Technology of Ferroalloys with Alkaline-Earth Metals

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19.1 CALCIUM AND ITS ALLOYS

19.1.1 Properties of Calcium and Its Systems

Calcium is a typical representative of the group of alkaline-earth metals of the periodic table (serial number 20 and atomic weight 40.08). The configuration of the outer electron shell of the Ca atom is $2s^2$, the melting temperature is 839°C, and the boiling temperature is 1495°C. Calcium is allotropic: α-Ca with an FCC lattice (a = 0.558 nm) that is stable below 443°C, and ß-Ca with a BCC lattice (a = 0.448 nm) that is stable in the 443° to 842°C range. The density of calcium is 1.54 g/cm^3.

Even though calcium is practically insoluble in iron and steels, it is extensively used to control the composition and shape of oxygen, sulfur, and nonmetallic inclusions. Pure calcium is too reactive and vaporizes easily, so it is not easy to apply it directly. Therefore, calcium is used in steelmaking in the form of calcium silicon (SiCa), calcium manganese silicon (SiMnCa), and more complex master alloys (CaSiBa, CaSiBaAl), as well as calcium carbide (CaC_2).

In the Ca-Si system, calcium forms several silicides: Ca_2Si (25.95% Si), probably Ca_5Si_3 (28.31% Si), CaSi (41.20% Si), Ca_3Si_4 (48.3% Si), and $CaSi_2$ (58.36% Si) (Fig. 19.1a). Not all silicides have reliable thermodynamic functions, and this calculated phase diagram may show only the most stable and well-studied phases (Fig. 19.1b).

With carbon, calcium forms one stable carbide, CaC_2 (62.54% Ca), which has a melting point of ~2430 K and a density of 2.204 g/cm^3. Calcium carbide is also widely used in the chemical industry, in the organic synthesis used to produce synthetic rubber, and to produce calcium cyanamide ($CaCN_2$). The phase diagram Ca-C has not been put together yet, and it is assumed there is very little mutual solubility of Ca and C. The carbide CaC_2 is known to exist in four modifications: I, in the range 450°C; triclinic II, below 25°C and above 250°C; III, in the 350° to 435°C range; and IV, above 435° to 500°C (temperatures of these phase transitions are overlaid due to different levels of purity in the materials).

The system Ca-O has several compounds: CaO (calcia), CaO_2 (peroxide), CaO_4 (hyperoxide), and CaO_6 (ozonide). All but CaO (71.42% Ca) are usually unstable. Calcia (lime) has a melting point of 2613°C, a boiling point of ~3000°C, and a density of 3.37 g/cm^3. Solubility of oxygen in solid calcium is negligible (Fig. 19.2). The high-temperature part of the diagram is not yet well defined, and there are opinions that CaO-Ca liquid might have a miscibility gap near the CaO-rich corner.

The equilibria in the CaO-SiO$_2$ system (Fig. 19.3) are very important in steelmaking and ferroalloys processing. As follows from the phase diagram of this system, the interaction of CaO with SiO$_2$ leads to a number of silicates—3CaO·SiO$_2$, 2CaO·SiO$_2$, 3CaO·2SiO$_2$, and CaO·SiO$_2$—which are characterized by relatively high thermodynamic stability. Orthosilicate 2CaO·SiO$_2$ melts congruently at 2130°C, and monosilicate CaO·SiO$_2$ melts congruently at 1544°C.
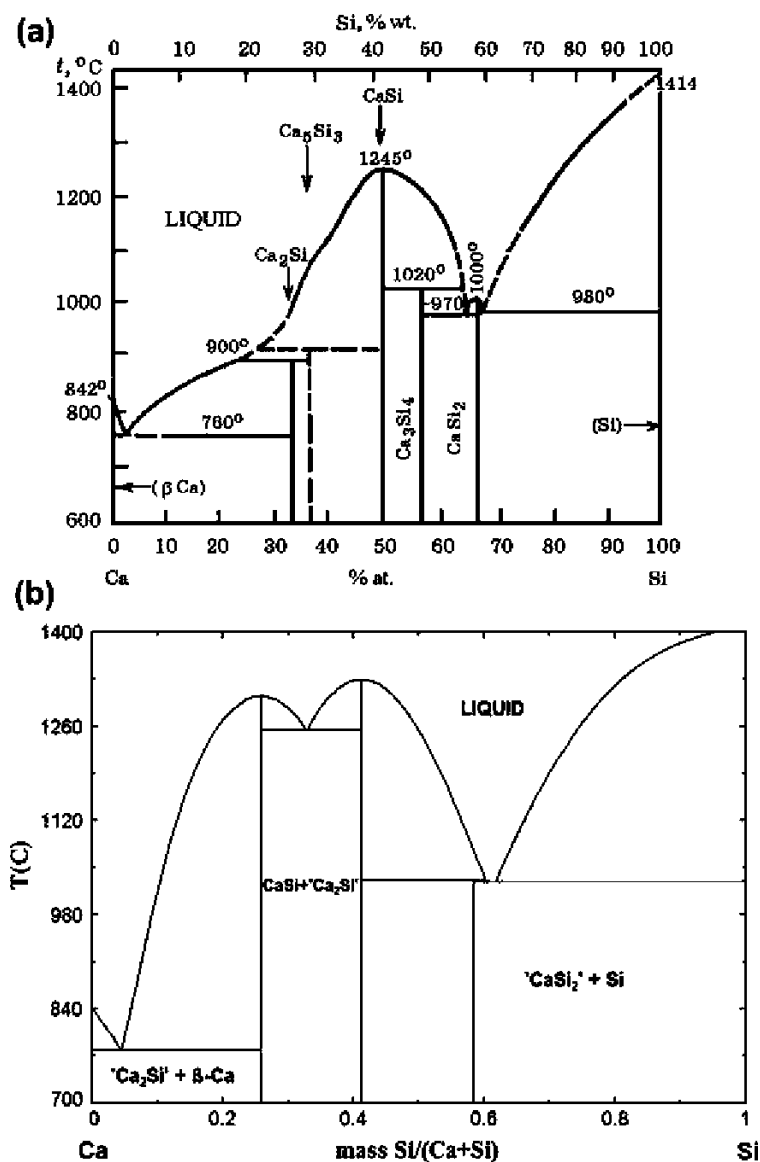
FIGURE 19.1   The system Ca-Si by different sources: based on experiments (a) and calculated from known thermodynamic data (b).

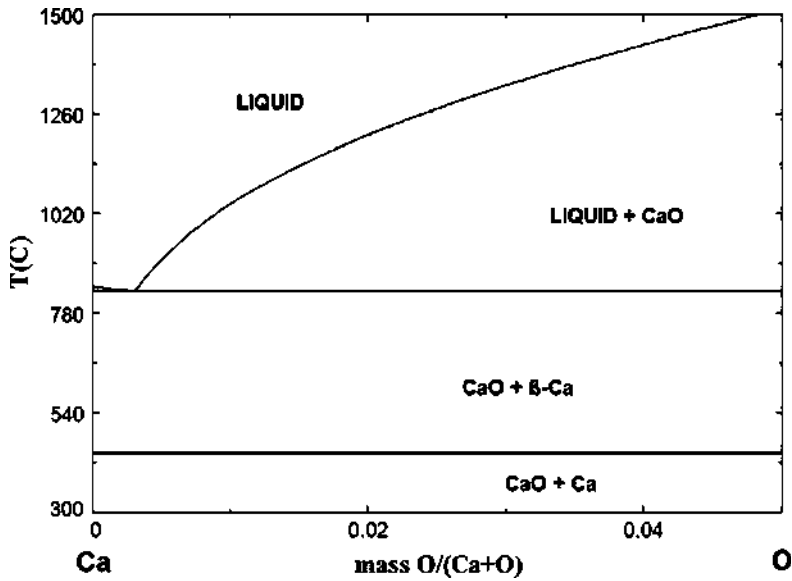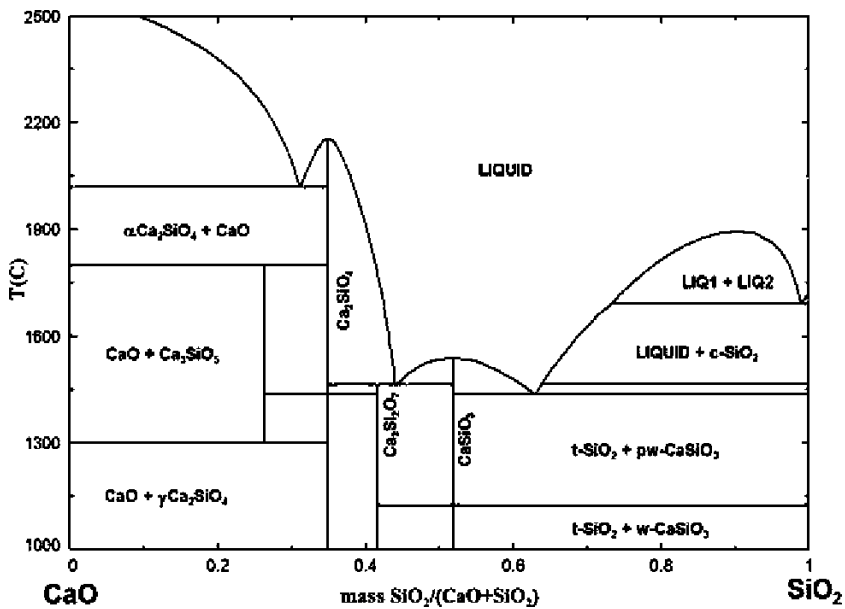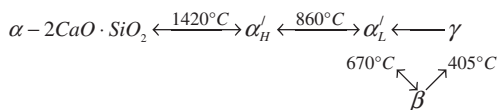**FIGURE 19.2** The system Ca-O.

