Chapter 7

Manganese Ferroalloys Technology

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Chapter Outline

7.1 INTRODUCTION TO MANGANESE FERROALLOYS

7.1.1 History and Background of Manganese

Manganese is a relatively common element in the earth's crust. The average concentration reaches nearly 0.1%, and it is the twelfth most abundant element and fourth most abundant of the metals in commercial use. Manganese occurs in nature mainly in the form of oxide, carbonate, and silicate minerals. Paintings pigmented with manganese oxide can be traced back 17 000 years. Later, in ancient Greece, the presence of manganese in steel gave the Spartans superior steel weapons. In 1774, Swedish chemist Carl Wilhelm Scheele was the first to recognize that manganese is a separate chemical element, and in the same year his colleague Johan Gottlieb Gahn isolated an impure sample of the element by reduction of MnO_2 (pyrolusite) with charcoal. In 1816, it was found that adding manganese to iron made it harder, without making it more brittle. At the beginning of the 19th century, scientists began to explore the use of manganese in steelmaking, with patents being granted for its use.

Because about 90% of all manganese produced is consumed in the steel industry, the world demand for manganese depends directly on the needs of the steel industry, which is typical for most ferroalloys. There are numerous grades of steel, and each grade requires a different amount of manganese. The average unit consumption of manganese per ton of steel is currently about 10 kg. There is some direct consumption of manganese ores and sinter in the blast furnaces where pig iron is produced, but manganese is mainly consumed in the form of ferromanganese, silicomanganese, and manganese metal. Only about 5% of the manganese used in steel production is introduced into the blast furnace.

7.2 PROPERTIES OF MANGANESE AND ITS COMPOUNDS

7.2.1 Properties of Manganese

There are four modifications of manganese known at ambient pressure: complex cubic structure α-Mn (a = 0.89124 nm, 58 atoms in the basic lattice,

density 7.44 g/cm^3) below 727°C; complex cubic β-Mn in the range 727° to 1090°C (a = 0.6289 nm, 20 atoms in the basic lattice, density 7.29 g/cm^3); FCC γ-Mn at 1090° to 1138°C (a = 0.3855 nm at 1100°C, density 6.37 g/cm^3); and those above 1138°C—BCC δ-Mn (a = 0.3075 nm at 1143°C, density 6.28 g/cm^3). The melting point of manganese is 1244°C and the boiling point is 2150°C. It can have valences from 1+ to 7+, of which 2+ and 4+ are the most common. The pure metal is grayish white, resembling iron, but it is harder and very brittle. Manganese (Mn) and iron (Fe) are close neighbors in the periodic system, with element numbers 25 and 26 and atomic weights of 55 and 56, respectively.

Manganese is added to steel for the following reasons: it is used as an alloying element to improve strength, toughness, and hardness; it is used for sulfur control whereby it combines with sulfur and controls the morphology of sulfides; and, lastly, it is used for oxygen removal. Manganese stabilizes the austenite in steel, although it is less potent than nickel. It lowers the temperature of austenite transformation into ferrite and improves the response of steel to quenching. The effect of manganese in forming austenite is improved by combining it with nitrogen, which is also an austenite-forming element (Matricardi and Downing, 1995).

Manganese plays a key role in steels because of its ability to combine with sulfur: manganese sulfide avoids the hot shortness of the steel and prevents the interstitial liquid formation of iron sulfide.

Manganese is a milder deoxidizer than silicon and aluminum but enhances their effectiveness due to the formation of stable manganese silicates and aluminates. Silicomanganese (SiMn) is a more effective deoxidizer than is the case with individual additions of ferrosilicon and ferromanganese. Deoxidation with silicomanganese results in cleaner steel as the liquid manganese silicate formed coalesces and thus separates more easily from the melt, compared to solid SiO_2 formed during ferrosilicon deoxidation. This feature also reduces the problems with nozzle clogging during casting.

7.2.2 Interaction of Manganese with Oxygen and Carbon

Manganese forms several oxides, of which only monoxide (MnO) is stable at high temperatures. The unstable higher oxides MnO_2, Mn_2O_3, and Mn_3O_4 predominate in manganese ores. Higher manganese oxides such as Mn_2O_7 are very unstable and easily decompose even at room temperatures. MnO_2 and Mn_2O_3 dissociate in solid state to lower oxides when heated. Figure 7.1 shows areas corresponding to oxides and metal stability at different oxygen potentials versus temperature, and Figure 7.2 presents the phase equilibria diagram at 1 atm air (0.21 atm oxygen partial pressure).

Reduction of MnO to liquid metallic manganese is far more difficult than reduction of FeO to iron; and reduction of MnO to form solid manganese, analogous to the sponge iron formation in the Fe-O system, is not practically possible.
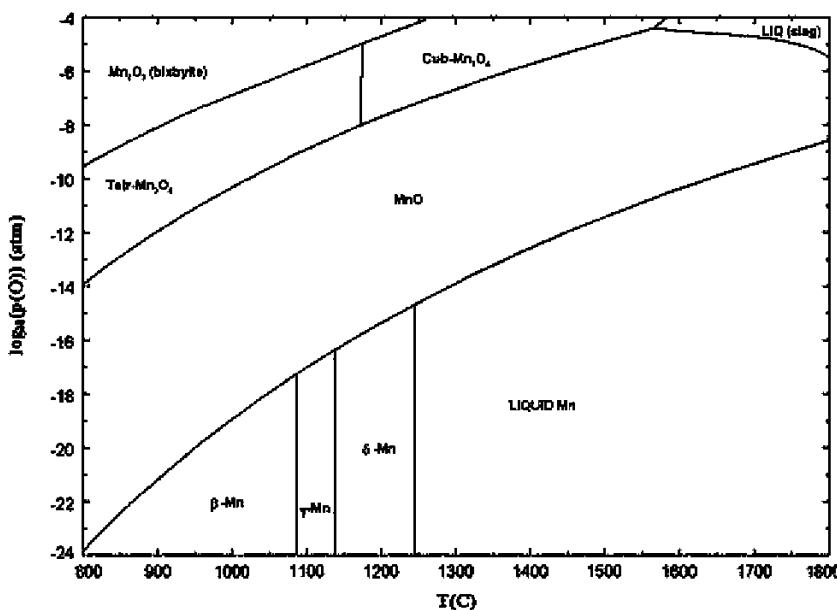
**FIGURE 7.1**   The stability phase diagram of the Mn-O system.
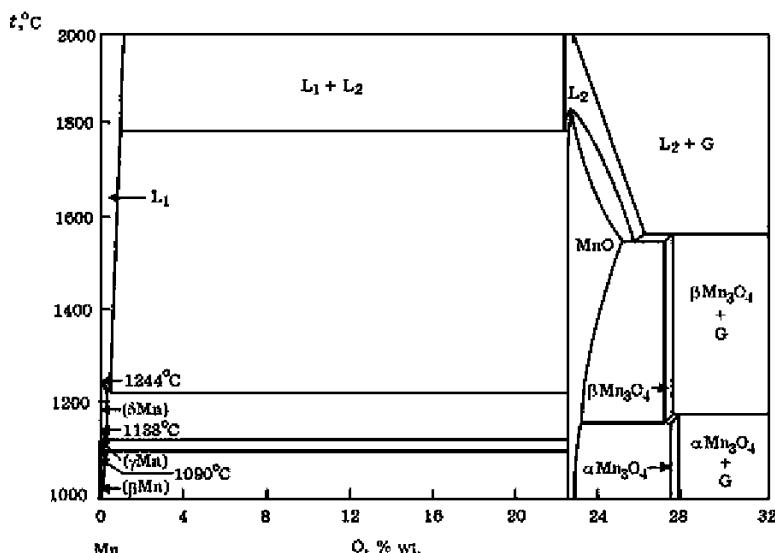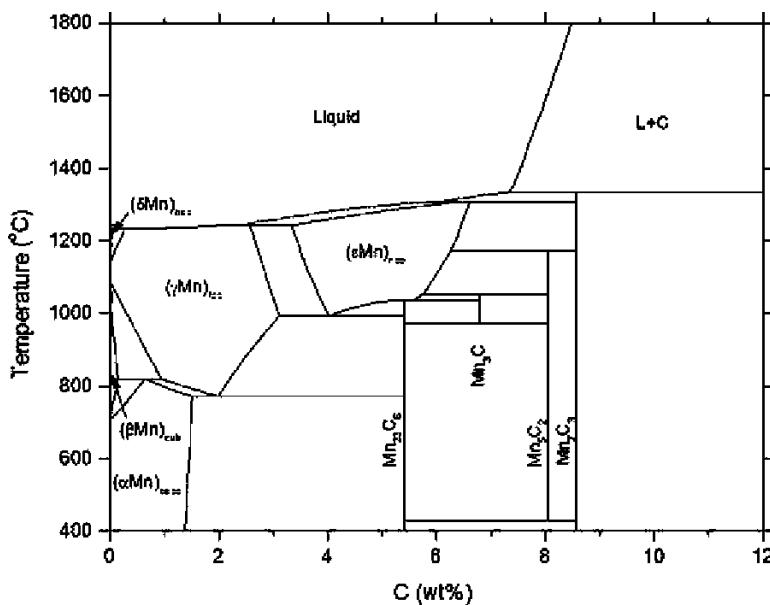
FIGURE 7.2   The phase equilibria in the Mn-O system at 1 atm air conditions.

FIGURE 7.3   Calculated Mn-C phase diagram using the SINTEF ferroalloy database *(Olsen et al., 2007).*

The Mn-C equilibrium phase diagram is shown in Figure 7.3. Manganese and carbon are completely miscible in liquid state, but, as opposed to the Fe-C system, the liquidus temperature increases with increasing carbon content from 1237°C up to 1297°C at 7.34% C. This composition corresponds to alloy in equilibrium with graphite and the carbide Mn_7C_3. Stable carbides are formed during solidification—for example, $Mn_{23}C_6$, Mn_3C, and Mn_7C_3. Most manganese carbides (particularly Mn_5C_2) are unstable in reaction with moisture, but it is found that 5% Fe is sufficient to stabilize the alloy in wet air and 10% Fe is sufficient to avoid reaction with water. Among manganese carbides, Mn_3C is the most stable in respect to environmental conditions.

7.2.3 Interaction of Manganese with Other Elements

In the Mn-Fe system, manganese stabilizes austenitic structure forming a large area of FCC γ–(Fe, Mn) (Fig. 7.4). Both manganese-rich and iron-rich solid solutions have a wide range of homogeneity. There is complete miscibility in the liquid state, and the system shows very small deviation from ideal behavior. Manganese and iron are not found to form any stable intermetallic compounds.

Manganese and silicon are completely miscible in the liquid state. The minimum eutectic temperature at the Mn-rich side is 1038°C at $X_{Si} = 0.175$ (11.2 wt% Si). Several silicides are formed during solidification (Fig. 7.5). Manganese silicide compositions (Gasik et al., 2009) have been updated—for
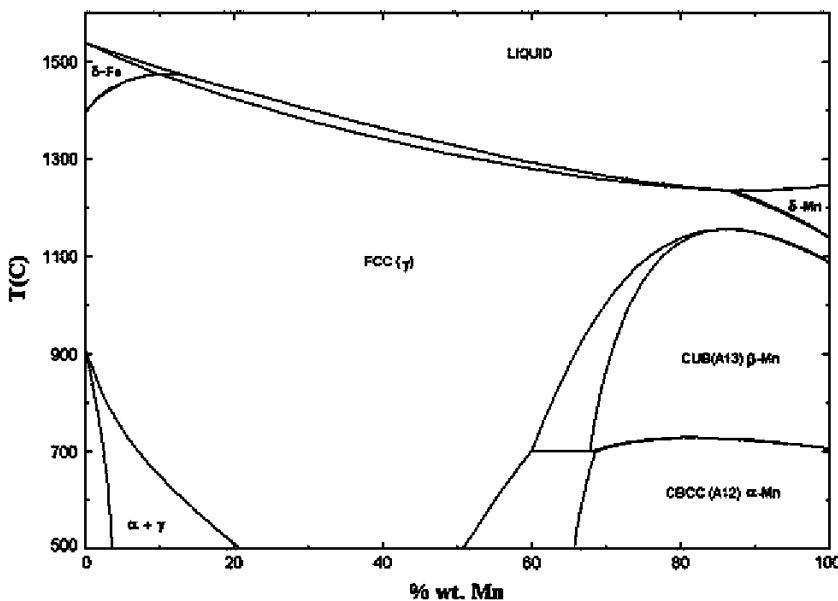
FIGURE 7.4   The phase equilibrium diagram of the Fe-Mn system.
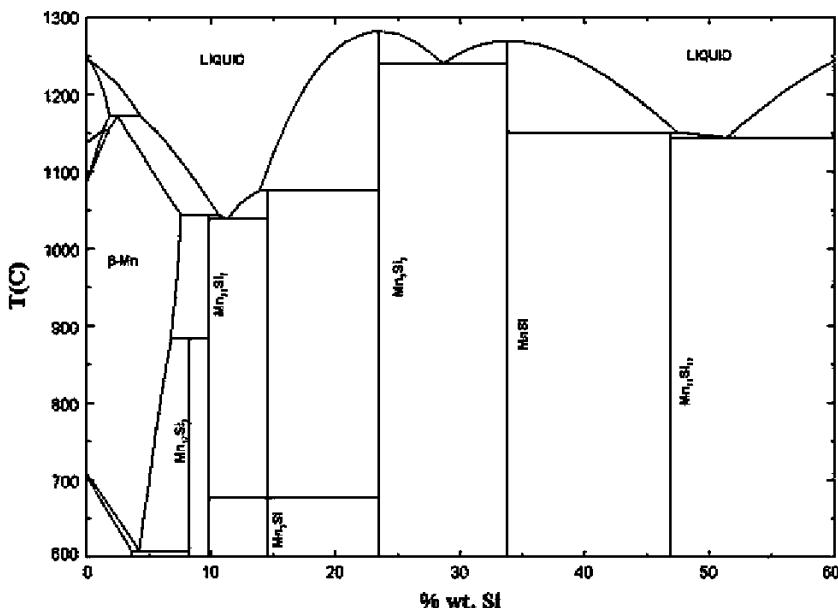
**FIGURE 7.5**   The phase equilibria in the Mn-Si system (up to 60% wt. Si).

instance, the MnSi$_2$ formula is being expressed now more correctly as Mn$_{11}$Si$_{19}$, Mn$_6$Si as Mn$_{17}$Si$_3$ (R-phase), and Mn$_9$Si$_2$ as Mn$_{33}$Si$_7$ (υ-phase). Some of these silicides have a certain homogeneity range, particularly at high temperatures (not shown in Fig. 7.5).

