactions in this case is not enough, so the perovskite must be preheated up to 600° to 700°C, reaching the temperature of the mixture ~300°C. The recovery degree of titanium in the process is approximately 75% to 80%. Figure 15.11 shows a flow sheet schematic of melting ferrotitanium with its postreduction from liquid slag.

Although reduction by aluminum is feasible due to high reaction heat, it is not economical to consume extra aluminum just for the reduction of iron (to provide necessary heat). Thus, an alternative method includes heating the melt

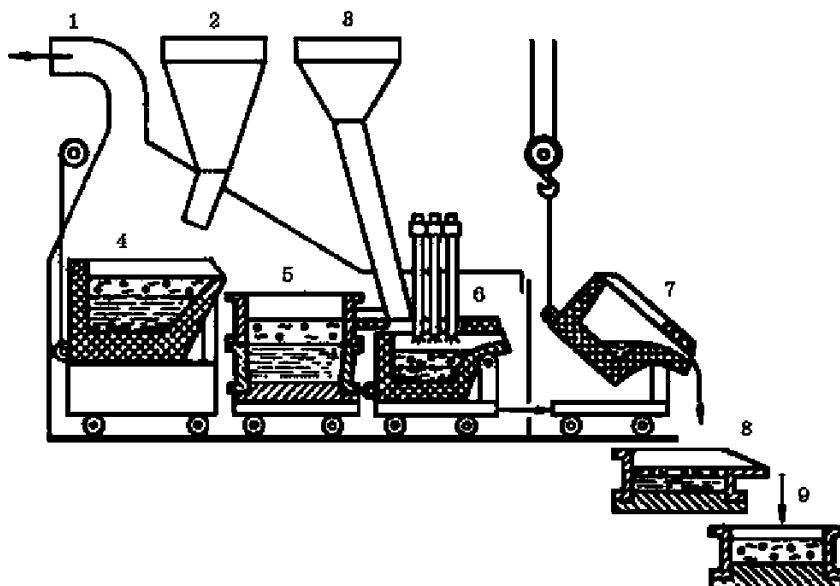


FIGURE 15.11 Scheme of ferrotitanium production from liquid slag: 1, gas extraction hood; 2, charge feeder for the smelting of ferrotitanium; 3, charge feeder for titanium recovery from the slag; 4, hearth for smelting ferrotitanium; 5, molds for metal and slag; 6, electric furnace to reduce the slag; 7, removable furnace hearth; 8, skimmer; 9, mold.

in an electric furnace to add the energy needed to finalize reactions and to ensure metal and slag conditioning.

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