FIGURE 19.3 The system CaO-SiO$_2$.

Orthosilicate $2CaO \cdot SiO_2$ has a complex polymorphism, which is of a high metallurgical relevancy:

$$\alpha - 2CaO \cdot SiO_2 \xleftrightarrow{1420°C} \alpha'_H \xleftrightarrow{860°C} \alpha'_L \longleftarrow \gamma$$

$$670°C \searrow \quad \nearrow 405°C$$
$$\beta$$

The transformations $\alpha \to \alpha'_H$ and $\alpha'_L \to \beta$ are reversible, whereas $\beta \to \gamma$ and $\gamma \to \alpha'_L$ are not. The $\beta \to \gamma$ transformation is accompanied by a volume increase of 12%, leading to excess stresses and cracking of the material. This causes excess dusting and difficulties in handling highly basic orthosilicate-rich slag from the production of metallic manganese and low carbon ferrochromium.

19.1.2 Technology Used for Smelting Calcium Carbide

The equipment used for the smelting of calcium carbide is similar to that employed in electric furnaces used for other forms of ferroalloys processing, where carbon is used as a reductant. Calcium carbide is also an intermediate product in the smelting of calcium–silicon alloy. Technical grade calcium carbide is crystallized from the melt and contains ~80% CaC_2 and 10% to 15% CaO (Fig. 19.4). Commercial calcium carbide is a gray-black material due to the presence of residual carbon. The reaction of CaC_2 with water is known to generate acetylene gas (C_2H_2), and therefore the product must be kept in dry storage.

The modern technology used for the production of calcium carbide is based on the reduction of calcium oxide (lime) to CaC_2 by carbon for the overall reaction $CaO + 3C = CaC_2 + CO$. During this process, impurities such as sulfur
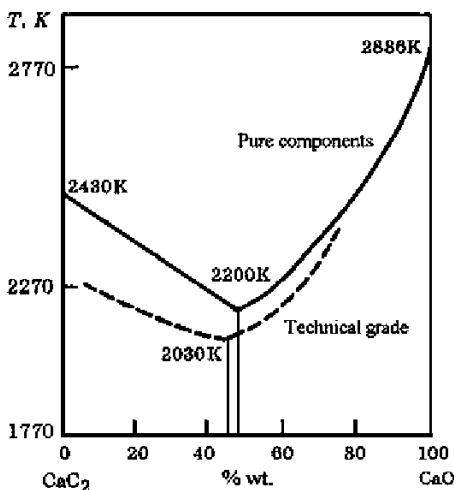

FIGURE 19.4 The liquidus in the system CaC_2-CaO.

and phosphorus, contained in the charge components, are also reduced and dissolved in molten calcium carbide. Calcium and sulfur form a sufficiently strong compound, CaS (which decreases the quality of the carbide product). Calcium and phosphorus also form the phosphide Ca_3P_2, which is easily decomposed by moisture resulting in hydrogen phosphide (phosphine, PH_3), a very poisonous gas. The PH_3 content in acetylene is usually limited <0.08% vol.

Other undesirable impurities in CaC_2 come from lime and coke ash (Al_2O_3, SiO_2). Therefore, the lime should contain at least 92% to 95% CaO and less than 1% to 2% CO_2. The content of solid carbon in the coke should be 85% to 89%, and it should be dried to a moisture level <1%. The particle size of the lime used is 8 to 10 mm, and the particle size of the coke is 8 to 25 mm. The quality of technical grade calcium carbide (aside its acetylene-generating ability and PH_3) is determined by the sulfide phase (<0.5% to 1%) and free carbon (<1%).

Calcium carbide is produced in ore-reduction electric furnaces with a round or rectangular bath and a capacity of 60 to 80 MVA (Fig. 19.5). Rectangular bath dimensions are about $10.9 \times 8.9 \times 5.6$ m with rectangular self-backed electrodes of 3200×850 mm cross-section. The furnace is covered with water-cooled elements. The charge-feeding funnel (~300 mm) is placed around each
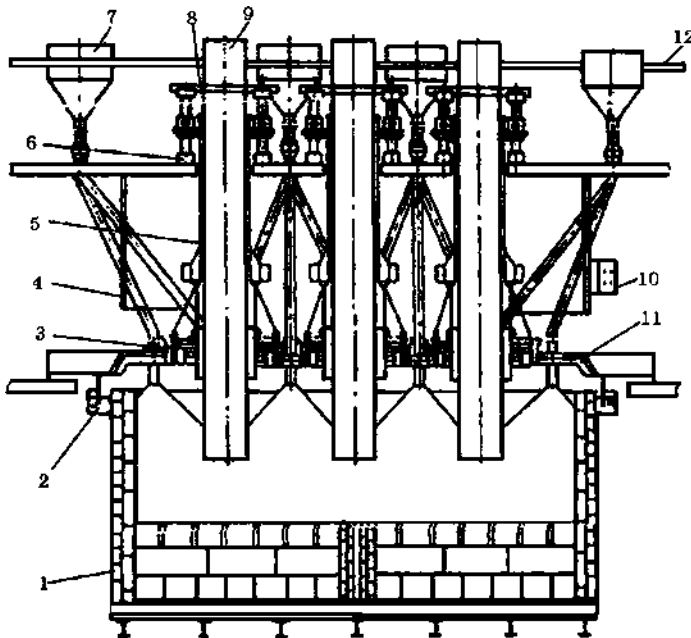
FIGURE 19.5   Closed electric furnace for calcium carbide production with rectangular bath type: 1, furnace lining; 2, sand seal; 3, dry seal; 4, hood; 5, electrode guide; 6, mechanism for moving the electrode; 7, charge feeder; 8, displacement mechanism (bypass) of electrodes; 9, electrodes; 10, power feeder; 11, furnace cover; 12, top level of the electrodes.

electrode. The main gas collectors are located between electrodes (catching up to 80% of the top gas). For a furnace power capacity of 60 MVA, the voltage is between 87 and 167 V and the average current range is 80 to 120 kA. For a furnace capacity of 80 to 85 MVA, the maximum voltage is 202 V. These values may vary for different furnace designs and electrical supply system versions.

For every ton of calcium carbide, about 250 to 330 m^3 of gas is released (72% vol. CO, 5 CO_2, 7 to 8 H_2, <0.1 CH_4, balance N_2). Dust content in the gas is 100 to 150 mg/m^3 and it is removed by scrubbers (cleaning of 1000 m^3 of gas consumes 2.7 to 3.5 m^3 water). The calcium carbide melt is tapped through a tap hole into the water-cooled drums.