With phosphorus, manganese forms several stable phosphides such as Mn$_3$P, Mn$_2$P, Mn$_3$P$_2$, and MnP, but no solid solutions (Fig. 7.6). In the liquid state there is a strong interaction between Mn and P atoms.

With sulfur, manganese forms two stable sulfides, MnS and MnS$_2$. Sulfide MnS has a high melting temperature of 1610°C, and this is one of the reasons why manganese addition is effective for reducing the harmful effect of sulfur in steels. As with phosphorus, sulfur is practically insoluble in solid manganese.

Nitrogen and manganese form rather complex equilibria (Fig, 7.7). Besides nitrides Mn$_4$N, Mn$_5$N$_2$, Mn$_3$N$_2$ (also expressed as Mn$_6$N$_4$), and Mn$_6$N$_5$, there are wide homogeneity ranges in austenitic γ-Mn and ξ-Mn$_5$N$_2$ phases. These equilibria are important for processing nitrided manganese ferroalloys.

From the point of view of manganese ferroalloys processing, one of the most important systems is Mn-Fe-Si-C, as it eventually forms the basis of all manganese alloys. These alloys are high-, medium-, and low-carbon ferromanganese, often abbreviated to HC-, MC-, and LC-FeMn, as well as silico-manganese (SiMn) and to some extent metallic manganese (>96% Mn). Pure manganese has a high vapor pressure in its liquid state (above 1246°C), although the boiling point is 2060°C, so the addition of iron, silicon, and carbon has an appreciable effect on decreasing Mn vaporization at temperatures used for production and refining processes.
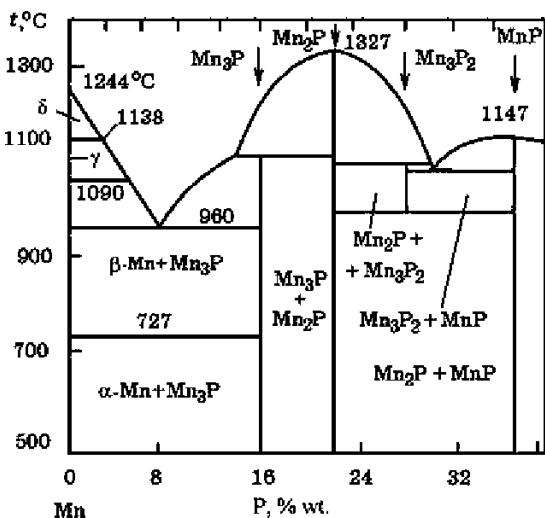
FIGURE 7.6 The phase equilibria diagram Mn-P.
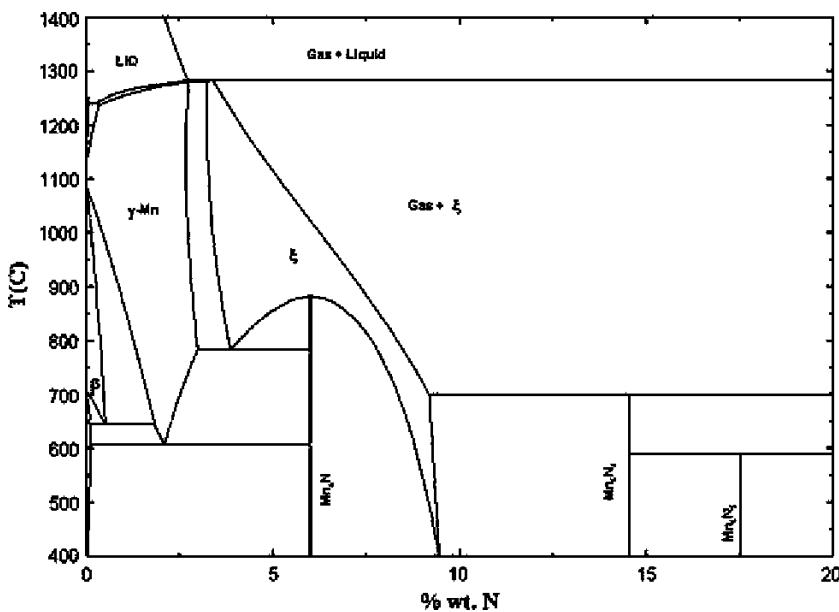
FIGURE 7.7   The phase equilibria diagram Mn-N at 1 atm pressure.
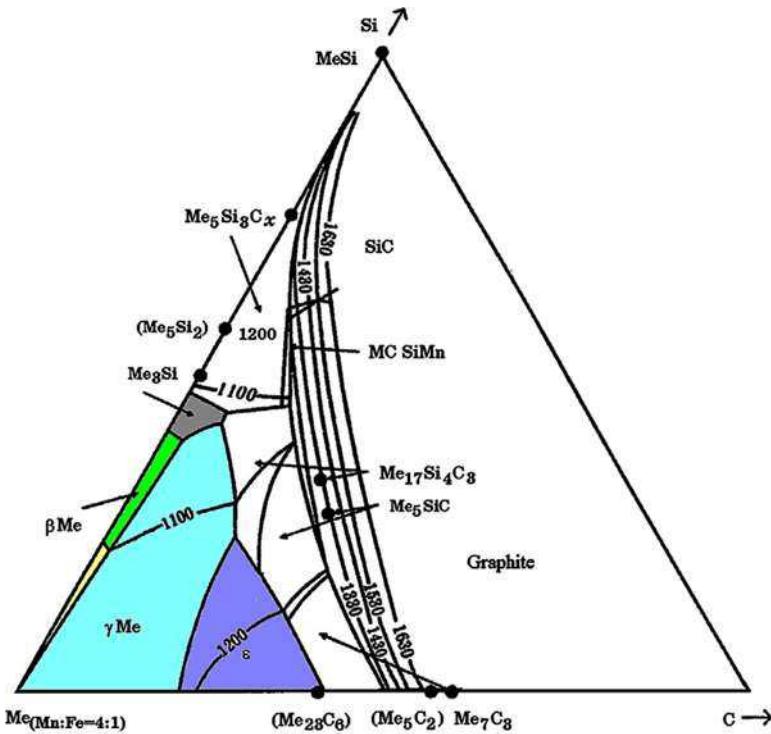
FIGURE 7.8   The liquidus projection in the Mn-Fe-Si-C system (weight ratio Mn/Fe = 4).

Tang and Olsen (2002) analyzed phase equilibria and reactions in the Mn-Si-C system. Contrary to the Fe-Si-C system, in the Mn-Si-C system carbon solubility is higher, but it also decreases with an increase of silicon content. As for iron, for liquid Mn-Si-C alloys with low silicon content ($<$16% to 23% Si wt., depending on temperature), the equilibrium solid phase is carbon (graphite), whereas at higher concentrations it is silicon carbide. Graphite and SiC might coincide in equilibrium where the Nowotny phase $Mn_5Si_3C_x$ may appear (Olsen et al., 2007). Figure 7.8 represents the liquidus projection of the Mn-Fe-Si-C system in the metal-rich corner for the ratio Mn/Fe = 4. Complex silicocarbides [Mn, Fe]$_{17}$Si$_4$C$_3$, [Mn,Fe]$_3$SiC might appear in equilibrium with graphite.

7.2.4 Manganese in Oxide Systems and Slags

Manganese monoxide forms two compounds with silica: rhodonite $MnSiO_3$ and tephroite Mn_2SiO_4 (Fig. 7.9). They have rather low melting temperatures and this is one of the reasons why manganese-silicate charge components usually melt first before reducing to metal.

The main slag elements when producing FeMn and SiMn alloys are Mn-, Si-, Ca-, Mg-, and Al- oxides. Calculated liquidus projection relations for the ternary $MnO-SiO_2-CaO$ system are shown in Figure 7.10. Many commercial ores will, after agglomeration and prereduction, also fall into the system $MnO-SiO_2-Al_2O_3$. Calculated phase and liquidus relations for the $MnO-SiO_2-Al_2O_3$ system are shown in Figure 7.11.
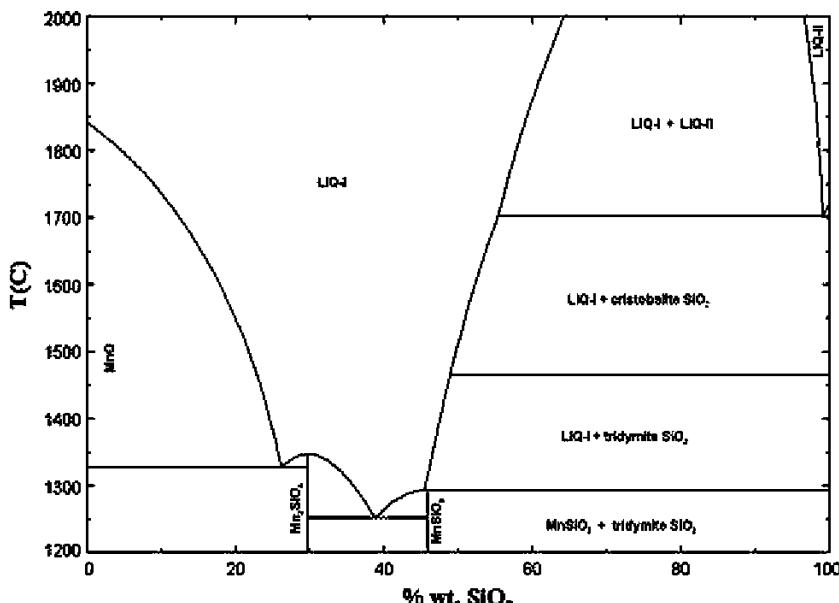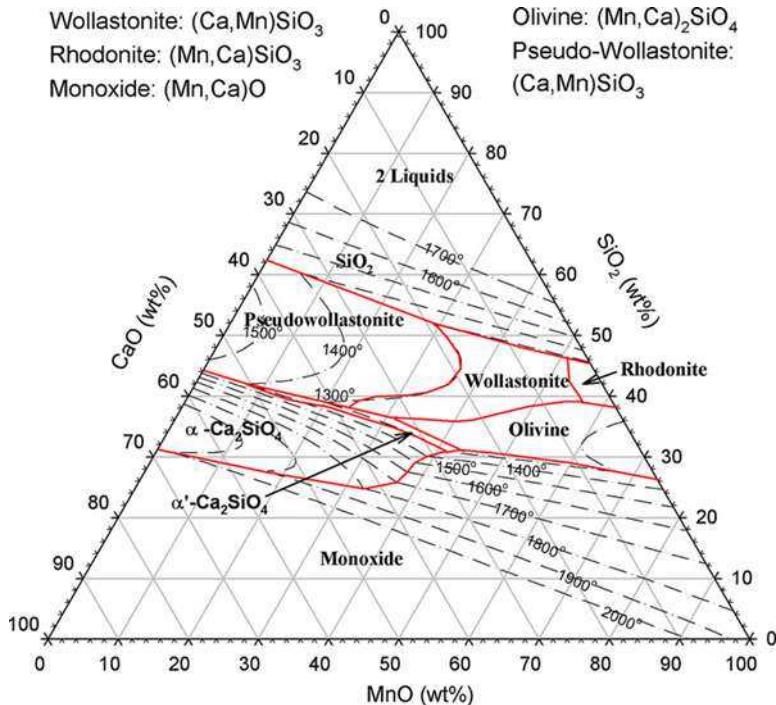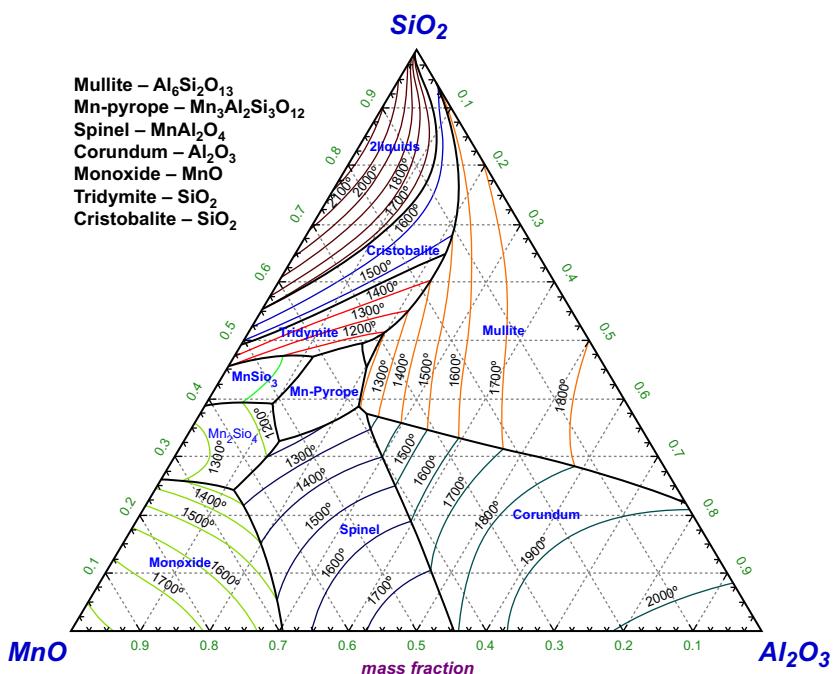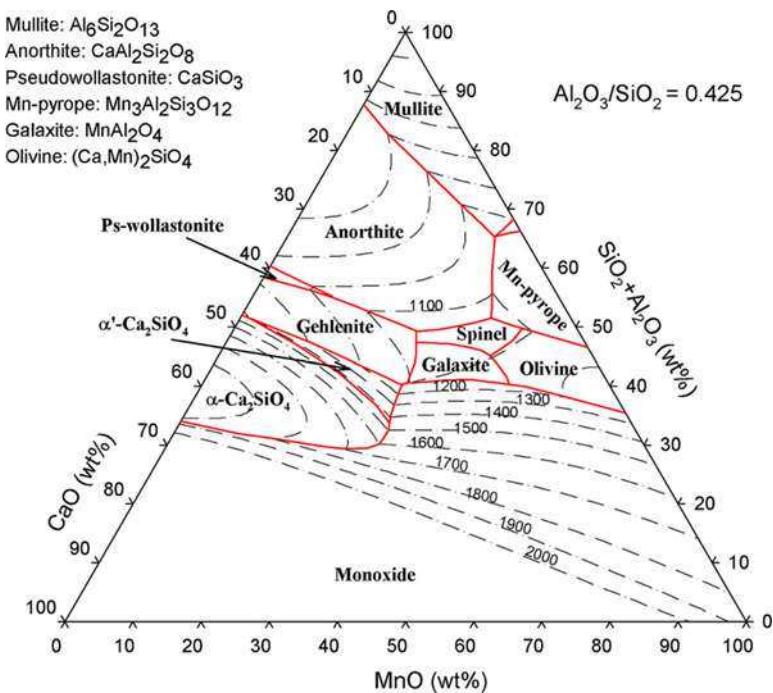
FIGURE 7.9   The phase equilibria diagram in the MnO-SiO$_2$ system.

