SILICON AND SILICON ALLOYS, CHEMICAL AND METALLURGICAL

1. Introduction

Silicon, a low density chemical element having nonmetallic characteristics, is the second, after oxygen (50.5%), most abundant element in the lithosphere. Silicon occurs naturally in the form of oxides and silicates and constitutes over 25% of the earth's crust (see SILICA, INTRODUCTION).

The commercial production of silicon in the form of binary and ternary alloys began early in the twentieth century with the development of electric-arc and blast furnaces and the subsequent rise in iron (qv) and steel (qv) production (1). The most important and most widely used method for making silicon and silicon alloys is by the reduction of oxides or silicates using carbon (qv) in an electric arc furnace. Primary uses of silicon having a purity of greater than 98% are in the chemical, aluminum, and electronics markets (for higher purity silicon, see SILICON, PURE). Typical properties of silicon are shown in Table 1 (2,3).

Silicon is soluble in aluminum in the solid state to a maximum of 1.62 wt % at 577°C (4). It is soluble in silver, gold, and zinc at temperatures above their melting points. Phase diagrams of systems containing silicides are available (4,5).

More than half of the elements in the Periodic Table react with silicon to form one or more silicides. The refractory metal and noble metal silicides are used in the electronics industry. Silicon and ferrosilicon alloys have a wide range of applications in the iron and steel industries where they are used as inoculants to give significantly improved mechanical properties. Ferrosilicon alloys are also used as deoxidizers and as an economical source of silicon for steel and iron.

2. Silicon

2.1. Production. Silicon is typically produced in a three-electrode, a-c submerged electric arc furnace by the carbothermic reduction of silicon dioxide (quartz) with carbonaceous reducing agents (6). The reductants consist of a mixture of coal (qv), charcoal, petroleum coke, and wood chips. Petroleum coke, if used, accounts for less than 10% of the total carbon requirements. The majority of the carbon is provided in the form of coal or charcoal. Low ash bituminous coal typically has a fixed carbon content of 55–70% and an ash content of <4%. Typical carbon contribution of coal is 65%. Charcoal, as a reductant, is highly reactive and varies in fixed carbon from 70–92%. Typical carbon contribution from charcoal is 80%. Wood chips are added to the reductant mix to increase the raw material mix porosity, which improves the SiO (g) to solid carbon reaction. Silica is added to the furnace in the form of quartz, quartzite, or gravel. The key quartz requirements are friability and thermal stability. Depending on the desired silicon quality, the total oxide impurities in quartz may vary from 0.5–1%. A simplified silicon furnace diagram is shown in Figure 1.

The overall reaction for the production of silicon is expressed as follows:

$$SiO_2 + 2C \rightarrow Si^0 + 2CO \tag{1}$$

Typical raw material mix to produce one metric ton of silicon consists of 2500−3000 kg quartz, 1200−1400 kg of low ash coal and/or charcoal, and 1500−3000 kg wood chips. From 11 to 14 MWh of electrical power, and prebaked carbon electrodes of 90−140 kg, are consumed.

The production of silicon takes place via two key intermediates, silicon monoxide, SiO, and silicon carbide, SiC. In the high temperature zone of the furnace below and around the electrode, SiC reacts with SiO_2 to produce silicon, SiO, and carbon monoxide, CO, according to equation 2. As the gaseous SiO and CO ascend through the charge bed, the SiO reacts with the carbon reductants to produce silicon carbide according to equation 3. The carbon and silica in the charge bed can also react directly to produce SiC according to equation 4. SiO can also be produced by an equimolar reaction of SiO_2 with carbon according to equation 5.

$$SiC + SiO_2 \rightarrow Si^0 + SiO + C \tag{2}$$

$$SiO + 2\,C \rightarrow SiC + 2\,CO \tag{3}$$

$$SiO_2 + 3\,C \rightarrow SiC + 2\,CO \tag{4}$$

$$SiO_2 + C \rightarrow SiO + CO \tag{5}$$

The silicon carbide, produced in the middle zone of the furnace, is pushed down by stoking and reacts with SiO_2 to produce silicon. The silicon produced is periodically or continuously tapped. Rising SiO reacts with the carbon in the bed and is converted to SiC and the process repeats itself.

A typical 20-MW, a-c furnace is fitted with three 45-in. (114.3-cm) prebaked amorphous carbon electrodes equilaterally spaced, operating on a three-phase delta connection. The spacing of the electrodes is designed to provide a single reaction zone between the three electrodes. The furnace is rotated to give one revolution in two to four days or it may be oscillated only. Rotation of the furnace relative to the electrodes minimizes silicon carbide buildup in the furnace.

The open-top furnace is fitted with a hood to collect the silicon monoxide and carbon monoxide emerging from the furnace. The gases are oxidized by introducing air, which also results in oxidation of the carbon materials on top of the furnace. The off-gas, consisting of silica fume and carbon particles, is passed through radiation pipes and a drop-out box, where the heavy carbon particles are removed. The fume particles are collected in the baghouse and the gases are discharged to the atmosphere.