19.1.3 Smelting Technology Used for Calcium–Silicon Alloy

Calcium–silicon (also referred to as ferro–silicon–calcium, FeSiCa)—which contains 10% to 35% Ca, 5% to 25% Fe, and the balance made up of Si—is the most commonly used calcium ferroalloy. It may contain 0.2% to 1% C, up to 1% to 2% Al, and below 0.02% to 0.03% P. There are also other alloys, such as calcium–manganese–silicon (16% to 20% Ca, 14% to 18% Mn, 53% to 60% Si, and the balance made up of Fe [<10%]) plus other residuals as noted earlier, although they are less commonly used. In industrial practice, there are three different ways to melt calcium–silicon alloy, of which reduction by carbon is the most common (Berdnikov et al., 2008). It utilizes a combined simultaneous reduction of calcium and silicon from their oxides. In the second method, the reduction of CaO is realized by silicon contained in the added ferrosilicon alloy. The third method utilizes a reduction of silicon from quartzite by carbon coming from CaC_2.

19.1.3.1 The Method of Reduction by Carbon

In this process, the charge consists of metallurgical lime (>87% CaO, <0.01% P) with a lump size of 40 to 100 mm, quartzite (95% SiO_2) of 25 to 200 mm size, coke (<11% to 13% ash) of 5 to 20 mm size, and black coal. A strict requirement on sulfur content in the components is imposed, as calcium and sulfur form a thermodynamically stable sulfide, CaS. The sulfur content in CaSi alloy may reach 0.2%. The main sources of sulfur are quartzite (50% to 55%), coke (20% to 30%), and coal (10% to 15%). The high-calcium grades (20% to 35% Ca) are obtained by reducing the lime and quartzite with coke in open electric furnaces of 16.5 MVA. The process can be represented by the scheme $CaO + 3SiO_2 + 7C \rightarrow [CaSi_2 + Si]_{Fe} + 7CO$. The reduction process is facilitated due to the formation of thermodynamically stable associates close to $CaSi_2$, which lowers the activity of calcium and silicon and improves the recovery of these elements from their oxides. Intermediate products are formed (SiC and CaC_2) in this process, and therefore excess carbon in the charge has to be avoided to eliminate the overgrowth of carbides in the furnace bath.

A sample charge load consists of 85 kg lime, 200 kg quartzite, 30 kg coal, 50 kg charcoal, and 85 to 95 kg coke. When melting alloys of low-calcium grades (10% to 15% Ca), ~40 kg of iron chips are added to the charge. The exact composition of the charge is calculated taking into account the practical efficiency of recovery use for each element. For example, for the charge for alloy with 30% Ca the extraction efficiency of calcium is normally taken as 67% and of silicon, 75%.

Special attention has to be paid to control the slag formation processes, because the slag has a higher density than metal and it is deposited on the bottom of the bath. Its excessive accumulation leads to disorders in the operation of the furnace. The composition of the slag varies according to the grade of the alloy. The low-grade alloys (~15% Ca) have preferentially basic slags (60% to 70% CaO, 25% to 30% SiO_2), whereas high-grade alloys (~30% Ca) have acidic slags (15% to 20% CaO, 40% to 55% SiO_2) with extra carbide content (<10% SiC, <10% to 15% CaC_2). Slags with a high content of calcium carbide have higher fluidity and reduced sulfur concentration, but the drawbacks are poor separation of the slag from the metal and thus more difficult tapping.

An electric furnace with 14 MVA of power operates at a 50 to 60 kA current. Even if the process is within its optimal parameters limits, the bath accumulates autogenic ("frozen") lining over time, consisting of a half-reduced charge (oxides and carbides). This requires periodic stops and relining of the furnace. In industrial practice, to avoid delays, the problem is partly solved by periodically changing the furnace operation for smelting of 45% ferrosilicon. The tapping of the alloy and slag in the normal course of melting is performed (every 2 h) into a carbon-lined walled and fireclay bottom ladle. The approximate composition of the CaSi alloy obtained by this carbon reduction process is 28% to 31% Ca, 60% to 68% Si, 3% to 4% Fe, 1% to 2% Al, 1% to 1.5% C, <0.1% S, and <0.02% P.

The sulfur and aluminum presence in the CaSi alloy is the result of the use of carbon reductants with high sulfur and ash (Al_2O_3) contents. At high temperatures, alumina is reduced by carbon and forms carbide Al_4C_3, which dissolves into the alloy. Therefore, the use of components with a high content of impurities (such as Al_2O_3) in the smelting of calcium–silicon is limited to keep a permissible level (<2% wt. Al).

19.1.3.2 The Method of Reduction by Silicon

This method is based on the use of ferrosilicon as a reductant, giving the overall reaction $(CaO) + [Si]_{FeSi} \rightarrow [CaSi_2 + Si + FeSi_2] + (2CaO \cdot SiO_2)$.   Because the chemical affinity of silicon for oxygen is lower than that of calcium, the reaction can proceed in the direction of obtaining calcium–silicon only in the case of a substantial reduction of the activity of calcium. This specifies high silicon and lower calcium content in the final alloy. Reaction equilibrium is achieved at relatively low concentrations of calcium, so the method can be used

to obtain lower grades of calcium–silicon (referred to as FeSiCa) with calcium at less than 20%.

The calcium–silicon smelting is carried out in open furnaces as a batch process. The typical composition of the charge has 200 kg lime, 196 kg ferrosilicon (Fe-75% Si), and 30 kg fluorspar (CaF_2). The use of fluorspar is necessary to reduce viscosity of the highly basic slag and to improve conditions for the separation of melt products from the slag. The recovery of calcium is only 20% to 30% (calcium also partially vaporizes) and the utilization of silicon from the ferrosilicon is about 75% to 85%. From the charge materials, into the alloy are transferring approximately 25% to 35% Al, 15% to 30% S, 15% to 35% P, and 25% to 30% Mg. The actual chemical composition of FeSiCa is (% wt.) 15 to 19 Ca, 55 to 65 Si, 18 to 22 Fe, <1 Al, <0.01 S, <0.02 P, and <0.07 C.

The quality of FeSiCa made by silicon reduction is higher than that resulting from carbon reduction, especially in respect of sulfur and carbon contents. Comparative technical and economic indicators of the smelting of calcium–silicon by carbon and silicon reduction are given in Table 19.1. Calcium–silicon alloy is normally supplied to steel mills in different sizes (<2, 2 to 5, 5 to 20, and 20 to 200 mm lumps). Fine sizes of the alloy are not very efficient for steel deoxidation due to significant losses of calcium (low density and high activity with respect to atmospheric oxygen and oxides of the ladle slags). Better use of calcium–silicon is achieved when it is applied in the form of cored wire.

TABLE 19.1 Comparison of Charge Materials per 1 Ton of the CaSi Alloy (15% and 30% wt. Ca) for Different Methods of Smelting

Category	15% Ca	30% Ca	15% Ca	30% Ca
	Carbon Reduction		Silicon Reduction	
Materials, kg				
Quartz	1436	1875	—	—
Lime	456	748	960	940
Coal	281	265	—	—
Charcoal	244	370	—	—
Dry coke	388	600	—	—
Ferrosilicon 65% Si	—	—	917	805
Iron chips	318	—	—	—
Electrode paste	107	134	—	—
Graphitized electrodes	—	—	12.5	10.5

19.1.3.3 The Method of Reduction by Calcium Carbide

The first method for smelting CaSi by carbon reduction described earlier relies on the simultaneous reduction of Si and Ca from quartzite and limestone, but despite its apparent simplicity, this method has some significant drawbacks. It is difficult to apply it to the smelting of calcium–silicon with more than 30% Ca due to the autogenic lining accumulation in the furnace bath. Fused products resulting from the interaction of SiO_2 and CaC_2 form deposits on the bottom and on the walls. Because CaSi alloy has a lower density than these deposits, it collects under the electrodes and over the bottom deposits, disturbing the electrical conditions (also causing shortcuts) and furnace operation. As noted previously, for these reasons the furnace is periodically switched to the smelting of ferrosilicon (Fe-45% Si) to bring the bath back to the desired state for the subsequent smelting of calcium silicon.

These disadvantages are largely eliminated upon implementation of the two-step calcium–silicon smelting process. The first stage of this process consists of manufacturing technical grade calcium carbide, which is smelted from lime and coke charge (as described in Section 19.1.2). The second step is the smelting of the charge composted of calcium carbide and quartzite, where the reduction follows the scheme $CaC_2 + SiO_2 \rightarrow [Ca\text{-}Si] + 2CO$.

To produce calcium–silicon with 30% to 35% Ca using this method, the charge materials required for 1 ton of the alloy are (kg) 1700 to 2000 quartz, 600 to 1000 calcium carbide, 560 to 580 coke, and 170 to 200 charcoal. A typical furnace of 2.5 MVA makes 3500 tpa of calcium–silicon, which is enough to deoxidize ~1 million ton of steel. Smaller furnaces can be also used, and a comparison of these furnaces using this production method is shown in Table 19.2.