FIGURE 7.10 Calculated phase and liquidus relations for the MnO-SiO₂-CaO system using the FACT oxide database.

FIGURE 7.11 Calculated phase and liquidus relations for the MnO-SiO₂-Al₂O₃ system using the FACT oxide database.

FIGURE 7.12 Calculated phase and liquidus relations for the $MnO-SiO_2-CaO-Al_2O_3$ (weight ratio $Al_2O_3/SiO_2 = 0.425$) system using the FACT oxide database.

In many manganese ferroalloys smelting and agglomeration processes, basic fluxes like lime or dolomite are often added. This shifts phase equilibria and leads to new, important phase fields. Examples of calculated phase and liquidus relations for the $MnO-SiO_2-CaO-Al_2O_3$ (weight ratio $Al_2O_3/SiO_2 = 0.425$) system are shown in Figure 7.12.

7.3 MANGANESE ORES PROCESSING AND REDUCTION

7.3.1 Manganese Ores

Manganese occurs in nature in the form of minerals. More than 300 minerals are said to contain some manganese, but only a small number have high manganese content. The manganese mineralogy is complex because manganese occurs in divalent, trivalent, and tetravalent states. The most common manganese minerals are oxides, carbonates, and, appearing less frequently, silicates and sulfides (Matricardi and Downing, 1995). Manganese minerals of significant abundance and economic importance are listed in Table 7.1.

TABLE 7.1 Most Known Manganese Minerals

Mineral	Chemical Formula	Mn Content
Oxide Types		
Pyrolusite	MnO_2	63.2
Vernadite	$MnO_2 \cdot H_2O$	44−52
Braunite	$3(Mn,Fe)_2O_3 \cdot MnSiO_3$	48.9−56.1
Braunite II	$7(Mn,Fe)_2O_3 \cdot CaSiO_3$	52.6
Manganite	$\gamma\text{-}MnOOH$	62.5
Psilomelane	$(K,Ba)(Mn^{2+}Mn^{4+})_8O_{16}(OH)_4$	48.6−49.6
Cryptomelane	$(K,Ba)Mn_8O_{16} \cdot xH_2O$	55.8−56.8
Hollandite	$(Ba,K)Mn_8O_{16} \cdot xH_2O$	42.5
Todorokite	$(Ca,Na,K)\,(Mn^{2+}Mn^{4+})_6O_{12} \cdot xH_2O$	49.4−52.2
Hausmannite	$(Mn,Fe)_3O_4$	64.8
Jacobsite	Fe_2MnO_4	23.8
Bixbyite	$(Mn,Fe)_2O_3$	55.6
Carbonate Types		
Manganocalcite	$(Mn,Ca)CO_3$	<20−25
Oligonite	$(Fe,Mn)CO_3$	23−32
Rhodochrosite	$MnCO_3$	47.6
Silicate Types		
Rhodonite	$MnSiO_3$	42
Tephroite	Mn_2SiO_4	54.4
Sulfide Types		
Alabandine	MnS	63.2
Gauerite	MnS_2	46.2

Braunite and braunite II are common complex silicate minerals usually occurring in association with bixbyite, hausmannite, and pyrolusite in deposits such as the Postmasburg and Kalahari manganese deposits of South Africa where braunite is the principal manganese mineral. Rhodochrosite is a common carbonate mineral in various ores.

There are only a limited number of workable deposits of manganese ores. The most important land-based manganese ore deposits are located in the Republic of South Africa, Australia, Gabon, Brazil, China, India, and in the Commonwealth Independent State (CIS) countries of Ukraine, Kazakhstan, and Georgia. The manganese ores are characterized by their content of manganese, iron, and various impurities. The main types of ores are metallurgical (>35% Mn; high-grade ores with a manganese content above 48% are within this category), ferruginous (15% to 35% Mn; high levels of iron), and mangano-ferrous ores (in fact, iron ores with 5% to 10% Mn). The metallurgical ores are mainly used for direct production of high carbon ferromanganese and silicomanganese alloys, whereas the last two categories are used especially in blast furnaces for adjusting the manganese content of produced pig iron. There might be a substantial variation of ore composition even within the common deposit. For example, Georgian Tchiatura-oxide type ores have 15% to 43% Mn, 13% to 58% SiO_2, 2% to 4.5% Fe_2O_3, and 0.7% to 5.5% Al_2O_3 with the average manganese content ~27% (Gasik et al., 2009; Matricardi and Downing, 1995).

Metallurgical grade ores are produced from open pit and underground operations by conventional mining techniques. Ores are crushed and screened, and washed if necessary. Heavy media separation can be used for ores with a high content of silica and alumina gangue. The average manganese recovery in this operation is usually between 60% and 75%.

Metallurgical grade manganese ores contain typically 40% to 50% manganese. Another important parameter is the manganese-to-iron ratio (Mn/Fe), which is required to be >7.5 by weight for the production of standard ferromanganese alloy with 78% Mn. Extra iron might always be introduced as steel chips and recycled scrap. There are also limitations on alumina and silica contents, as excessive slag formation in the furnace increases the electric energy consumption. Ores and concentrates with more than 10% SiO_2 are suitable for use in SiMn production. In some deposits, high phosphorus content is also a concern, and it must be removed before smelting because most of the phosphorus remains in the finished product. South African manganese ores are characterized by low phosphorus content, but, for example, Nikopol ore deposits (Ukraine) have 0.15% to 0.30% P in oxide-type ores and up to 0.6% P in carbonate-type ores (Gasik, 1992). Other physical and chemical properties are also important, such as the level of volatiles and the excess oxygen content. Sulfur is not a problem, neither for metallurgical nor for environmental reasons, as sulfur forms manganese sulfide, which is dissolved and usually removed with the slag.

Most of the mines have sinter plants, where fines are agglomerated. Sintered material is well suited for use in ferromanganese furnaces because it is mechanically strong and thermally stable, allowing the gas to disperse evenly throughout the preheating and prereduction zone. The sintering also results in saving energy if the ore is of the carbonate type. If, on the other hand, oxide-type ores are sintered, most of the beneficial heat from the exothermic

prereduction that usually takes place inside the furnace is lost and the energy consumption will increase. However, the use of fluxed sinter, by the addition of dolomite or MgO-contained materials, has been introduced and shown to improve both sinter plant and smelting operations (Kutsyn et al., 2012).

A blend of manganese ores is, in most cases, used when manganese ferroalloys are produced either in electric submerged arc furnaces or in blast furnaces. The choice of ores depends on chemical and physical properties as well as on economic factors. Table 7.2 shows the average analyses of some important metallurgical ores (Gasik, 1992; Gavrilov and Gasik, 2001; Matricardi and Downing, 1995; Olsen et al., 2007; Samuratov et al., 2010; Tangstad et al., 2004). It is evident that there are important differences in the chemical composition of the various ores. For example, some ores have an unfavorable Mn/Fe ratio but rather low phosphorus content, so a proper ore dressing process must be applied on a case-by-case basis.

After mining, ore is crushed and screened into various particle size fractions ranging from fines (<6 mm) to lump ore (<75 mm). The proportion of fines is often as high as 30% to 70% of the total. Screened ores are upgraded by various methods to produce concentrates. The most common physical separation methods are washing, high-intensity magnetic separation, separation by gravity concentration, and separation by flotation, which makes use of the different surface properties of the minerals. An example for particle size distribution for Nikopol ore concentrates is shown in Table 7.3 (Gasik, 1992).

7.3.2 Agglomeration Processes

Experience has shown that smooth and efficient operation of manganese ferroalloys smelting furnaces is achieved when close sizing control is practiced on the raw materials. The raw materials must secure good permeability for the gas to be distributed through the burden. Fines in the raw materials are particularly detrimental, causing poor charge porosity, which will result in high power consumption per ton of alloy, excessive fume and dust losses, and low productivity. Alloy producers prefer lump and agglomerated ores. High-quality fines are often agglomerated, normally by the use of a sintering process either at the mine or at the customer's plant.

Sintering, pelletizing, and briquetting are three principal technologies used for the agglomeration of ores and concentrates.

Pelletizing is a more difficult process for manganese ores than for most iron ores. It requires higher temperatures ($>1150°$ to $1250°C$) to produce strong enough manganese ore pellets, which makes it a more expensive process. On heating of green pellets, manganese dioxide (MnO_2) and manganic oxide (Mn_2O_3) dissociate in endothermic reactions that impose additional fuel consumption. Fine grinding of the material would also be necessary for pelletizing. Consequently, pelletizing appears to be a rather expensive solution for manganese ore, particularly compared with iron ore, although there are

TABLE 7.2 Typical Compositions of Some Manganese Ores (major components)

Deposit	Type	Mn	SiO_2	Fe_{tot}	MgO	Al_2O_3	CaO	H_2O	P
Nikopol (Ukraine)	Oxide	29–43	11–24	1–3	0.8–2	1.4–3.3	4–10	0.5–2.5	0.15–0.3
	Pyrolusite	47.5	8.6	0.65	0.6	1.6	2	<1	0.2
	Carbonate	22–28	13–16	1.5–3	1.5–2.2	1.7–2.3	7–13	0.5–1.5	0.3–0.6
Tchiatura (Georgia)	Oxide	30–44	6–17	0.7–4	1–2.5	1.3–2.6	3.8–5.5	n.r.	0.1–0.4
	Pyrolusite	28	17.6	1.3	1.5	2.9	8.2	n.r.	0.20
	Carbonate	23–25	16–17	1.3	2.5	2	10	n.r.	0.15
Comilog (Gabon)	Pyrolusite	46–51	4–8	3–4.7	<0.3	5.5–7.5	<0.2	<9	<0.1
Groote Eylandt (Australia)	Pyrolusite	48.8	7	4.2	0.1	4.2	0.1	2.7	0.1
Gloria (South Africa)	Carbonate	39.1	5.7	5	3.8	0.3	12.7	0.4	0.02
Mamatwan (South Africa)	Carbonate	37.8	4	4.6	3.5	0.5	14.7	1	0.02
Zapadny Kamys (Kazakhstan)	Fe-Mn type	17–19	40–42	5–6	1–1.5	5–6.5	1.2–1.7	n.r.	0.035

n.r., not reported.

TABLE 7.3 Typical Particle Size Distribution, % wt., of Beneficiated Nikopol Manganese Ores

Size Class, mm	Gravitational Oxide Concentrates	Oxide-Carbonate Concentrate
+25	2.5−10.5	—
25−8	10−33	—
8−5	15−36	—
5−3	5−20	63−68
3−0.5	14−42	17−20
0.5−0.2	5−14	—
−0.2	<3.5	13−16

known attempts to pelletize fine manganese ores (flotation enriched) into 12 to 15 mm size pellets using low-temperature drying.

Briquetting is of less importance for conventional concentrates but is of some interest for agglomeration of manganese-bearing wastes and undersized ore and carbon materials at the production plant. The sintering and pelletizing processes are associated with high capital investment and the high cost of grinding and burning. Briquetting is, in contrast, a cold bonding process and consequently less capital intensive than pelletizing, and it does not need extra milling of materials. Bitumen, cement, molasses, and lime, alone or in combination, have been tested as binders for making briquettes. Reasonable results have been reported for briquetting of concentrates with 3% to 6% humidity (using 7% to 10% lignosulfate as a binder) when pressing at 9 to 10 MPa and drying at 130° to 140°C (Gasik, 1992). The presence of carbon reductant raises the briquette softening temperature up to 1250° to 1400°C.

Agglomeration by sintering has become the leading technology for processing manganese ore. Phase transformations in manganese sinter are not as well known as respective ones in iron ore sintering, which are hindered by a lack of reliable information of the equilibria in complex oxide systems. For instance, in the CaO-MnO-MgO system the solid phase is only of the monoxide type (MeO), but in the presence of MnO there is a miscibility gap leading to separation of CaO-rich and MgO-rich solutions (Woermann and Muan, 1970). It might be caused by manganese oxidation, as in this system oxygen potential should be below 10^{-9} atm to ensure the stability of Mn^{2+}. This system, with addition of silica, is even less studied, especially in the solid-state regions relevant for sinter production. Mechanisms of low-temperature transformations

at 600° to 1200°C as well as the exact mineral structure of some forming phases (donpeacorite, kanoite, substituted pyroxene, and clinopyroxene) are still a subject of discussion (Bohlen et al., 1980; Kutsyn et al., 2012; Petersen et al., 1984; Phase equilibria diagrams, 2001).

The traveling grate technology is the traditional way to produce manganese sinter, such as at the TEMCO ferroalloy smelter plant (Australia), Samancore Manganese Mamatwan mine (South Africa), COMILOG manganese mines (Gabon), and Vale mines (Brazil). This equipment is most suitable for larger capacities. Alternatives are the new steel belt sintering technology developed for smaller capacities (Outokumpu Corp., Finland) or stationary pan sintering (Vale in Mo i Rana, Norway and previously also by Eramet Sauda, Norway). The down-draught sintering in stationary pans is an old established practice capable of producing good-quality sinter for smaller tonnages.

Sintering and pelletizing upgrades the manganese content of the ore through the loss of oxygen from manganese oxides and other volatile species as bound water and carbonates. An example of nonfluxed and fluxed compositions of agglomerates is shown in Table 7.4 (Gasik, 1992; Kutsyn et al., 2011).

Agglomerate compositions similar to those shown in Table 7.4 usually result from the mixture of proper ores and concentrates, depending on the raw materials parameters and requirements for final basicity, stability, and composition. As an average, about 1 to 1.3 t of sinter is processed per 1 m^2 of the sinter machine in 1 hour. One ton of ready sinter usually requires 1.2 t of manganese concentrate, 120 kg of coke, 5.6 Nm^3 of natural gas, and 85 to 95 kWh of electric energy (Gasik et al., 2009). A burden less oxidized, but with better physical characteristics and favorable mineral composition, may result in improved furnace operation compared with an oxidized burden of poor physical quality. When manganese ferroalloys are manufactured on a scale that does not allow the use of large sinter plants at the metal producer's plant as in iron making, the sintering of fines is often carried out at the mine. Sintering at the metallurgical plant makes it possible to use fine ores that are otherwise unusable, as well as fines produced by rescreening classified ores, bag-house dust, sludge from gas cleaning plants, and fines from screening of carbon materials. Coke fines are used as the main energy source in the sintering process. If the smelting furnace is covered and equipped with CO gas collection, the CO gas

TABLE 7.4 Example of Composition of Nonfluxed (AMN) and Fluxed (AMO) Manganese Sinters from Nikopol Ores, % wt.

Type	Mn	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	P	S	K_2O+Na_2O
AMN	43−50	19−28	2−4	2−3	2−4	1−2	0.12−0.2	0.1−0.2	1−2.5
AMO	36−40	16−25	3−6	2−3	3−8	6−10	0.15−0.2	0.1	1−2.5

can also be used as energy in the sintering plant and for preheating the smelter feed. Sinter is extensively degraded during handling and transportation and should therefore be produced near the utilization point. Addition of proper fluxes (higher MgO contents) was shown to improve mechanical properties of fluxed sinter and resist its degradation in storage (aging due to calcium orthosilicates) by creation of a larger fraction of monoxide phase (Kutsyn et al., 2012).

7.4 MANGANESE FERROALLOYS

7.4.1 Manganese Alloy Specifications

The primary use of manganese is in the steel industry where manganese is added mainly in the form of ferroalloys. Several different types of manganese alloys have been developed and are being marketed (Matricardi and Downing, 1995). These alloys may be divided into the following major categories:

- Ferromanganese FeMn, high- (HC), medium- (MC), and low-carbon (LC)
- Silicomanganese SiMn (or ferrosilicomanganese FeSiMn)
- Metallic manganese Mn
- Nitrided manganese alloys (nitrided manganese MnN and silicomanganese SiMnN)

The number of alloy specifications is large. Some suppliers list more than 20 different products. The alloys vary in manganese, carbon, silicon, phosphorus, and nitrogen content. Because of the scarcity of low phosphorus manganese ores, many users, especially alloy steel manufacturers, will pay a premium for low phosphorus alloys. Typical examples of alloy specifications for most commercially used manganese ferroalloys are shown in Table 7.5 (Gasik, 1992, Gasik et al., 2009; Olsen et al., 2007).

High-carbon FeMn is the traditional form of manganese added to steels, but its application is mostly limited to unalloyed and low-alloyed carbon steels. Medium and low carbon ferromanganese are used where the carbon content must be controlled and cannot be reduced after the addition of the ferroalloy. These grades are mainly produced by oxygen refining of high carbon ferromanganese and by a silicothermic process involving the reaction between silicon in crude SiMn alloy and manganese ore. The consumption of refined alloys with reduced carbon content is increasing due to increasing production of low carbon steels. In 2010, the worldwide production of refined ferromanganese (< 2% C) was 1.5 Mt. The use of silicomanganese is expected to advance at a faster rate than high carbon ferromanganese consumption. Silicomanganese adds less phosphorus, carbon, aluminum, and nitrogen to the steel compared to a mixture of standard high carbon ferromanganese (HC FeMn) and ferrosilicon with 75% Si (FeSi75). Standard quality silicomanganese (SiMn) is used in most silicon and manganese-containing steels where the combination of carbon,

TABLE 7.5 Typical Composition of Major Commercial Manganese Alloys (maximum content, wt. % unless shown otherwise)

Alloy	Grade	Mn	C	Si	P	S	N
HC-FeMn	78	78−82	7.5	1	0.05*; <0.2−0.35	0.03	
	75	>75	<6−7	<4−6	0.05*; 0.45	0.03	
	70	>70	7	6	0.06	0.03	
MC-FeMn	88	85−95	2	3	0.4	0.03	
	85C1	85	1−1.5	1	<0.1−0.3	0.03	
	75C2	75	1.5−2	2−2.5	<0.2−0.35	0.03	
LC-FeMn	90	95	0.2	1	0.07	0.05	
	85C0.5	85	0.5	2	<0.2−0.3	0.03	
FeSiMn (commercial)	Si25	>60	0.5	25−35	0.05	0.01	
	Si22	>65	1	20−25	0.1	0.02	
	Si17	>65	2.5	15−20	0.1	0.02	
	Si12	>65	3.5	10−15	0.2	0.03	
FeSiMn	Crude[†]	Bal.	<0.05−0.15	>27	<0.05−0.07	0.02	
Metal Mn	998[‡]	99.8	0.04	—	0.003	0.003	
	997[‡]	99.7	0.06	—	0.05	0.10	
	965	96.5	0.10	0.8	0.05	0.05	
	95	95	0.20	1.8	0.07	0.05	
MnN	92N6[‡]	92	0.1	—	0.005	0.1	>6
	87N6	87	0.2	1.8	0.07	0.05	>6
	89N4	89	0.2	1.8	0.07	0.05	>4
	91N2	91	0.2	1.8	0.07	0.05	>2
SiMnN	7N	>60	3.5	9−17	0.1	0.02	>7
	5N	>60	3.5	9−17	0.1	0.02	4−7

*For premium grades only.
[†]As reductant for smelting Mn, max. 2.3% to 2.8% Fe.
[‡]Only for Mn made by electrolysis.

manganese, silicon, and trace elements fits the final steel analysis in an economical way. The use of low carbon silicomanganese in stainless steels and alloy steels provides a more economical production route, where a combination of manganese and silicon is required in a low carbon steel product.

Metallic manganese is produced by two methods: electrolytic and electrothermal. Electrolytic manganese is the purest form of manganese and has a minimum content of 99.8% Mn. This hydrometallurgical method is not considered here. Electrothermal manganese is produced by the reduction of dephosphorized manganese slag melt with silicon from crude SiMn in the presence of flux (lime). For this purpose, SiMn has a limited amount of iron (Gasik, 1992). It is used in the production of aluminum and copper alloys, for special grades of stainless steel and other special steels, and for electronic applications. Aluminum alloys constitute the largest nonferrous metallurgical use of manganese. Manganese improves the corrosion resistance of aluminum. Aluminum alloys with a Mn content of 1% or more are widely used in beverage cans and in food-handling equipment. Manganese bronzes are copper-based alloys, strengthened by small additions of manganese (up to 4.5%). These alloys are used for marine propellers and fittings as well as gears and bearings.

7.4.2 Impurities in Manganese Alloys

The trend toward the production of higher-quality steels with fewer impurities increases the pressure on producers of manganese alloys to improve the quality of their products by tighter specifications on harmful elements—particularly carbon, sulfur, and phosphorus (see Table 7.5). Commercial production of manganese alloys from ordinary raw materials inevitably introduces many impurities in the final metal, although in smaller amounts. Typical concentrations of a number of these constituents are given in Table 7.6.

7.5 SMELTING TECHNOLOGIES FOR MANGANESE ALLOYS

7.5.1 Basics of Reduction Processes

Manganese ores will always contain some iron oxides. Reduction of the iron oxides in the ore is probably almost complete when the temperature reaches 1200°C. The product will be a carbon-saturated iron alloy with an increasing content of manganese at increasing reductions in temperature. The last reduction step, $MnO \rightarrow Mn$ metal, will take place in the liquid state with MnO being dissolved in the oxide melt and the produced manganese metal continuously dissolved in the liquid carbon-saturated Mn-Fe-C metal. Both MnO and SiO_2 are partially reduced from the slag to form the metal phase.

Besides manganese oxides and silica, the manganese ores normally also contain Al_2O_3, CaO, and MgO. Coke ash also contains SiO_2, Al_2O_3, and smaller amounts of CaO and MgO. In addition, CaO- and MgO-containing

TABLE 7.6 Typical Concentration of Other Impurity Elements in Manganese Ferroalloy (Olsen et al., 2007)

	wt. %		ppm												
Alloy	O	N	Al	Ca	Mg	Ti	Cr	Co	V	Ni	Cu	Zn	S	B	H
HC FeMn	0.2	0.03	50	100	300	80	200	220	400	220	130	80	20	< 5	20
MC FeMn	0.4	0.12	50	100	3000	40	350	270	400	280	150	10	40	< 5	15
LC FeMn	0.4	0.12	50	100	2000	50	750	290	450	280	170	10	30	< 5	15
MC SiMn	0.15	0.005	150	200	350	2000	320	110	250	300	75	15	90	220	15
LC SiMn	0.15	0.005	150	100	200	2500	300	70	250	300	75	15	30	220	15

fluxes are usually added to the raw material mixture. These oxides will end up in the slag phase. They are considered to be irreducible, and they maintain their mutual ratio in the slag during the reduction process, this being of great importance for the thermodynamic and physical properties of the slag phase.

As follows from the Fe-Mn-Si-C system equilibria (e.g., see Fig. 7.8), graphite remains the stable phase coexisting with carbon-saturated alloy melts until the Si-content reaches a certain value (approximately 18% for Mn-Si melt; this depends on temperature). Then silicon carbide replaces graphite as the stable carbon-containing phase.

The important factors that control the degree of manganese reduction are the slag basicity, which in practice is expressed as $(CaO+MgO)/(Al_2O_3+SiO_2)$, and CO partial pressure. An increase of basicity and a decrease of CO pressure will reduce the MnO content of the slag considerably (Olsen et al., 2007). Even though experimental results may provide a basic image of the equilibrium compositions of metal and slag for a given system, it will still be difficult to determine the exact quantities and compositions of the reaction products. The reason is that the final state of a given system is dependent not only on chemical equilibrium but also on stoichiometric restrictions (i.e., the materials balance).

Carbonates present in the charge or added as flux decompose between 300° to 900°C. The higher manganese oxides that predominate in manganese ores (MnO_2, Mn_2O_3, and Mn_3O_4) are relatively unstable and easily reduced in solid state. These are exothermic reactions producing a considerable amount of heat and thereby preheating the charge materials in the furnace. Iron is always present in manganese ores, and the reduction of iron oxides runs parallel to the reduction of higher manganese oxides. At temperatures above 1150°C, reduced iron forms a liquid alloy, dissolving carbon and assisting in the reduction of manganese due to lower Mn activity in the metal phase. Considerable smelting of the remaining oxide mixture starts at ~1250°C, and the final reduction of MnO to manganese metal will take place with solid carbon in the coke bed. This is also the case for the reduction of silica to silicon metal. Some carbon will dissolve in the metal up to carbon saturation.

The manganese reduction reaction is highly endothermic and will consume approximately two thirds of the supplied electric energy for HC FeMn production and one third for SiMn production. The CO gas will heat the descending raw materials in the furnace. Because a reduction of the higher manganese oxides with CO gas is exothermic, these reactions will contribute to the temperature increase in the prereduction zone.

7.5.2 Outline of Industrial Practice
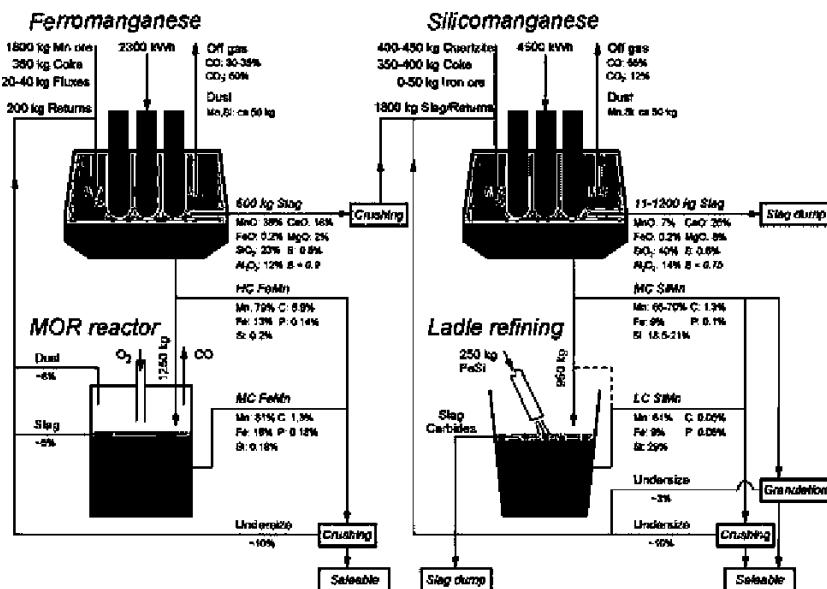
Manganese ferroalloys are commercially produced by the carbothermic reduction of manganese oxide ores in submerged arc furnaces (SAFs). The blast furnace process is still marginally used for high carbon FeMn production, where the coke serves as a reducing agent as well as an energy source. Blast

furnace smelting has serious disadvantages, such as high coke consumption (~1500 to 2000 kg/t of alloy, which is five to six times higher than in electric furnaces) and high losses of manganese in slag and off-gases. The electric furnace practice offers several advantages, such as a higher overall yield of Mn from the ores, less carbon consumption, lower-quality reducing agents, and greater flexibility in its ability to produce different grades of alloys. In addition, basically the same furnace might be switched to a flexible production of either HC FeMn or SiMn on demand.