19.2 MAGNESIUM

19.2.1 Properties of Magnesium and Its Systems

Magnesium is an element of group II of the periodic table of elements; its atomic number is 12, its atomic weight is 24.305, and it belongs to the group of alkaline earth metals (AEMs: Be, Mg, Ca, Sr, Ba, Ra). The configuration of the outer electron shell is $3s^2$, and the typical oxidation degree is +2, rarely +1. Magnesium has a hexagonal crystal lattice (a = 0.321 nm, c = 0.520 nm). Its melting point is 650°C, and its density is 1.74 g/cm³ (20°C), 1.54 g/cm³ (700°C). The equation of the temperature dependence of vapor pressure (in mm Hg) above liquid Mg has the from lg $P_{Mg} = 16.7974 - 7844.2/T + 2.548 \cdot 10^{-4} \cdot T - 2.728 \cdot lgT$ (407–1390 K). Like calcium, magnesium is practically insoluble in iron and steels. It might be used for deoxidation and sulfur removal (Zhuchkov et al., 1977), but its main metallurgical use is for the inoculation of cast irons.

In the Mg-O system, the stable oxide formed is MgO with a melting temperature of 2827°C, a boiling temperature of 3600°C, and a density

TABLE 19.2 Technical Parameters Comparison for Small-Scale Calcium–Silicon Smelting Using the Two-Step Technology

Furnace Transformer, MVA (x phases)	0.63	1.2	1.5	2.5	2.5 (x 3)	
Maximal current, kA	6.7	11.4	11.7	17.5	35.2	
Graphitized electrodes, diameter in mm	300	400	400	500	610	—
Self-baked electrodes, diameter in mm	—	—	—	—	—	850
Average production capacity, tpa	800–900	1200–1500	1800–2000	3000–4000	10,000–12,500	
Hearth length, m	11.6	12	12	13.5	16.7	
Hearth width, m	6.1	7.2	7.2	7.85	10.8	
Hearth height, m	8.5	12.6	12.6	12.6	14.1	15.8

of 3.58 g/cm^3. Oxide MgO has a substantial vapor pressure at high temperatures. Other oxides reported to exist are MgO_2, MgO_4, and Mg_2O, but they are not stable in the typical conditions required for ferroalloys processing.

In the system Mg-C, two stable carbides are known: MgC_2 and Mg_2C_3. The density of MgC_2 is 2.204 g/cm^3. The interaction of magnesium carbide with water or water vapor proceeds similarly to that for CaC_2, leading to the formation of C_2H_2 and the mixture of hydrocarbons. Monocarbide MgC has been observed, but only at high pressures (a few GPa). The phase dominant diagram of the Mg-O-C system is shown in Figure 19.6 at 1 atm total pressure and 1600°C. As the figure shows, pure magnesium can only be reduced to carbides or to magnesium gas, which requires low oxygen partial pressures and low CO pressures.

The system Mg-Si has one stable silicide, Mg_2Si (36.56% Si), which congruently melts at 1102°C (Fig. 19.7). There is practically no solubility of Mg in Si or otherwise. Two metastable silicides of MgSi and $MgSi_4$ compositions have been mentioned but without enough detailed data to allow a reassessment of the phase equilibria.

With sulfur, magnesium forms a stable sulfide, MgS, with a melting temperature of about 2200° and a density of 2.86 g/cm^3. With CO_2, magnesium oxide forms carbonate, $MgCO_3$, which dissociates back to MgO and CO_2 at high temperatures. With silica, magnesium oxide (Fig. 19.8) forms two stable silicates: $2MgO \cdot SiO_2$ and $MgO \cdot SiO_2$.
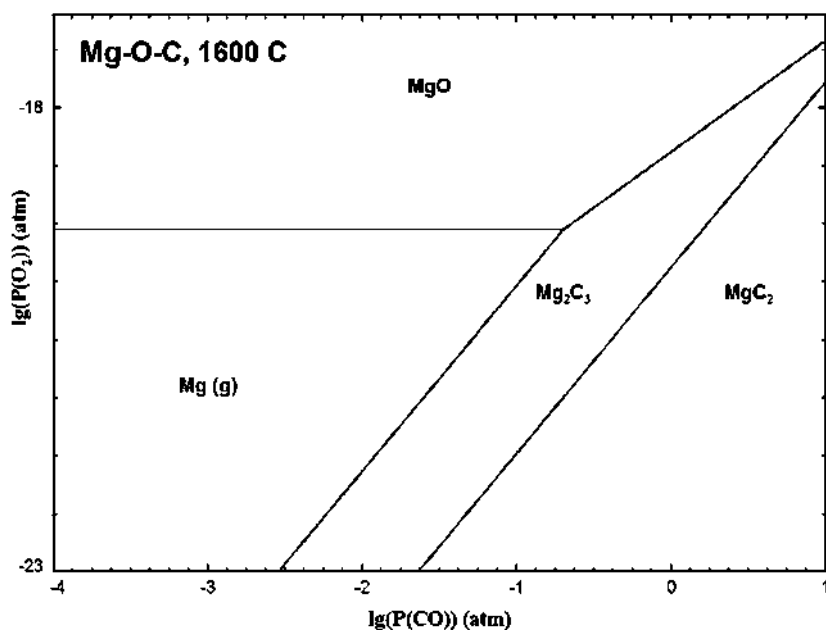
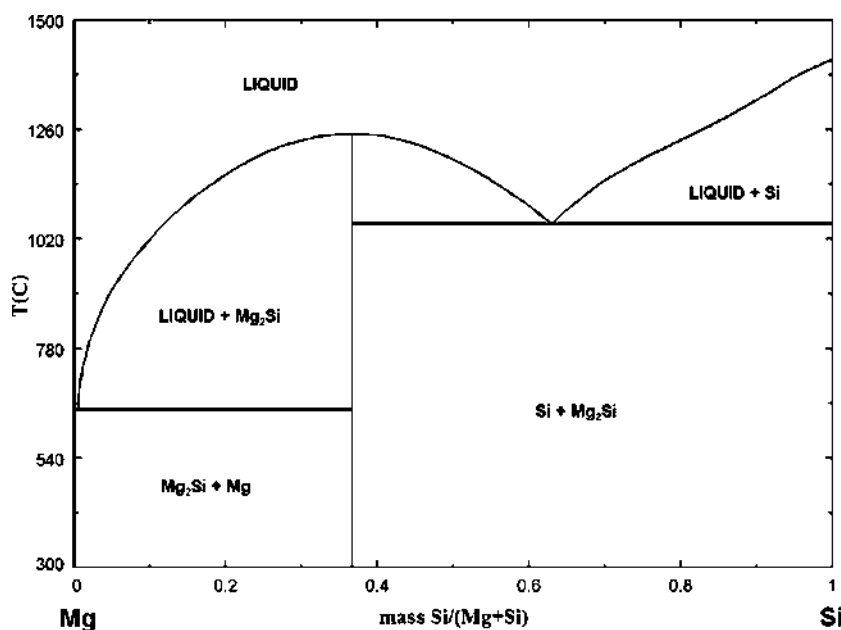**FIGURE 19.6**   Mg-O-C dominant phases diagram at 1600°C.

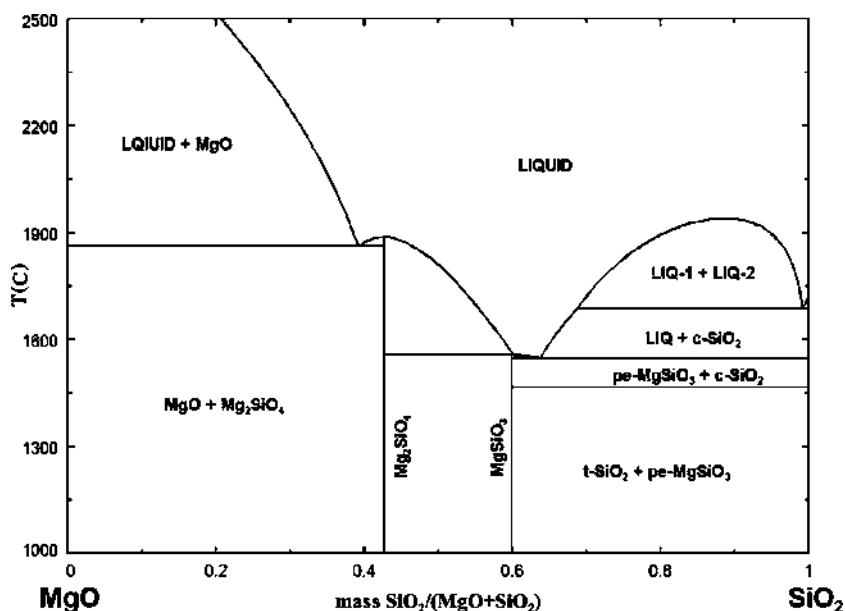**FIGURE 19.7**   Mg-Si system diagram.