All manganese ferroalloys are processed, in principle, by either the discard slag method (sometimes called the flux process) or the duplex (also known as the flux-less) method. These two methods are not, however, directly dependent on the number of added fluxes but rather on the final basicity of the slag. Both can be realized with or without fluxes, depending on the raw materials. The first method is quite similar to the blast furnace practice and it aims to reduce manganese into the alloy in one stage, usually with assistance of basic fluxes (CaO, MgO) or using a basic ore decreasing silica activity in the slag and increasing the activity of MnO. For high-carbon ferromanganese discard slag practice (flux), manganese recovery is ~80%, and about 15% to 20% MnO remains in the slag, which is dumped, as it is not economical to recover more manganese at such concentrations.

The second method, the duplex process, is more common. There is normally a blend of several ores to achieve a required composition of produced metal and slag. The tapped slag will contain as much as 30% to 50% MnO. The MnO-rich slag is reprocessed for the production of silicomanganese or metal manganese in the second stage (Fig. 7.13). In this way, the MnO content of the discarded slag can be reduced to ~5% MnO, and an overall manganese recovery is increased to 85% to 90% with less coke required.

The interior of a furnace producing high carbon ferromanganese consists of two main zones: the top prereduction zone (low temperature) and the lower coke bed zone (high temperature). In the prereduction zone, raw materials are heated through heat exchange with ascending hot gases, and solid-state reduction of higher manganese oxides to MnO by CO gas takes place. Due to the exothermic nature of these reactions, temperature increases lead to melting of the partially reduced manganese ore (Tangstad et al., 2010). In the coke bed zone, prereduced and molten ores and fluxes fuse together to form an oxide melt (slag). This zone has a bed of solid coke, liquid slag, and liquid metal. These phases may be present in various configurations depending on the history of the operation. The coke bed starts approximately at the tip of the submerged electrodes. The relative amount of coke in the charge mix determines whether the coke bed increases, decreases, or is stable in size. In addition to being the chemical reduction agent coke also acts as the heating element of the process where the electric current runs and joule energy is produced, determining temperature distribution. The production rate, product quality, and stability of the furnace operation are mainly determined by parameters in the coke bed.

FIGURE 7.13 Duplex (double stage) production of HC FeMn and SiMn, with refining processes (Olsen et al., 2007).

Due to the different densities of coke, slag, and metal, the various layers are often described in the literature as consisting of separate layers. However, from excavations of single-phase pilot-scale furnaces and industrial furnaces, it has been proven that coke is present all the way down to the metal layer, due to the weight of the above located charge materials. The slag-to-coke ratio in the coke bed increases with decreasing distance to the metal layer. Also, vertical columns of almost pure slag have been found in the center of the coke bed. The structure of this zone may vary from "dry coke" (with no slag) to coke lumps more or less evenly dispersed in the slag, which hence have no mutual contact. The shape and size of the coke bed may also vary from horizontal layers to bell-shaped and conical shapes depending on raw materials, slag chemistry, and most of all on the preceding furnace operation (i.e., whether the coke volume in the furnace is increasing, decreasing, or is in a stable state). The electrode tips are normally located around the upper level of the coke bed, and the current distribution is mainly determined by conditions in this zone. If raw materials are changed in type, the existing ore inside the furnace will be replaced much faster than the existing coke. Depending on the coke bed volume, a complete change to new coke in the furnace may take several weeks.

The generation and transfer of heat in the furnace determine the performance. Electric energy must be converted into heat in those regions where the thermal energy is mainly consumed. Enough energy should be supplied

to the lower regions to give sufficient conditions of slag and metal for easy tapping. The main factors that affect the energy distribution and consequently the process temperature are a naturally electric energy supply, a balance of enthalpy of chemical reactions, and internal heat exchange and transfer of heat by circulating substances, such as Mn(g), K(g), and CO-rich gases.

For normal furnace operation, the electrodes are submerged relatively deep in the furnace, and due to the large difference in electric resistivity, most of the current will run through the coke bed. The main part of the electric energy is dissipated in the coke bed area close to the electrodes. This means that the rate of raw material flow and metal production is at its maximum close to the electrodes, where also the gas flow rate will be high. Despite the turbulence and high temperature gradients in the reaction zone, it has been found during the excavation of furnaces that the slag composition changes gradually throughout the coke bed; hence, it is believed that the horizontal movement of coke, slag, and gas is very small.
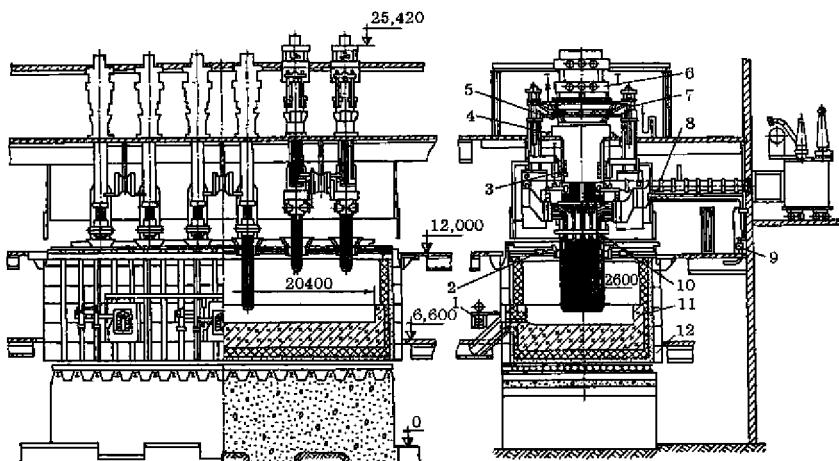
Commonly, bulk manganese alloys are produced in three-phase submerged arc furnaces, which have a three-electrode (Søderberg type, or self-baking) circular or a six-electrode rectangular geometry. Most of the modern production of manganese alloys takes place in covered furnaces rated from 20 to 90 MVA power capacity (Table 7.7).

Examples of the construction of the last two furnaces described in Table 7.7 (Gasik et al., 2009) are shown in Figure 7.14 (rectangular type) and Figure 7.15 (circular type).
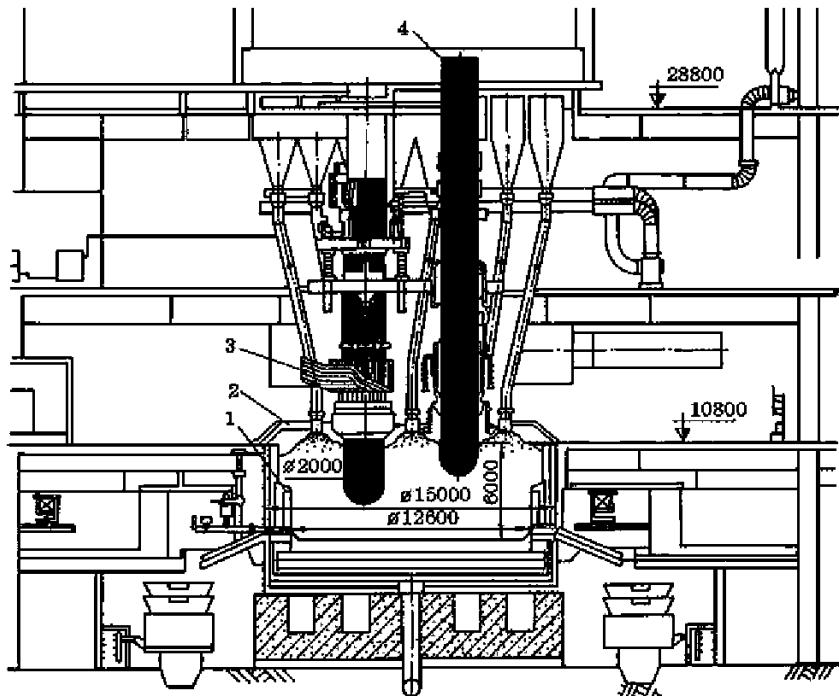
TABLE 7.7 Parameters of Some Industrial Furnaces for Smelting of HC FeMn from Plants in Norway and Ukraine (Gasik, et al., 2009; Olsen et al., 2007)*

Furnace Type	Circular	Circular	Rectangular	Circular
Rated power, MVA	45	45	63	75
Electrodes	3	3	6	3
Electrode section, mm	Ø 1700	Ø 1900	3000 x 750	Ø 2000
Electrode current, kA	120	133	112	160
Electrode pitch, mm	4000		3300	4300
Hearth depth, mm		8800	3190	7300
Hearth size, mm	Ø 12000	Ø 15000	20340 × 6000	Ø 15000
Power factor			0.91	0.92

Empty cells mean no data have been provided.

FIGURE 7.14 Rectangular 63 MVA furnace for manganese ferroalloys (dimensions in mm): 1, tap hole device; 2, furnace cover; 3, electrode holder support; 4, gaskets; 5, hydraulic shift system; 6, electrode shift mechanism; 7, hydraulic lift; 8, "short net" (secondary circuit); 9, water cooling system; 10, electrode holder; 11, lining; 12, furnace shell.

FIGURE 7.15 Circular furnace (75 MVA) for manganese ferroalloys (dimensions in mm): 1, carbon blocks lining; 2, furnace cover; 3, short net; 4, electrode.

The raw material mix is transported to hoppers above the furnace from where it is fed by gravity through chutes passing through the furnace cover. Produced slag and metal may be tapped simultaneously from the same tap hole, or separately in different slag and metal tap holes arranged at a vertical distance of 0.5 to 1 m.
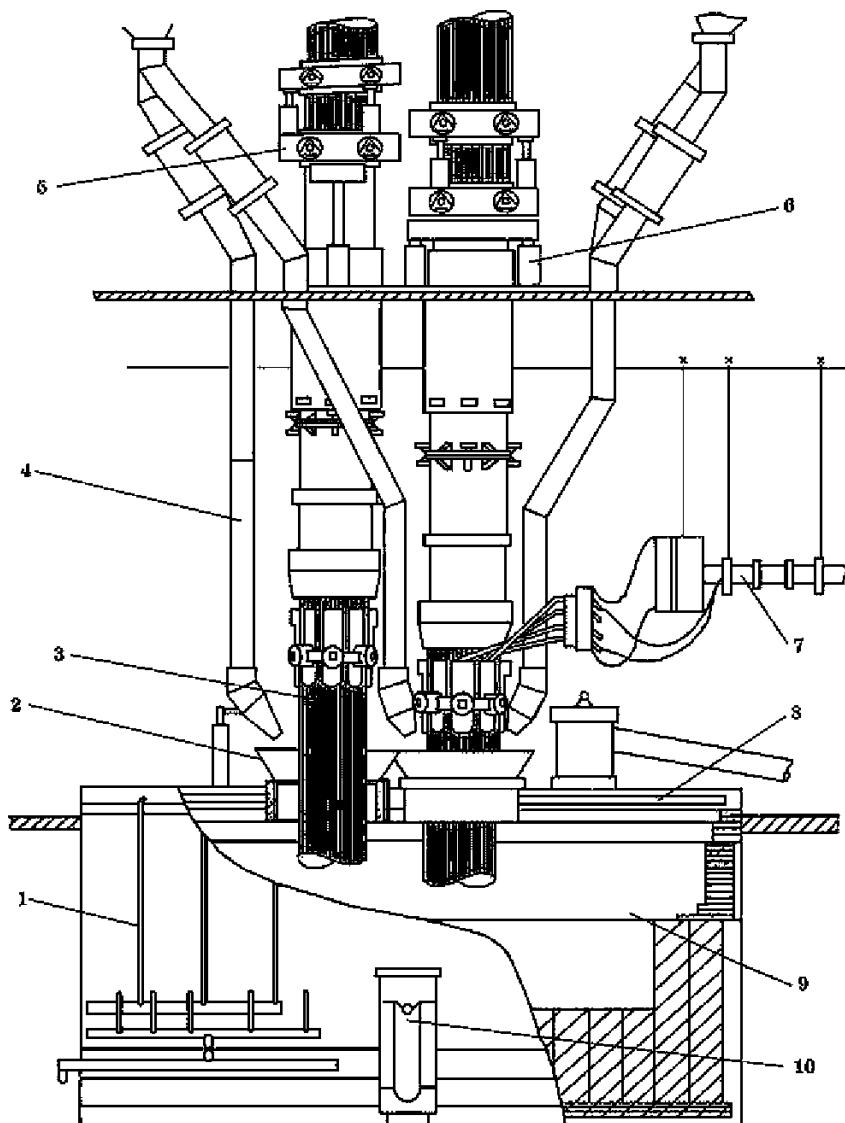
When high-phosphorus (>0.2% P) manganese ores are utilized, it is not usually feasible to remove phosphorus at the stage of ore-dressing or agglomeration. In this case, the electrometallurgical method is sometimes used first to reduce phosphorus and iron from the oxide melt with a minor amount of coke into a by-product metal, leaving most of the manganese in the refined slag, which then will be used for further processing into FeMn, SiMn, or metal manganese. The process is carried out in circular closed furnaces (Fig. 7.16) continuously, with periodic tapping of slag (38% to 42% Mn, 0.010% to 0.017% P) and metal (50% to 55% Mn, 1% to 3% Si, balance Fe, C, and P). There, ~90% of the total amount of phosphorus and iron present is reduced into the metal.

7.6 TECHNOLOGY OF FERROMANGANESE

7.6.1 High-Carbon Ferromanganese Production

High carbon ferromanganese is commercially produced by the carbothermic reduction of manganese ores, primarily in electric submerged arc furnaces. The produced metal typically contains around 72% to 82% Mn and 7% C (see Table 7.5), and the slag contains around 40% MnO (duplex process). An increasing part of the metal is refined to medium or low carbon ferromanganese after smelting. Different raw material components are weighed out based on chemical analyses of ores, fluxes (dolomite, limestone), and carbonaceous agents (coke), and on the desired composition of alloy and slag. These basic fluxes are added to give the slag suitable chemical properties, smelting temperature, and viscosity in order to secure good furnace operation and a high manganese yield. Blending ores from different sources is a common practice—for instance, to obtain a specific Mn to Fe ratio in the metal (e.g., 7:1 for high carbon ferromanganese with 78% Mn). Independent producers in ore-importing countries have considerable flexibility in the blending of ores to produce a given product at the lowest production cost. For instance, the Fe and P content of the metal is determined and controlled by the composition of the ore mix, as iron oxides and undesired oxides of phosphorus are easily reduced. Also, the slag basicity is important because it controls smelting properties and the content of unreduced MnO in the slag.

Examples of HC FeMn smelting by flux and flux-less processes are shown in Table 7.8 (Gasik, 1992). Note that the parameters of these processes greatly depend on the ores used, furnace type, slag basicity, and furnace operation methodology.

FIGURE 7.16 General view of the 22.5 MVA furnace for phosphorus removal from the manganese slag: 1, furnace shell; 2, charge feeding funnel; 3, self-baking electrodes; 4, charge feeding ducts; 5, electrode holding and shifting mechanisms; 6, hydraulic shifting cylinders; 7, short net; 8, furnace cover; 9, hearth; 10, tap hole and guide.

Optimized ferromanganese furnace operation assumes a necessary high load, a minimum of coke and energy consumption, stable and expected metal and slag composition with a high yield of manganese and minimized greenhouse gases, and noxious compounds emissions. Whereas the power consumption is

TABLE 7.8 Comparison of Basic Parameters of Smelting of HC FeMn by Different Process Types (per 1 ton of alloy with 78% Mn; n.r. = not reported)

Parameters	Discard method	Duplex method		
	Plant A	Plant B	Plant C	Plant D
Specific consumption, kg/ton				
Concentrate or agglomerate (48% Mn)	1950−2060	2750−2970	n.r.	n.r.
Coke	550−580	350−420	360	306
Iron ore pellets	110	85	−	−
Limestone	700	−	−	−
Electrode paste	10−21	12−22	12	6.6
Electric energy, kWh/ton	3300−3900	2200−3500	2400	2150
High−MnO slag (48% Mn basis), kg/ton	−	900−1300	n.r.	n.r.
% Mn in slag	12−15	35−38	31.2	33.1
Slag/metal ratio	1.2−1.3	0.8−0.9	0.64	n.r.
Manganese yield, %	76−82	97−99	76.7	81.5

determined mainly by reactions in the prereduction zone, the stability of the operation is determined by the coke bed size and the reactions taking place in the coke bed zone. A biased carbon balance (coke loads that are too high or too low) will result in erroneous electrode positions and an upset of the heat distribution between the charge zone and the reaction zone. This will most often lead to operational problems with less metal yield and a lower load, and thus reduced tonnage. These factors are important for the economy of the process.

If the correct mixture of ores and fluxes fails to be added, this will be easily detected by the slag and metal analyses and may be corrected relatively quickly. However, if the added quantity of carbon is incorrect, this may not be readily noticed. Even with good chemical analyses and weights of raw materials, there can easily be 1% to 2% inaccuracy in the carbon quantity added. In a 40 MW FeMn furnace producing 400 tons of HC FeMn per day with a coke consumption of 330 kg coke per ton of alloy, a total of 132 tons of coke will be added every day. With an inaccuracy rate of 2%, the furnace may be "undercooked" or "overcooked" by ±2.6 tons/day. After 2 weeks of "overcoking" there will be a buffer of more than 35 tons of coke in the furnace. Hence, even if a good mass balance is calculated, this is only one of several necessary means to secure the right quantity of raw materials.

7.6.2 Production of Commercial Silicomanganese (FeSiMn)

Silicomanganese (SiMn) is also produced by the carbothermic reduction of raw materials in electric submerged arc furnaces of the same type as used for the production of HC FeMn. The size of the SiMn furnaces is usually in the range 15 to 63 MVA (actual power 13 to 57 MW), giving 80 to 340 tons of alloy per day. Operation of the SiMn process differs from the FeMn process, as higher process temperatures are needed to attain the wanted silicon specification content in the metal (see Table 7.5). Basically there are no differences between commercial and crude SiMn production except the charge composition and process temperature. The SiMn production is often integrated with the manufacture of HC FeMn so that the high-MnO slag from the HC FeMn production (or from the phosphorus removal smelting) is reprocessed in the production of SiMn. In this way a high total yield of manganese is achieved (see Fig. 7.13).

In addition to manganese slag, Mn ore (agglomerate), and coke, other components of the charge are quartzite, FeSi or Si-melts, or off-grade qualities. The ratio of raw ore to Mn slag varies from plant to plant, depending on the ore quality and availability (for high-grade ores with low phosphorus production, the use of MnO-rich slag might not be required). The major flux used is dolomite or dolomite-limestone.

During smelting, iron and manganese oxides are reduced first, as in the HC FeMn process, but the reduction of silicon requires higher temperatures ($1600°$ to $1650°C$). Carbon-saturated alloys are in equilibrium with either graphite ($<20\%$ to 23% Si) or SiC (at higher silicon concentrations), whereas a major amount of carbon is combined into Nowotny's phase $(Mn,Fe)_5Si_3C_x$ (Gasik et al., 2009). The higher the silicon content, the lower the carbon level would be, similar to the Fe-Si-C and Cr-Si-C systems. As high silicon content in the alloy requires more energy, for SiMn alloys $>30\%$ Si addition of silicon wastes from the ferrosilicon industry is being practiced (Olsen et al., 2007). These wastes are relatively cheap sources of silicon, so this practice can even be favorable for the production of standard SiMn because it greatly reduces the specific energy consumption and consequently increases the production capacity of the furnace. The example of the SiMn smelting parameters is shown for 33 to 63 MVA furnaces in Table 7.9 (Gasik, 1992; Gasik et al., 2009; Olsen et al., 2007). The specific power consumption for the production of standard SiMn from a mixture of Mn-ore, HC FeMn, slag, and Si-rich metallic remelts is typically 3500 to 4500 kWh/ton of metal, depending primarily on how much of the metallic part of the charge is added to the feed. The power consumption will increase with the Si-content of the metal produced and also with the produced amount of slag per ton of metal.

Although the use of high-MnO slag with low phosphorus might ensure lower phosphorus content in SiMn, an excess supply of the slag is not feasible as it has a relatively low melting temperature compared with Mn-ores. Therefore, a too-

TABLE 7.9 Example of SiMn Smelting Parameters (basis 17% Si in the alloy)*

Parameters	Phosphorus Content in SiMn, %			
	<0.20	0.25–0.35	0.40–0.55	>0.60
Specific Consumption, kg/ton				
Manganese ore (48% Mn basis)	900–1200	1250–1400	1350–1400	1650–1670
Manganese slag (48% Mn basis)	650–850	300–360	150–180	—
Coke	310–415	320–425	320–410	320–395
Quartzite	250–285	260–330	260–305	260–300
Flux (dolomite, limestone)	100	<50	—	—
Recycled materials and Mn slags	160–200	200–235	190–250	150–220
Electrode paste	27–30	24–26	24–26	23–25
Electric energy, kWh/ton	3900–4300	3800–4100	3800–4000	3600–3900
Maximal Mn content in slag, %	10–12	11–12	11–13	12–13
Slag/metal ratio	1.6	1.5	1.4	1.3
Manganese yield, %	75–77	79–81	80–82	82–85

*Phosphorus content roughly indicates the share of low-P, high-MnO slag used in the charge, which affects other parameters.

high share of MnO slag will tend to give lower process temperatures, which will limit the practically achievable Si-level (usually <20% Si).

The economy of silicomanganese smelting is enhanced by minimizing the Mn loss as metal inclusions and MnO dissolved in the slag. The discarded slag from the SiMn process normally contains 5% to 10% MnO for the best practice (Olsen et al., 2007), although in some plants low-grade raw materials do not allow this level to decrease below 11% to 14% MnO (Gasik, 1992). To reduce the overall losses of the processes, any amount of metal fines and remelts from the production process are usually recycled back to the furnace. Industrial experiments have demonstrated that a reasonable increase of MgO in the slag would improve manganese recovery significantly. For example, Kutsyn et al. (2012) have shown that the addition of waste slag from ferronickel smelting in an SiMn flux-less process increased MgO in the slag up to 10% to 12% and allowed a decrease of MnO in tapped slag from 30–35% to 15–20% with optimal coke additions. It is expected that MgO additions shift slag mineral equilibrium composition toward the primary monoxide phase (MeO) instead of olivine or rhodonite (MeSiO$_3$), thus enhancing the activity of MnO for reduction.

7.6.3 Post-Tap Hole Processing for FeMn and SiMn

Both ferromanganese and silicomanganese furnaces are tapped every 2 to 3 hours. Even for duplex practice, there is a substantial amount of slag (Tables 7.8 and 7.9), so especially in the case of larger furnaces there are often separate tap holes for slag and metal. In the case of tapping through the same tap hole, slag and metal have to be separated outside the furnace, either by a skimmer in the runner or by cascade tapping. Both methods utilize the difference in density of slag and metal.

By the use of a skimmer, the flow from the furnace is blocked in such a manner that slag and metal are forced in different directions. In cascade tapping, a ladle for metal and one or more slag pots are placed in series, so that the flow from the furnace cascades from one container to the next. Separation occurs as the metal stays in the ladle, whereas the slag passes on to the pots. At the end of the tap, some slag remains in the ladle. The remaining slag has to be removed (e.g., by tilting the ladle and dragging off the slag with a manual or mechanical rake).

The typical temperature of the slag when it leaves the furnace is 1400° to 1500°C for HC FeMn and 1550° to 1650°C for SiMn (~19% Si). The metal temperature is ~50°C lower in both cases. The liquidus temperature at which the metal starts to solidify is for all alloys in the range of 1200° to 1300°C. For HC FeMn, the temperature interval between tapping and solidification is limited to ~100°C, which is enough to avoid extensive buildups ("sculling") on the ladle walls. However, for SiMn this value might exceed more than 300°C, which causes additional challenges. Casting at such high temperatures leads to slow solidification and creates more carbides precipitates. The solubility of carbon strongly depends on the temperature, and during cooling and solidification a considerable

number of carbides will precipitate and float toward the top of the melt. In this case, the final metal will be strongly segregated with carbide-forming elements. This phenomenon is the most troublesome at high silicon contents (>20%), because below this limit carbides will not form at these conditions.

7.6.4 Production of Manganese Metal

For manganese metal (see Table 7.5), carbon and iron contents are limited, so contrary to HC FeMn and SiMn production, carbon cannot be used here as a reductant. Manganese metal is thus produced by silicon reduction of high-MnO slag from which phosphorus has been removed. The silicon source is usually crude silicomanganese alloy, which differs from commercial SiMn mainly by limited iron content. The liquid Si-rich metal is mixed with liquid MnO slag with the addition of flux (CaO). The three-stage technology of metal manganese production is shown in Figure 7.17 (Gasik, 1992).
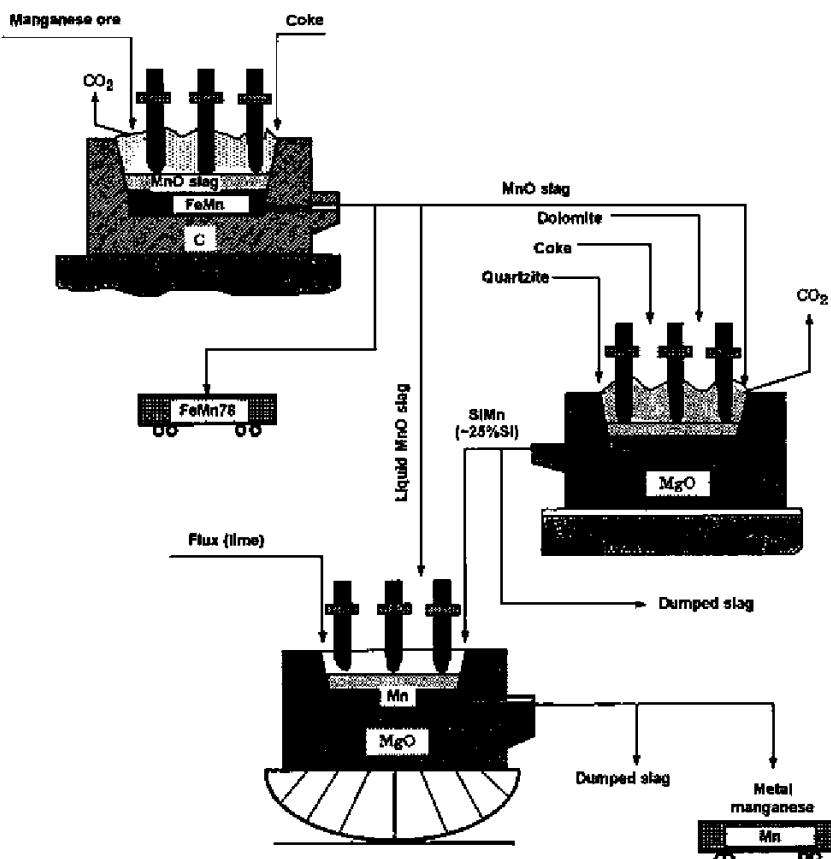
The first stage is very similar to the smelting of HC FeMn in large furnaces by a process like the one described above, and it includes production of HC FeMn (<0.70% P) and high-MnO slag (36% to 38% Mn, 20% SiO_2 and <0.012% P). The slag is tapped and split into two streams: one (liquid slag) is transferred and poured into a neighboring furnace for Mn production, and the second is solidified and then used for the smelting of crude SiMn alloy.

This solid slag is mixed with quartzite, coke, and dolomite flux to produce SiMn. Again, the chemistry of the process is similar to that used for the production of commercial SiMn, but here the attention is paid to iron, carbon, and phosphorus control. Due to this limitation, self-baking electrodes cannot be used and are substituted by graphitized electrodes; also, furnace lining is made of magnesite instead of carbon blocks (Gasik et al., 2009) (Fig. 7.18).

The charge for SiMn smelting consists of 800 kg of slag, 270 to 290 kg quartzite, and 340 to 360 kg of coke. During smelting, the yield is about 60% for Si and 83% to 85% for Mn. Target silicon content in the alloy is >25% Si, normally 27% to 29% Si. Slag formed in this stage has up to 10% to 11% MnO and is partially recycled in commercial SiMn and FeMn smelting.