**FIGURE 19.8** MgO-SiO$_2$ system phase diagram. Pe, pseudoenstatite; c, cristoballite; t, tridymite.

Magnesium exists in nature in various minerals: carbonates MgCO$_3$, (Ca, Mg) CO$_3$, chlorides (MgCl$_2 \cdot$6H$_2$O), sulfate (MgSO$_4 \cdot$H$_2$O), silicates (3MgO$\cdot$2SiO$_2 \cdot$2H$_2$O), magnesium oxide (periclase, MgO), hydroxide Mg(OH)$_2$, and so on. Worldwide magnesium production is based on the firing of MgCO$_3$ and on extraction from seawater or brines. The product from firing contains 75% to 96% MgO total, and from seawater and brines it usually contains more than 97%.

19.2.2 Technology for Producing Magnesium and Ferroalloys

The major type of magnesium ferroalloy is in the form of magnesium–ferrosilicon (FeSiMg) with 5% to 10% Mg and calcium–silicon–magnesium (25% to 30% Ca, 50% to 55% Si, and 10% to 15% Mg). Minor types are also different master alloys such as Ni-15% Mg, with (<30% Si) or without silicon. Pure magnesium is manufactured by electrolysis of the chloride compounds.

There are several ways to make magnesium alloys by the reduction of magnesium from MgO or calcined dolomite in a vacuum smelting process using silicon (from FeSi) as a reductant. The vacuum–thermal process in general is described by the overall reaction

$$2(\text{CaO} \cdot \text{MgO}) + [\text{Si}]_{\text{FeSi}} = 2\text{Mg}(g) + (2\text{CaO} \cdot \text{SiO}_2) + [\text{Fe}].$$
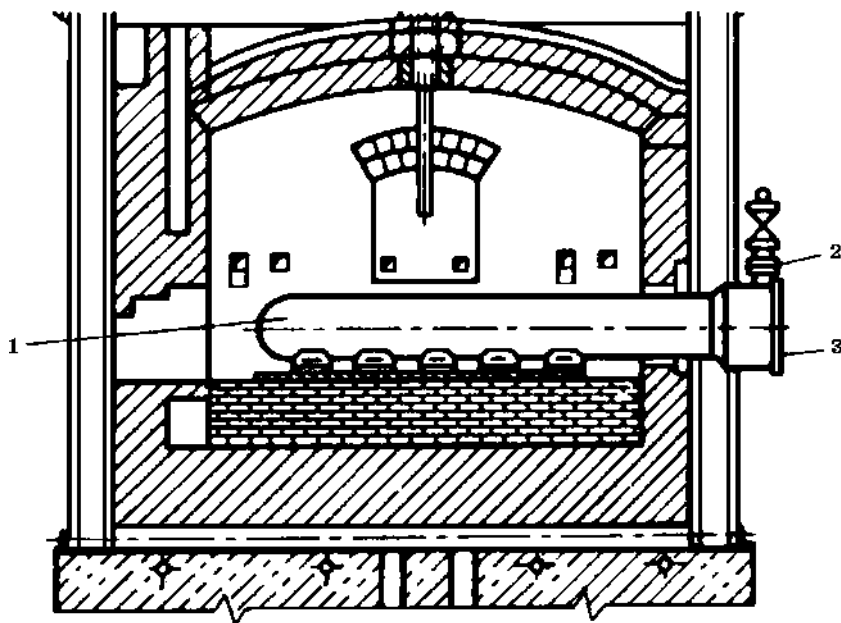
FIGURE 19.9 Production of magnesium by silicon reduction in a vacuum retort: 1, retort; 2, valve; 3, cover.

In the reaction zone, Mg evaporates, passes, and cools down in a metal retort area (Fig. 19.9) where it is condensed. Besides the use of silicon (ferrosilicon) as a reducing agent, aluminum can be used. Due to the evaporation–condensation route, this method can be used to obtain magnesium of technical purity.

To process FeSiMg alloy, the reduction by silicon from FeSi is used at normal pressure in an arc furnace. The charge is composed of magnesite (MgO), limestone, dolomite, ferrosilicon (Fe-75% Si), and fluorspar (CaF_2). The process in general can be represented by the following scheme:

$$(MgO, CaO) + [Si]_{FeSi} \rightarrow [Ca\text{-}Mg\text{-}Si\text{-}Fe] + (CaO\text{-}MgO\text{-}SiO_2).$$
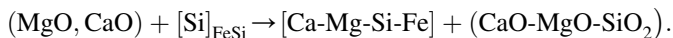
The maximum Mg content in the alloy (2.3% to 2.6%) is obtained when the ratio in the mixture MgO:CaO = 0.3 and the ratio $CaF_2/(CaO+MgO) = 0.1$ to 0.15. Excess of fluorspar in the charge leads to a loss of silicon due to the reaction $2CaF_2 + Si = SiF_4(g) + 2Ca$.
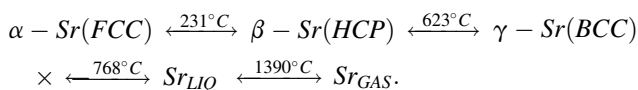
There is also the technique of processing Ca-Mg-Si-Fe alloys by dissolution of magnesium ingots (produced by the electrolytic method) in the liquid ferrosilicon. According to industrial experience, in the first stage the charge composed of Fe-65% Si, Fe-75% Si, CaO, and magnesite is melted to obtain an alloy with 2% to 3% Mg (using the process described earlier). In the second

stage, magnesium content is adjusted to 6% to 7% by dissolving extra magnesium ingots in this alloy. This FeSiMg alloy contains 5% to 7% Mg, 53% to 65% Si, and a balance made up of iron. The disadvantages of this method, however, are substantial losses of magnesium and the generation of intense smoke and sparks.

19.3 STRONTIUM

19.3.1 Properties of Strontium and Its Systems

Strontium is an element of group II of the periodic table of elements. Its atomic number is 38, its atomic weight is 87.62, the configuration of the outer electron shell of an atom is $5s^2$, and it belongs to the alkaline-earth metals (AEMs) group. The typical oxidation of strontium is +2, rarely +1. Strontium metal exists in three allotropic modifications, the transformation of which takes place at the following temperatures:

$$\alpha - Sr(FCC) \xleftrightarrow{231°C} \beta - Sr(HCP) \xleftrightarrow{623°C} \gamma - Sr(BCC)$$
$$\times \xleftarrow{768°C} Sr_{LIQ} \xleftrightarrow{1390°C} Sr_{GAS}.$$

In the system Sr-O the stable oxide formed is strontium oxide (SrO), colorless crystals with a density of 4.7 g/cm^3 and a melting point of 2660°C. Under the high pressure of oxygen, SrO may ignite to form peroxide (SrO_2). Strontium and strontium oxide react with water, forming hydroxide $Sr(OH)_2$, colorless hygroscopic crystals with a melting point of 535°C and a density of 3.632 g/cm^3. In the system Sr-C, the most stable solid carbide is SrC_2.

In the system Sr-Si, several silicides are formed: SrSi (24,23% Si) and $SrSi_2$ (38,99% Si) (Fig. 19.10). Silicides SrSi and $SrSi_2$ melt congruently at 1140° and 1150°C, respectively. The system has three eutectic temperatures of 700°, 1044°, and 1000°C. The existence of Sr_2Si and Sr_5Si_3 has also been reported.

Strontium oxide with CO_2 forms strontium carbonate ($SrCO_3$), which exists in several polymorphic modifications. The low-temperature stable phase (α) with a rhombohedral structure is stable below 925°C, and the high-temperature hexagonal phase (β) is stable within the 925° to 1416°C range. The third cubic phase (γ) forms under higher pressure of CO_2 (> 2MPa).

With silica, strontium oxide forms several silicates (e.g., $2SrO \cdot SiO_2$, $SrO \cdot SiO_2$). The melting point of $2SrO \cdot SiO_2$ has not been exactly determined, but it is above 1700°C (Fig. 19.11). The compound $SrO \cdot SiO_2$ melts congruently at 1580°C, and the lowest eutectic temperature in this system is 1358°C.

With alumina-SrO, several compounds exist, namely $4SrO \cdot Al_2O_3$, $3SrO \cdot Al_2O_3$ (melting point 1660°C), $SrO \cdot Al_2O_3$ (melting point 1790°C), $SrO \cdot 2Al_2O_3$ (melting point 1820°C), and $SrO \cdot 6Al_2O_3$ (melting point 1900°C), Fig. 19.12. Aluminate $4SrO \cdot Al_2O_3$ has two modifications: a high-temperature
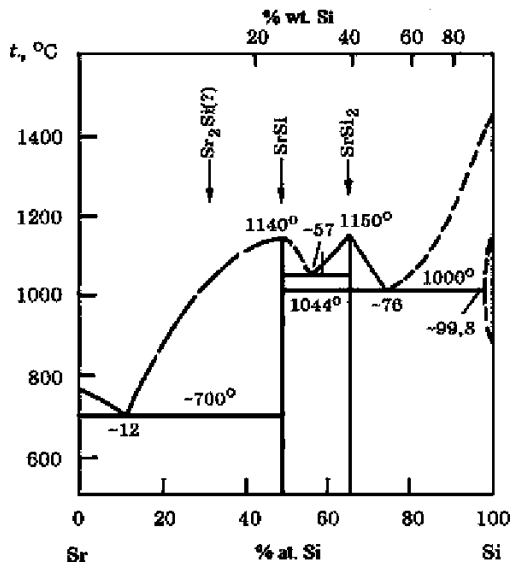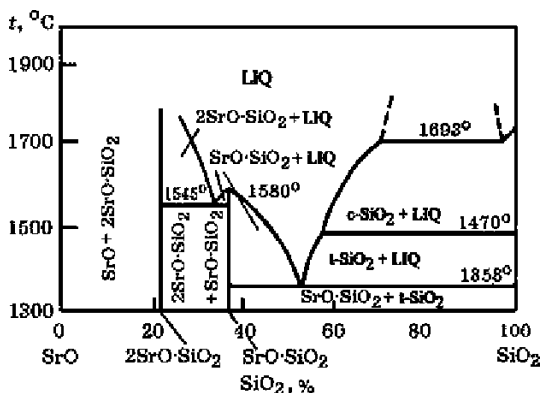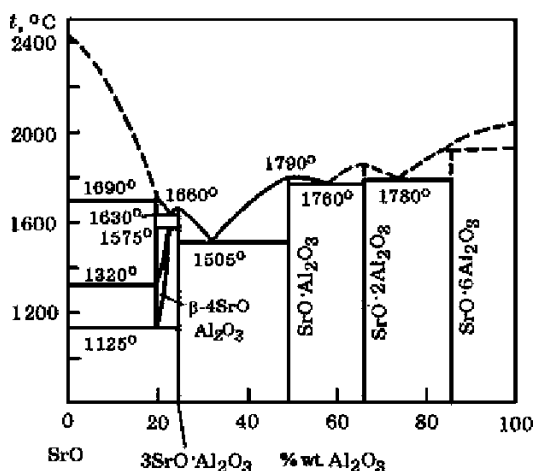
FIGURE 19.10   Sr-Si phase diagram.

phase (β-4SrO·Al$_2$O$_3$), stable in the 1320° to 1690°C range, and a low-temperature phase (α-4SrO·Al$_2$O$_3$), stable in the 1125° to 1320°C range. The lowest eutectic temperature in this system is 1505°C.

The total content of strontium in Earth's crust is estimated as 3.4·10^{-2}% (by weight). Strontium is known to form about 40 minerals, of which only two are of practical relevance, namely celestine (SrSO$_4$) and strontianite (SrCO$_3$). Strontium is present as an isomorphous impurity in a variety of magnesium, calcium, and barium minerals, such as (Sr,Ca)$_2$B$_{14}$O$_{23}$·8H$_2$O, and it is also


FIGURE 19.11   SrO-SiO$_2$ phase diagram.

FIGURE 19.12 SrO-Al$_2$O$_3$ phase diagram.

found in different natural mineral species. Part of the strontium in the oceans is concentrated in ferromanganese nodules (Gasik et al., 2009).

19.3.2 Smelting Technology of Strontium Alloys

Strontium raw materials are used mainly in the form of celestine (SrSO$_4$). Celestine concentrate contains about 86% SrSO$_4$. At high temperatures strontium sulfate interacts with carbon to form strontium sulfide (SrS):

$$SrSO_4 + 4C = SrS + 4CO,$$
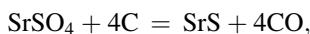
but in the presence of SiO$_2$ this reduction proceeds to strontium silicide:

$$SrSO_4 + 4C + SiO_2 = SrSi + SO_2 + 4CO.$$
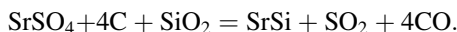
In areas of carbon deficiency, silicates of strontium can additionally form into the slag: $SrSO_4 + SiO_2 + C = (2SrO \cdot SiO_2) + CO + SO_2$.

For a complex ferroalloy containing strontium and barium, concentrates of strontianite (SrCO$_3$) and BaCO$_3$ are used. A typical concentrate grade has a lump size of up to 10 mm and a chemical composition (% wt.) of 5 to 6 SrO, 15 to 17 BaO, 20 to 22 CaO, and 23 to 25 SiO$_2$; the rest of the components are mainly MgO, Na$_2$O+K$_2$O, and FeO.

Ferrosilicostrontium alloy is processed in small electric arc furnaces with a capacity of 160 kVA at 30 V and a nominal current of 1500 A. The charge consists of celestine ore, quartzite, coke, and iron chips. The resulting FeSiSr alloy contains 8% to 10% Sr, 48% to 59% Si, and a balance made up of iron. The slag/metal ration in this process is ~1.5. Industrial experience shows that specific energy consumption is high and strontium extraction is low, so there is a need to improve the technology (Liu and Yang, 1998).

19.4 BARIUM

19.4.1 Properties of Barium and Its Systems

Barium is an element found in Group II of the periodic table of the elements. Its atomic number is 56, its atomic weight is 137.33, it belongs to the group of alkaline-earth metals, and it has a density of 3.78 g/cm^3. The configuration of the outer electron shell of an atom of barium is $6s^2$, and its main oxidation state is +2, rarely +1. Barium exists in two allotropic modifications: α-Ba below 375°C and β-Ba between 375° and 727°C.

In the Ba-O system, the most stable oxide is barium oxide (BaO) (89.57% Ba), which is made up of colorless crystals with a cubic lattice (a = 0.5542 nm) and a density of 5.7 g/cm^3. When heated in an oxygen environment, BaO forms barium peroxide (BaO$_2$) at about 500°C, with a hexagonal lattice (a = 0.534 nm, c = 0.677 nm) and a density of 4.96 g/cm^3. At higher temperatures, BaO$_2$ thermally dissociates to form BaO and O$_2$. The peroxide BaO$_2$ is the main component of the charge for manufacturing Al-Ba master alloys. The melting point of BaO is 2017°C, but it sublimates before reaching melting temperature. Barium oxide (BaO) forms during the dissociation of barium carbonate (BaCO$_3$) at 700° to 900°C.

Barium carbonate (77.69% BaO), like strontium carbonate, exists in three modifications: up to 840°C α-BaCO$_3$ with orthorhombic lattice (a = 0.639 nm, b = 0.883 nm, c = 0.528 nm); in the range 840° to 960°C, β-phase with a hexagonal lattice; and 982°C, γ-BaCO$_3$ with a cubic lattice. BaCO$_3$ forms solid solutions with SrCO$_3$, CaCO$_3$, and BaO.

Barium hydroxide Ba(OH)$_2$ exists in two modifications; the low-temperature modification transforms into the high-temperature form at 246°C. Hydroxide decomposes to BaO and H$_2$O when heated above 800°C. Barium peroxide, carbonate, and hydroxide are considered to be toxic materials and regulations limit their allowable concentration in the air.