The last stage includes mixing of liquid MnO slag, crude SiMn, and flux (CaO). Here, manganese oxide is reduced by silicon: $MnO + Si + CaO \rightarrow 2Mn + CaO \cdot SiO_2$ (formed SiO_2 is bound in the slag by lime to decrease its activity and to assist the reduction process). Lime addition also improves the thermal effect of manganese reduction.
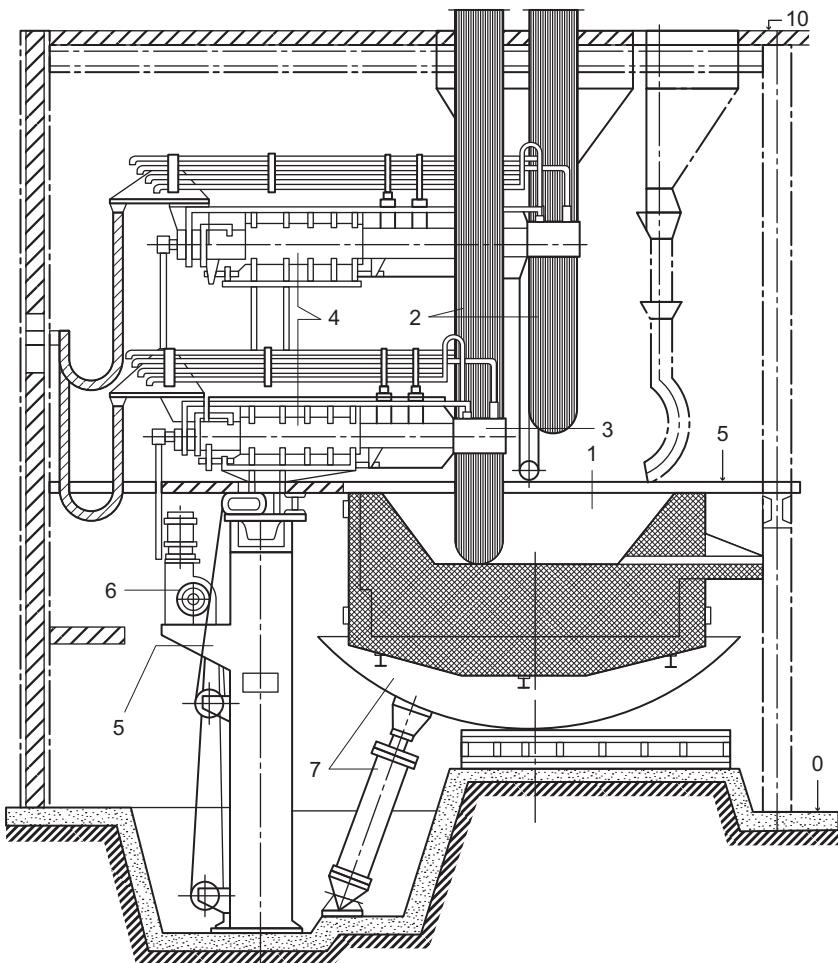
The process is carried out in a tilting furnace (see Fig. 7.18), the same as used for SiMn smelting (5 to 7 MVA capacity). It includes the following steps: preparatory stage, loading of ~one third of the total SiMn amount on the bottom, pouring of liquid MnO slag, loading of lime, melting, loading of the remaining ~two thirds of SiMn, complete melting (and reaching the required temperature), and blowing of the melt by oxygen to remove extra

FIGURE 7.17 Three-stage technology of metal manganese: (1) production of dephosphorized MnO slag and HC FeMn, (2) smelting of crude SiMn, and (3) smelting of metal manganese from liquid slag and SiMn *(From Gasik, 1992.)*

silicon from the metal melt. The process time is about 3 to 3.5 h and it requires 2040 to 2090 kg of MnO slag, 640 to 660 kg of crude SiMn, 1600 to 1650 kg of lime, and 2550 to 2600 kWh of electricity per 1 ton of manganese (Gasik, 1992). These values indicate that the slag-to-metal ratio in this stage is high, 3.6 to 4 depending on the required Mn grade and the quality of the charge materials.

The resulting metal manganese has 96% to 97% Mn, $<0.15\%$ C, $<1.2\%$ to 1.4% Si, $<2\%$ Fe, $<0.02\%$ S, and $<0.05\%$ P. The slag from this stage has a rather high manganese content (11% to 14% MnO) and high basicity, which leads to excessive slag dusting upon cooling. This is due to phase transformation $\beta–2Ca \cdot SiO_2 \rightarrow \gamma–2CaO \cdot SiO_2$, giving $+12\%$ volume change. Different additions for slag stabilization have been suggested (Gasik et al., 2009).

FIGURE 7.18   Furnace of 5 MVA capacity for the smelting of crude SiMn and metal manganese: 1, hearth; 2, electrodes; 3, short net contacts; 4, electrode holder sleeve; 5, telescopic stand; 6, lifting mechanism; 7, tilting mechanism.

In some cases, the desulfurization of metal manganese is being carried out. The usual sulfur content in manganese is only 0.01% to 0.02%, but for several applications this is too high. For example, the processing of iron-free vibration-damping alloy Mn-Cu-Ni (75% Mn) or magnetic shape memory (MSM) alloy Ni-Mn-Ga requires less than 0.001% to 0.005% S in manganese. For sulfur removal, molten manganese is treated by using a synthetic slag (40% CaO, 20% Al_2O_3, 28% CaF_2, and 12% Na_3AlF_6), which has a high potential for sulfur removal (Gasik, 1992).

7.7 REFINING OPERATIONS FOR LOW-CARBON MANGANESE FERROALLOYS

7.7.1 Production of Low-Carbon Ferromanganese
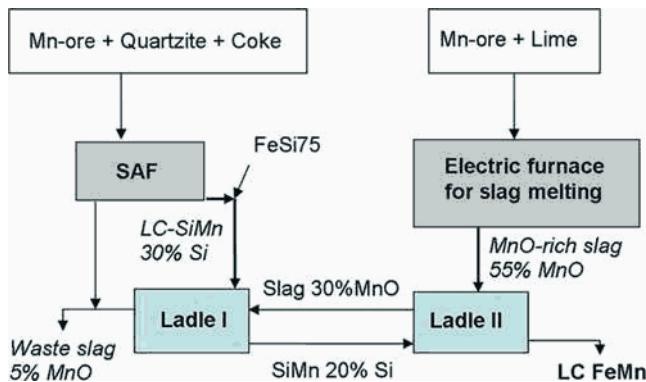
Low-carbon ferromanganese (LC FeMn) alloys are preferred, for example, for the production of low-carbon and other special grades of steel where close control of carbon is essential. Two principal methods of producing LC FeMn are in commercial operation. The first method includes the silicothermic reduction of manganese ore and MnO-rich slag, and its chemistry is very similar to that in the processing of metal manganese described previously. The second method involves blowing of the high carbon FeMn alloy with oxygen. This manganese oxygen refining process (MOR) has been in use in Norway and the United States since 1976. This process is in principle similar to the oxygen steelmaking processes.

7.7.1.1 Silicothermal Reduction

The first method utilizes SiMn as a reductant, and its composition determines the final carbon concentration in the alloy. It appears that SiMn with more than 22% Si at 1500°C is required to produce LC FeMn with a maximum of 0.8% C. Lime flux is added to increase basicity ($CaO/SiO_2 = 1.1$ to 1.3) and to decrease SiO_2 activity in the slag. The process might be realized in two versions. In the first version, the high-MnO slag with low phosphorus content is produced as for flux-less HC FeMn and metal manganese processes. Then slag (and possibly an manganese ores mixture) is reduced by a mixture of commercial and crude SiMn, for which usually some crashed SiMn undersieves are additionally used to decrease costs (Gasik, 1992). As the allowable iron content in LC FeMn is higher than in metallic manganese, this allows use of lower-grade SiMn and the manganese yield is normally higher than in the metal manganese three-stage process (see Fig. 7.17).

In the second version of the process, the SiMn is reduced outside of the furnace, in the ladles (Fig. 7.19), and two ladles with a counterflow of slag and SiMn are used to enhance the process. Two separate furnaces are used, one slag smelting furnace for preparing the oxide melt containing 55% MnO, and the other a conventional submerged arc furnace for producing the silicomanganese alloy.

Because the silicothermic reduction of slag is exothermic, the heat of the reaction is normally sufficient to cover the heat losses in the process. Any iron oxides in the manganese ore/slag will also be reduced, consuming silicon. An iron-free slag with a high content of MnO will give the highest content of Mn in the final alloy. As Figure 7.19 shows, some ferrosilicon is added to the metal to raise the Si content to 30%. This high Si metal meets in ladle I slag from ladle II with 30% MnO. Equilibrium is established to give a waste slag with 5% MnO and a metal with 20% Si. The partly reacted SiMn alloy, now with 20% Si, is mixed in ladle II with the MnO-rich slag mixture received from the slag-

FIGURE 7.19   Flow sheet diagram for the silicothermic production of LC FeMn.

melting furnace. Assuming that the slag/metal equilibrium is established, resulting in the 30% MnO slag and the final alloy product, LC FeMn, with 1% Si and less than 0.5% C, will be obtained (Olsen et al., 2007).

Due to thermodynamic conditions, 25% to 30% MnO in the final slag is necessary to obtain a final metal with 0.5% C and less than 1% Si, which might be the upper limit according to alloy specifications (Olsen et al., 2007). Fluxing of the slag with MgO and Al_2O_3 was found to lower the residual MnO concentration of the slag provided that equilibrium was established. A moderate addition of MgO has a favorable effect on the silicon–manganese distribution, indicating that the presence of MgO increases the activity coefficient of MnO and decreases the activity coefficient of SiO_2. To increase the rate and yield of the silicothermic process, ladles with a stirring capability such as a shaking ladle can be used in an effort to improve the efficiency of the process.

7.7.1.2 Decarburization of High Carbon Ferromanganese

In this process, HC FeMn alloy (~7% C, <1% Si) is decarburized by blowing the metal in its liquid state with oxygen gas or with oxygen-argon mixtures. This manganese oxygen refining (MOR) process is in many ways similar to the basic oxygen steel process (BOF) where liquid cast iron is decarburized by blowing with oxygen in a converter. One important difference is the process temperature: due to the high affinity of manganese for carbon and oxygen, the necessary temperature of the manganese refining process has to be >1750°C, which is 200° to 250°C higher than is needed for the steel process. The much higher temperature leads to several challenges, such as refractory attack, casting of superheated metal, and slag-metal separation. Another problem encountered is the high vapor pressure of manganese leading to excessive evaporation and oxidation by excess oxygen. Oxidized manganese is collected mainly as Mn_3O_4 in the gas cleaning system. The oxide dust can be agglomerated and recycled to the FeMn furnace for recovery of Mn. Some of the

TABLE 7.10 Mechanisms of HC FeMn Decarburization by Oxygen Blowing (MOR)

Stage	1	2	3
Temperature °C	1350 → 1550	1550 → 1650	~1650
Temperature increase rate	High	Average	Low
Oxygen reacts with	Mn > C	C > Mn	Mn > C
Mn loss rate	High	Low	High
Limiting mechanism	Oxygen transfer	Oxygen transfer	C transfer to gas/liquid interface

oxidized manganese may dissolve in a slag phase and thus fluxing agents can be added to adjust the properties of the slag. Additional silicon reduction of MnO (e.g., with FeSi75) will be necessary to recover Mn at the end of the process. MOR process slag often contains about 65% MnO, and it can also be recycled to the FeMn furnace together with other collected manganese values such as ladle sculls, splash, and spills. The economy of the MOR process is highly dependent on the recovery of manganese in the refined alloy. The total yield of manganese is typically about 92% (fume, 5%; slag, splash, and sculls, ~3%).

The MOR method allows practical achievement of ~0.5% to 1% C in the alloy if the temperature reaches 1800°C and CO pressure reaches 1 atm. Oxygen dilution with argon should be considered if further decarburization is desirable. The decarburization of ferromanganese takes place by three different mechanisms in sequence, summarized in Table 7.10 (Olsen et al., 2007).

It is believed that manganese is lost by evaporative mechanisms. The manganese vapor is oxidized to MnO mist by oxygen that was not consumed for CO formation. As the process continues, the manganese loss decreases gradually and reaches a minimum at the end of the first stage of decarburization. During the second stage, the rate of manganese loss increases slowly. Finally, after transition to the third period of decarburization, the loss of manganese again increases quickly with time (Olsen et al., 2007).

7.7.2 Production of Low-Carbon Silicomanganese

For required SiMn alloys with less carbon than usually obtained from the standard process, the effect of decreasing carbon solubility while increasing silicon content is utilized. Instead of separate smelting, LC SiMn is made by adding FeSi to standard SiMn in the ladle. As the silicon content in the melt increases, the equilibrium shifts toward the formation of silicon carbide (SiC).

Due to the lower density of the carbide compared to the metal, the precipitated particles will float to the top of the melt, where they can be captured by a slag layer, which subsequently is removed from the ladle.

Although it is possible to add FeSi or other silicon sources into the furnace, this might lead to unstable furnace operations. On the other hand, the ladle method increases the expenditure of FeSi due to losses of SiC to the slag. Thus, the plant optimum might be a combination of these two methods.

7.8 MANGANESE FERROALLOYS POSTPROCESSING

7.8.1 Casting

Manganese ferroalloys can be poured from the casting ladle either over the lip or through a bottom gate. Top pouring allows higher rates but has no good control on the captured unwanted inclusions of slag and carbides. Bottom tapping is the opposite: the flow rate is low and can, with the more sophisticated variants of gates, be throttled and stopped. Slag and carbides remain in the ladle, as they, due to lower density, tend to float in the opposite direction of the downward metal stream. The drawback is a somewhat higher cost of the equipment and occasional difficulties with opening the gate, but lip pouring is always a possible option.

High-carbon FeMn and SiMn alloys usually undergo layer casting, where the liquid metal is filled into a casting bay for a number of subsequent taps. Metal fines are used as the bed material, and new layers are cast on top of the preceding casts. With a bay area adjusted to the tap size and provided that this is fairly constant, it is possible to obtain a quite even thickness of the layers with the requested size in one direction. When full, the casting bay is emptied by a wheel loader and prepared for a new series. The method is suitable even for large tonnages. The metal may require some cooling before the bay can be emptied and reused.