With carbon, barium forms stable carbide phase BaC$_2$ (14.88% C), with properties similar to those of calcium carbide. Carbide crystallizes in a tetragonal lattice type of CaC$_2$, has a density of 3.895 g/cm^3, and melts above 2000°C with decomposition.

The system Ba-Si contains barium silicides BaSi (83.07% Ba) and BaSi$_2$ (71.03% Ba). The compound BaSi$_2$ melts congruently at 1180°C, and BaSi melts incongruently at 840°C (peritectic reaction). Two eutectic temperatures in this system are 630°C and 1020°C. The solubility of silicon in solid barium is very small and does not exceed 0.14% (at.).

Barium and sulfur form several sulfides, of which the most studied is barium sulfide (BaS) (81.07% Ba), which melts at 2200°C. Other sulfides of barium are Ba$_2$S, BaS$_2$, and BaS$_3$. The sulfide BaS crystallizes in a cubic lattice of the type NaCl (a = 0.6381 nm), which has a density of 4.252 g/cm^3. When stored in air, BaS absorbs CO$_2$ to form BaCO$_3$ and H$_2$S. Upon heating in air BaS oxidizes to

sulfate $BaSO_4$. Due to the high thermodynamic stability of barium sulfide, barium can be used for the desulfurization of iron and steel (Grigorovich et al., 2011; Han et al., 1992). In nature, barium is present in mineral barite ($BaSO_4$), which is used for the smelting of barium-containing ferroalloys. $BaSO_4$ dissociates upon heating to BaO, SO_2, and oxygen.

With aluminum, barium forms one stable compound, $BaAl_4$, melting congruently at 1097°C. On both sides of the aluminide line there are eutectics: at 1% (at.), Ba at 651°C; and at 70% (at.), Ba at 528°C (Fig. 19.13).
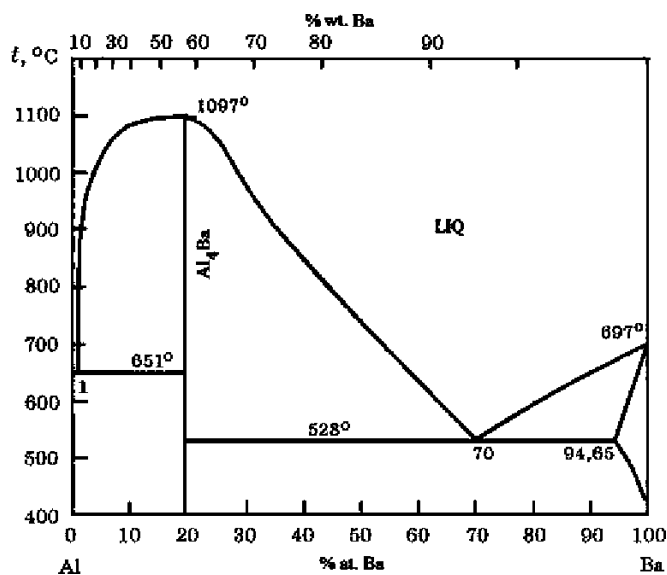

FIGURE 19.13   Al-Ba system.

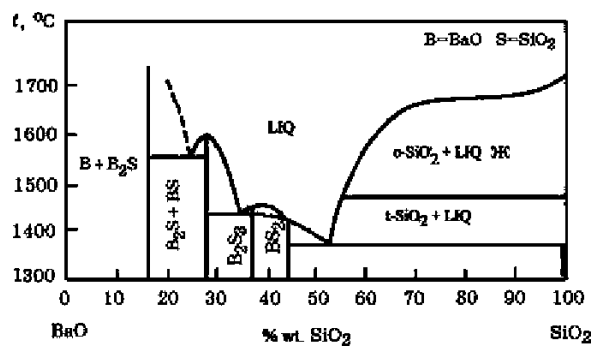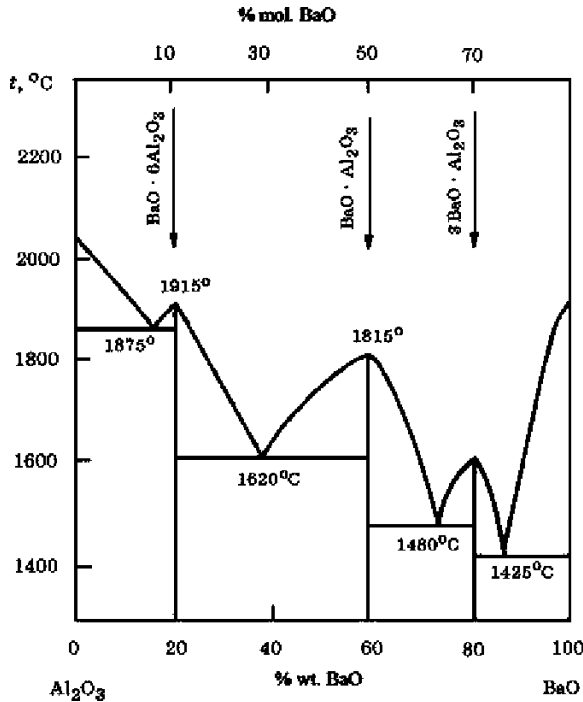FIGURE 19.14   Equilibrium phase diagram of the system $BaO-SiO_2$.

FIGURE 19.15   Equilibrium phase diagram of the system BaO-Al₂O₃.

The system BaO-SiO₂ is shown in Figure 19.14. In this system, several barium silicates are formed. Barium silicate 2BaO·SiO₂ has two phase modifications, the temperature of the transformation β ← → α is 1350°C, and the melting point is 1760°C. The system BaO-Al₂O₃ incorporates several aluminates of barium (Fig. 19.15).

19.4.2 Smelting Technology of Ferrosilicobarium

Ferroalloys with barium can be obtained by using carbon, silicon, and aluminum as reducing agents. The most economical method of smelting is the carbon reduction process with the use of barite concentrate (65.7% BaO), quartzite, and coke. The co-reduction of Ba and Si from this charge can be represented by the reaction $BaSO_4 + SiO_2 + 4C \rightarrow [BaSi] + 4CO + SO_2$.

Melting is performed in the electric arc furnace as a continuous process. The FeSiBa alloy obtained in this way has the following chemical composition (wt. %): 27 to 35 Ba, 46 to 52 Si, 0.15 to 0.3 C, 3 to 5 S, and the balance made up of Fe. The furnace slag contains 19% to 26% Ba, 25% to 37% SiO₂, 3% to 7% C, and 3% to 5% S.

The reduction of barium by silicon from Fe-75% Si could be described as $2BaO + [Si]_{FeSi} = [BaSi] + (2BaO \cdot SiO_2)$. This process produces FeSiBa alloy with up to 25% barium, and it is also possible to make a complex alloy containing both Ba and Ca. Melting is carried out in a batch process in an electric arc furnace. The charge load normally consists of 100 to 120 kg BaO, 190 kg Fe-75% Si alloy, 200 kg lime, and 50 kg fluorspar. The resulting complex has a ferroalloy chemical composition of (wt. %) 5 Ba, 15 Ca, 27 Fe; 1,5 Al; and the balance is made up of Si.

Ma et al. (1992) reported on the application of Fe-20% Si-40% Al-8% Ba alloy as a steel deoxidizer in a converter. Besides saving aluminum, improvements in shape of nonmetallic inclusions and in steel mechanical properties were obtained (the share of nonmetallic inclusions was decreased by 29% versus deoxidation with Fe-20% Si-50% Al alloy).

Kulinski and Gladala (1981) studied the production and application of complex ferroalloys with barium and calcium, using reduction of barium sulfate concentrate with lime with Fe-75% Si ferrosilicon. This results in high-silicon alloys (60 ±5 % Si) with 8% to 10% of both calcium and barium. The addition of manganese (<10%) was also found to be beneficial to the storage and use of alloys in steelmaking.

19.4.3 Smelting Technology of Al-Ba Alloys

Alloys of Al-Ba have a highly deoxidizing potential, as each component separately has a high affinity for oxygen dissolved in the molten metal (Mukai and Han, 1999). These master alloys can be used as structure modifiers for engineering steels and iron-based alloys. The basis of the process of smelting Al-Ba alloys is the reaction of oxides of barium with aluminum. Typical master alloys contain 40% to 45% Ba, <1% Si and Fe, and a balance composed of Al.