Refined qualities are usually cast and stored separately according to the analysis for each tap, and for this purpose casting in sand molds is suitable. This is a series of interconnected forms prepared in, for example, olivine sand. The liquid metal is filled from one end; optionally a skimmer between the first two forms can prevent slag and carbides from contaminating the rest of the set. Compared to layer casting, the thickness of the metal tends to increase and become more difficult to adjust even with careful preparations, and the cooling time is longer as the sand is a good insulator. Special attention should be given to superheated metal (e.g., MOR-treated FeMn with temperatures exceeding 1750°C). Removal of the large amount of surplus heat puts extraordinary demands on the casting equipment, and manganese fuming is considerable from the large surface of the cast.

When sufficiently cooled the metal blocks are removed from the molds by crane equipment or a wheel loader with forks. Notably, the timing of this

operation is often crucial, as too-hot metal "bleeds" and too "cold" metal breaks into pieces. If the available time between taps is insufficient for the molds to be emptied and prepared, casting is alternated between two sets of molds. The method is less suitable for large tonnages as it is rather space consuming and labor intensive (Olsen et al., 2007).

Other methods used to some extent involve chill cast and mold conveyors (3 to 10 m/min moving speed). These options require more sophisticated equipment and thus involve higher investment and operating costs. They are also more vulnerable and more often likely to be out of operation. However, they offer rather fast cooling and an even thickness of the metal, and the cast can be made thinner. Special cast iron molds are usually used, and the efficiency of this method is strongly affected by the lifetime of the molds.

7.8.2 Crushing and Sieving

For meeting the customer's demands in respect of the sizing of ferroalloy lumps, respective crushing and sieving procedures are utilized. Usually jaw and cone crushers in combination and roller crushers are used. The latter can be used for materials that already have the right size in one direction. Besides eliminating the secondary crusher, a notable feature of the roller crusher is that it generates fewer fines (Olsen et al., 2007).

Unavoidably, any crushing process gives a fraction of undersized material, which to a limited extent is sold, possibly at a discount. For manganese alloys the size limit of fines is usually set to 10 mm, although some customers accept fines as small as 4 mm at a full price. The remaining fines can be used as bed material or coolant additions in the ladle, or they can be recycled as feedstock on the furnace.

Table 7.11 gives typical size distribution of various crushed alloys, showing that 22% to 30% of the crushed metal must be recycled, one way or another. It should be noted that these numbers include bed materials, which, especially on HC FeMn and SiMn, might account for as much as 5%, thus reducing the actual generated fines figures accordingly.

An alternative "net shape casting" technique was developed to eliminate the need to subsequently crush the metal, similar to the process of granulation (water atomization) of ferrosilicon. The control of the flow rate of metal that enters water and a sufficient water amount to be present as coolant agent are critical parameters to monitor. For example, Elkem ASA developed a similar method for granulation of SiMn ("Mansil"). The granules produced are dense discs with a diameter up to 30 mm and thickness up to 10 mm. This was found to be close to the optimum size when considering the rate of dissolution of the alloy in liquid steel. The mechanical strength of these granules is high due to the rapid solidification, and the macrosegregation tends to be lower than with traditional casting methods. Finally, the fraction of undersized material (−3 mm) with this method can be as low as 3%.

TABLE 7.11 Examples of Size Distribution of Crushed Alloys (Including Bed Materials)*

| Fraction, mm | Alloy, % in Size Fraction | | Utilization | | | |
	FeMn	SiMn	Charge	Ladle	Bed Material	Sale
0−1	8.5−9.5	9.8	All			
1−4	3.5−5.7	9.4	Some	Some	Most	
4−10	7.3−11	10.3		Some	Most	Some
10−25	18−21.3	17.2				All
25−50	30.1−33.4	29.4				All
50−80	23.5−27.1	24.1				All

Equipment: jaw crusher and cone crusher.

7.9 NITRIDED MANGANESE FERROALLOYS

Nitrided manganese and silicomanganese (see Table 7.5) with 2% to 8% N are used for different steel grades, especially austenitic stainless grades (20Cr-10Mn-4Ni, 18Cr-12Mn-5Ni, etc.), which have 0.5% to 0.8% N and additionally may contain Nb and V, which improve steel properties at subzero temperatures. Manganese here is used, together with nitrogen, as an efficient nickel substitute (Gasik, 1992).

As nitrogen solubility in liquid manganese is much lower than in solid (particularly γ-Mn), the production method is based on the solid-state reaction of manganese with nitrogen. Crushed in a nitrogen atmosphere, manganese ($<$ 2 mm) is first put into trays and evacuated at 200°C and <150 Pa. Hydrogen contained in manganese is released, which makes higher active surface areas of the powder beneficial for the next reaction with nitrogen. Then the temperature is raised to 800°C and pure nitrogen gas is entered into the furnace. The reaction of nitrogen with manganese is exothermic, and the temperature in the manganese layer increases to 900° to 950°C with partial sintering of the grains. The product is cooled down in a nitrogen atmosphere and the whole process time is about 70 h (Gasik et al., 2009). Manganese yield is 97% to 98% in this process. Metal manganese from silicon reduction and from electrolysis might be used, resulting in different purity grades and manganese content. For 1 ton of MnN, the requirements are 1030 kg of metal manganese, ~150 m^3 nitrogen, and 1180 kWh electricity (depending on the vacuum furnace type and parameters).

Nitrided SiMn (14% to 25% Si) is used for similar purposes. Nitrogen here is usually present as complex nitride $Mn_{2.05}Si_{2.35}N_{3.6}$ and carbon as carbide

$(Mn,Fe)_{23}C_6$. As nitrogen is added, silicon and manganese contents in SiMnN decrease slightly (see Table 7.5). Solid-state nitriding is a very efficient method for obtaining complex ferroalloys with nitrogen, especially of the Fe-Mn-Cr-V-Nb-N system. Nitrogen content may be up to 10% wt., and these ferroalloys have been proven in steelmaking to be a universal source of nitrogen for stainless steels and alloys.

7.10 ENERGY USE IN MANGANESE FERROALLOYS PROCESSING

As in all electrothermal ferroalloys processing, the costs of manganese ferroalloys are directly correlated with the specific energy consumption (kWh/ton of alloy) due to a higher tonnage but, of course, also related to the cost of electrical energy.

From the point of the reduction process, the largest energy demand would be imposed when MnO is the only manganese oxide in the raw materials, as the reduction reaction is highly endothermic. On the other hand, reduction reactions of the higher manganese oxides (MnO_x, where $x > 1$) with CO gas are all exothermic. For instance, about 20% energy reduction for this process might be achieved if the Mn_3O_4 sinter is fully replaced by MnO_2 ore.

The addition of carbonate ores leads to higher energy consumption, as might be expected. Carbonates are normally present as the added fluxes ($CaCO_3$ and $MgCO_3$) and to a lesser extent as $MnCO_3$ in some manganese ores. Decomposition of the carbonates is endothermic: if 100 kg of $CaCO_3$ is added per ton of alloy produced in order to increase the total content of basic oxides, the energy consumption will increase by ~70 kWh. In practice, however, CO_2 produced from this reaction may react with carbon in coke according to the Boudouard reaction $CO_2(g) + C \rightarrow 2CO(g)$, and hence increase the specific energy consumption even more. The same effect is created by moisture present in raw materials: 10% of water in the charge would require an additional ~150 kWh to evaporate. Theoretically, the difference between high rates of the prereduction reactions, defined as 100% prereduced ore, will decrease electricity demand by about 400 kWh per ton of alloy compared to a very low prereduction rate. However, industrial practice shows a reduction of ~160 kWh/ton when the prereduction degree of the ore is between 20% to 60% (Ishak and Tangstad, 2007).

From the point of view of heat transfer in the process, higher temperature of the materials leaving the furnace would naturally require higher specific energy consumption. A rough estimation might be made as +50 kWh for an additional 100°C of tapped slag and metal temperature and +70–80 kWh for additional 200°C in off-gas temperature.

In silicomanganese smelting, more energy is required to reduce silicon, and the higher the % Si in SiMn, the higher the specific energy demands. For example, energy cost to produce 18% of silicon in the metal is about the same as the cost to produce 100% Mn. Hence, the cost of producing SiMn with 18% Si from oxides is about twice the cost of producing FeMn. Adding metal (cheap

TABLE 7.12 Example of the Energy Balance (off-gas temperature is taken as 150°C)

Input	kWh/ton	Output	kWh/ton
Electric energy	1992	Gas (sensible heat)	42
Carbon reductant	2708	Gas (chemical enthalpy)	776
		Metal (chemical enthalpy)	2897
		Metal (sensible heat)	363
		Slag (sensible heat)	181
		Slag (chemical enthalpy)	317
		Carbonates decomposition	122

silicon sources, remelts, etc.) to boost production is very efficient for decreasing specific energy numbers.

Other energy flow sinks are usually heat losses from the equipment (~20% of total) and cannot be significantly exploited. However, it is possible for the plant to control material losses: a 5% loss of metal in the slag will increase the apparent energy consumption by 5%. Table 7.12 shows an example of the process energy balance for FeMn smelting.

Besides the chemical enthalpy of the metal, the next major form of energy that can potentially be recovered is chemical potential in the gas, especially CO and hydrogen. In closed furnaces this value may be quite high, and many producers sell the gas directly as a by-product. The most challenging issues for recovering this energy are the dust in the gas and the relatively low and varying temperature in the off-gas. In Table 7.12, the off-gas is assumed to be at 150°C (equivalent to ~42 kWh/ton of alloy). If the off-gas temperature is increased to 600°C, its potential energy content will increase to 213 kWh.

The latent heat of slag and metal is usually lost to the surroundings as the metal and slag are cooled and solidified. However, some plants heat water with this energy, which is exploited in adjacent fish farming and the heating of houses, streets, and facilities around the plant.

7.11 POTENTIAL HAZARDS OF OPERATIONS

Some elements of risk are always attached to high temperature smelting and reduction processes. They could be of a general nature, such as accidents caused by metal and slag penetration through furnace and ladle linings, and danger of CO gas poisoning, CO gas explosions, and hot metal-water explosions. The production of HC FeMn in closed furnaces involves special hazards

due to occasional eruptions, blowouts, and explosions taking place inside the furnace. Blows or eruptions of minor strength may have no dramatic effect, but more violent eruptions (sudden ejection of solid, liquid, or gaseous products from the furnace interior), on the other hand, may have dramatic effects and cause great damage. A more violent and instantaneous ejection of material, accompanied by rapid gas expansion, is considered to be an explosion. Although the occurrence of such incidents is rare, they have caused extensive damage to equipment and severe injuries.

Virtually all reported serious eruptions have been traced to a set of conditions that resulted in a hangup or bridging of the charge materials so that their normal downward movement was interrupted or retarded. As electric energy continues to be supplied to the furnace with little or no movement of the charge due to the bridging, a cavity forms under and around the electrode, particularly after tapping of the furnace. When conditions change, allowing the bridge to collapse (usually during or shortly after a tapping), large quantities of unreacted mix may enter the superheated cavity. The effect of the sudden contact between relatively cold raw materials and the hot liquid slag is an instantaneous dissociation of oxides, carbonates, and moisture, followed by explosive reactions evolving oxygen, CO, and hydrogen. These reactions can be extremely violent, and as they normally take place rather deep in the furnace charge, large amounts of hot materials may be thrown out of the furnace by the gaseous reaction products.

Industrial experience has shown that such dangerous situations may arise when the furnace condition prevents an even distribution of the escaping gases in the charge and an even regular downward movement of the raw materials in the furnace. Excessive moisture in the charge materials, particularly if present with excessive fines, will tend to intensify the densification of the charge, promote mix segregation, and inhibit uniform downward movement of the charge. Any leakage of water into the furnace has the same effect, so moisture control is a vital item to monitor closely.

Bridge formation and blocked raw material movement may also be a result of excessive amounts of alkalis (Na, K) and zinc in the charge materials. ZnO is reduced in the furnace hot zone and gaseous Zn is formed. Zn vapor condenses in the colder part of the charge mix normally as ZnO. Banks and bridges are formed, and the flow of materials becomes nonuniform. Occasionally, the area under the bridge may be overheated and the bridge collapses, bringing some of the unreacted raw materials directly into the superheated zone. A similar circulation of alkalis (i.e., K_2O) may take place with the same result. The agglomeration effect of Zn- and K-vapor has also been investigated by Slizovskiy (2012).

To minimize the causes for densification and bridge formation (minimizing the effect of a bridge collapse if it occurs), the chemical composition of the raw materials is of major importance, especially the content of higher oxides and carbonates in the charge. The type of ore influences largely the amount of gas

produced in a possible blowout. A highly oxidized ore has traditionally been considered to be an advantage in ferromanganese smelting, as the net exothermic process through dissociation of oxygen and the subsequent reaction with carbon monoxide will result in reduced consumption of electrical energy. However, at the same time, the risk of explosions and eruptions connected with the use of highly oxidized ores has been recognized. Apparently, a certain threshold value exists for the content of high-oxidized ore in the burden, under which such ore can be used without any hazard.

The choice of reductants is clearly also of high importance for the prevention of explosions in furnaces. The number of fines in the reductants is probably of even higher importance than the content of ore fines for gas permeability and thereby for the general furnace condition and specifically for the bridging mechanism in the charge. Coke fines normally carry much more moisture than do ore fines, and coke dust itself represents an explosion hazard through the possibility of ignition.

When ferromanganese is produced in open furnaces, the operator can estimate the risks of eruptions by visual observation of the charge condition and mix-flow from the hoppers. Through easy access to the charge surface, the operator may be able to direct corrective intervention, such as the breaking of crusts and the distribution of charge on the furnace surface. With the introduction of closed furnaces, the operator's visual contact with the furnace top has been removed, taking with it the possibility of direct corrective intervention. Also, the furnace units have gradually grown in size, thereby dramatically increasing the severity of blows and eruptions when such events take place.

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