The charge is composed of barium peroxide ($BaO_2 > 93\%$), aluminum powder (fractions 0 to 0.1 mm ~20%, 0.1 to 1 mm ~70%, and 1 to 3 mm ~15%), and fluorspar ($CaF_2 > 95\%$). For 100 kg of barium peroxide, the load of aluminum is 56 kg and that of fluorspar is 11 kg.

The reduction of BaO_2 by aluminum is an exothermic process that is carried out in a cast iron mold with a diameter of ~1 m and a height of ~0.6 m with an extension sheet metal cover of 5 to 10 mm. The batch dose of the charge is 200 to 250 kg of barium peroxide. The charge is ignited and the process proceeds forming the liquid alloy, which is collected above the slag because of its lower density. The alloy block is cooled, crushed, and packaged.

19.5 METALLURGICAL LIME

Lime (CaO) is a very important component of many ferroalloys processes to form and adjust proper slag formation. The lime charge for the smelting of ferroalloys with reduction by silicon (metallic manganese, medium carbon

ferromanganese, low-carbon ferrochrome) as well as by carbon (ferrosilicon) must have the proper chemical composition: $<1.5\%$ to 2% SiO_2, $<0.03\%$ to 0.08% S, and $<0.02\%$ to 0.03% P, depending on the quality grade of the lime (Gasik et al., 2009). A strict limit on phosphorus content in lime is due to almost complete phosphorus reduction by either carbon or silicon and its transfer into ferroalloys. Allowable sulfur content in lime is higher than that of phosphorus, because sulfur is assimilated in basic slag, especially better with the higher the basicity of the slag.

The source for lime production is natural limestone. It is composed of mineral calcite—$CaCO_3$ (56% CaO, 44% CO_2)—and impurity oxides (MgO, SiO_2, Fe_2O_3). When heated to $900°$ to $1100°C$, it thermally dissociates by the reaction $CaCO_3 \rightarrow CaO + CO_2$ (gas). The most important feature of the crystal-chemical transformations during the thermal dissociation of calcite is the process of forming crystalline phases $CaCO_3$ and CaO. The dissociation reaction of calcite is localized at the interface of $CaCO_3$-CaO. As heating and isothermal holding of the reaction boundary move deeper into a piece of limestone, the $CaCO_3$ crystal lattice is transformed into the crystal lattice of CaO.

The size of the crystallites (grains) of obtained lime determines its chemical activity when lime is dissolved in slags. With the increasing firing temperature of limestone, lime crystal size increases, which leads to a decrease of its chemical reactivity. It is known that for cases in which lime should be more resistant to moisture, the firing temperatures must be high enough. The most stable lime is obtained by remelting it in electric arc furnaces to produce fused lime with rather large crystals.

Often limestone also contains magnesium carbonate $MgCO_3$, which also thermally dissociates upon heating with the formation of magnesia (MgO) and CO_2. The complex carbonate of calcium and magnesium is considered an equimolar mixture of $CaCO_3$ isomorphic with $MgCO_3$, or as a double compound, dolomite $(Ca, Mg)(CO_3)_2$. The thermal dissociation of dolomite proceeds in two stages: (1) the decomposition of dolomite into $CaCO_3$, MgO, and CO_2, and (2) the dissociation of $CaCO_3$.

There are different technologies of lime production. In the following two examples, lime is made in shaft-slit furnaces or in kiln furnaces.

The shaft-slit furnace example (Fig. 19.16) has a height of 22.5 up to the charging devices level and has three main zones from the top down: preheating (6.18 m), firing (6.5 m), and cooling (4.32 m). The length of the slit is 6 m but the width is not uniform: 1.7 m in the firing zone, 1.35 m in the heating zone, and 2.4 m in the cooling zone. The lining has a base of chromia–magnesia bricks.

The furnace is equipped with two tiers (rows) of burners. The lower tier in this case has 10 burners on each side of the shaft furnace, and the top (at the "square" oven) has 4 burners on each side. As furnaces are often build inside the ferroalloy plant, it is a common practice to mix the exhaust gas from fer-roalloys (FeSi, FeSiMn) production (80% to 85% CO, 3% to 5% H_2) as fuel to
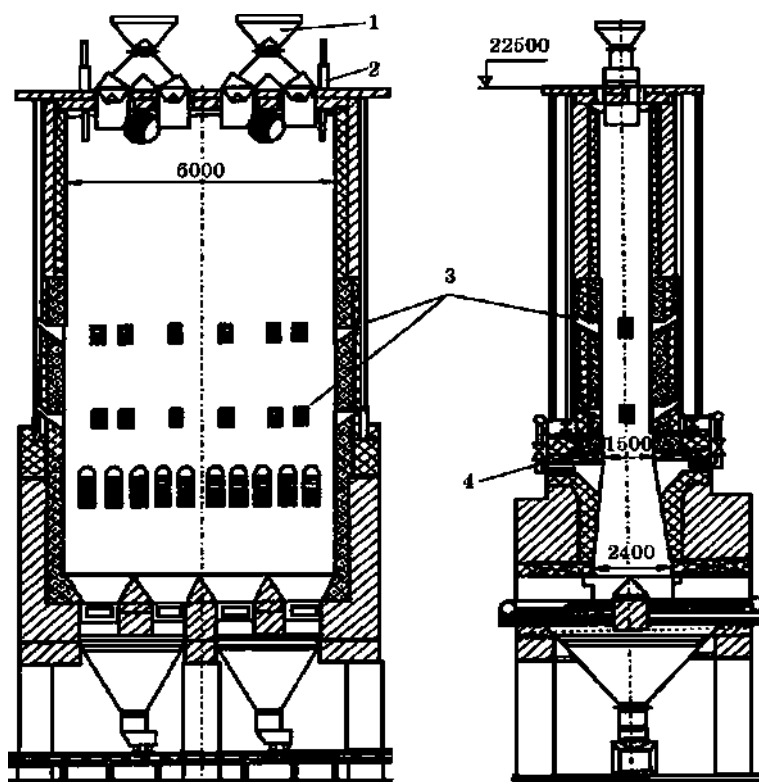
FIGURE 19.16 Shaft-slit furnace design: 1, tapered charging device; 2, limestone level indicator; 3, viewing window; 4, burner.

decrease the consumption of natural gas. For example, for a gas with 80% CO, its calorific value is about 6.6 Gcal/h for a 3000 m^3/h flow rate. The addition of 200 m^3/h of natural gas will complement the fuel calorific value with an extra 1.64 Gcal/h, which is similar to the value for a 1000 m^3/h flow rate of natural gas, if it were be used alone. The exhaust gases from the shaft-slit furnace have a composition of 27% to 30% CO_2, 0.6% to 1.2% O_2, 3% to 6% CO, and the balance made up of nitrogen.

Temperatures in the shaft-slit furnace are kept in the firing zone of 900° to 1100°C and in the heating zone of limestone 600° to 680°C. The temperature of the flue gases from the shaft furnace should not exceed 250°C. The productivity rate of the furnace much depends on the flow of gas. At the gas flow rate of 416 to 480 Nm^3/h, a furnace similar to the one shown in Figure 19.16 produces 50 to 60 tons of lime a day, consuming 105 t/day of limestone. Increasing the gas flow rate up to 1024 to 1056 Nm^3/h might raise the productivity level to 140 to 150 t/day with a daily limestone consumption of 250 t (Gasik et al., 2009).

Another method of making metallurgical lime is the use of rotary kiln furnaces. They have some advantages over shaft-slit furnaces in that they offer a higher level of process mechanization, easier operation, and a higher and more continuous performance of the limestone firing process. However, they also require higher investment and more fuel consumption per 1 ton of lime produced. The kiln is commonly 2.4 to 3.6 m diameter and 63 to 70 m length, heated by natural gas, with or without the additions of ferroalloy gas, resulting in a burner temperature of 1400° to 1500°C. The kiln has three main zones: preheating, firing (refractory lining temperature of 1200° to 1300°C), and cooling. Limestone with a lump size of 10 to 50 mm is almost completely dissociated at 1200° to 1250°C for 1.5 to 3 h kiln residence time.

To improve heat recovery, rotary kiln feeders are equipped with tubular heaters that utilize the waste heat of flue gases. They preheat limestone up to 150° to 200°C, which improves the kiln's thermal performance by 30% to 50%.

Lime can also be produced in fluidized bed process furnaces, but shaft-slit and kiln furnaces are more widespread for ferroalloy applications.

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