In a good arc furnace operation, tapped silicon recovery accounts for 80±10% of the inbound silicon in quartz. The remaining 15% exits the furnace in the form of SiO, which oxidizes to SiO_2 upon coming in contact with air. The energy required to produce silicon varies from 11−14 kWh/kg Si. Arc furnaces for silicon production are very inefficient from the standpoint of energy utilization. Only 31% of the total energy input to the furnace both in the form of electrical energy and chemical energy from the reductants (coal, charcoal, coke, wood chips) is used for reduction of quartz. The remaining 69% of the energy is lost, most of it in the form of by-product off-gas accounting for up to 52.5% of the input.

The quality of the silicon is controlled by careful selection of the raw materials. This is especially true for impurities such as Fe and Ti, which are more difficult to remove by refining. A typical analysis of tapped silicon gives 0.2–1.0% Ca, 0.2–0.9% Al, 0.25–0.8% Fe, and <500 ppm for Cr, Mg, Mn, Ni, Ti, V, Cu, Zr, P, and B. The specifications of various grades of silicon for the chemical and aluminum industry are summarized in Table 2.

2.2. Refining

In order to produce silicon that meets the requirements of the chemical, ie, silicones, and primary aluminum markets, the silicon produced in the arc furnace requires further purification. The quality of silicon for the chemical silicones industry is critical with respect to the levels of aluminum and calcium present, and the primary aluminum grade of silicon requires low levels of calcium, iron, and phosphorus. The impurity requirements for the secondary aluminum market are not as stringent, so long as the silicon content is >98.5%.

Advances in refining technology have improved the ability to meet silicon purity requirements. The concept of gas injection through a bottom plug for refining silicon alloys in a ladle was developed at Tinfos Jernverk A/S in Norway during the 1980s (7). Because silicon is refined by mixing air and oxygen with molten silicon, the use of a bottom plug provided significantly improved mass transfer between the impurities in the silicon melt and the oxide slag. This method yields nearly equilibrium levels of calcium and aluminum in silicon. Prior to the development of bottom plug technology, the silicon refining process efficiency was limited by the use of a lance for injection of gases from the top of the ladle. Use of bottom plug technology has commercially demonstrated reduction of calcium levels from 2 to <0.01% and aluminum from 1 to <0.1%.

In order to produce silicon for a given specification with respect to aluminum and calcium, the tapped metal is refined using a predetermined amount of oxygen. The oxygen is introduced to the molten bath as a mixture of oxygen, air, or SiO_2 (sand). The refining efficiency, a function of mass transfer between the silicon melt and the oxide slag, is improved by stirring the bath using the necessary amount of nitrogen, introduced as air. The amount of addition of oxygen as sand depends on tap temperature and heat generated by the oxidation of calcium and aluminum, which is also a function of the tap metal chemistry.

Contamination of chemical grade silicon with small amounts of the oxide slag is known to be detrimental to the silicon performance. The oxide slag must be removed from molten silicon by phase separation during casting. Recent advances in refining technology have recognized the need to reduce the oxide slag contamination by improving its tendency to separate. The separation can be improved by controlling the process to generate an oxide slag with suitable viscosity, density, and melting point. This can be accomplished by considering the interactions between calcium and aluminum levels, refining temperature, and casting temperature (8).

A thorough review of the principles of silicon and ferrosilicon refining has been published (9,10). The equilibrium ternary diagram between the SiO_2–CaO–Al_2O_3 slag and the Si–Al–Ca alloy at 1550°C is shown in Figure 2 (10). A typical casting operation is shown in Figure 3.

2.3. Technology Developments. The composite electrode technology is one of the most significant developments put into commercial practice in the early 1990s (11). The improved version of the Søderberg technology provides iron-free self-baking electrodes which have the potential to reduce electrode cost by as much as 50% without contributing additional impurities to the product (12).

Developments in the process computer control technology since the 1980s have been one of the leading factors in improving furnace operation and getting higher silicon recovery. The relationship of resistance and electrode spacing is also a key factor in furnace design optimization. These topics have been thoroughly discussed in the literature (13,14). Other process improvements for improved silicon recovery by carbon theory control via calcium in the tap stream have also been published (15). Calcium addition to a silicon furnace has also been found to improve the operation (16). The direct current closed furnace technology for smelting silicon represent an area where a significant amount of effort has been put forth to demonstrate newer technology on a pilot scale (17,18). A parallel effort on smelting silicon and ferrosilicon in a d-c furnace was also evaluated by the Silicon Technology Competitive Cooperative (STCC) (19), the membership of which consists of principal silicon and ferrosilicon producers in the United States.

In the area of silicon casting, water granulation on a commercial scale has been key (20), offering the advantage of uniform distribution of trace impurities within a silicon granule. Some chemical producers have found such silicon to give improved performance (21). Although water-granulated silicon minimizes silicon losses as fines and gives a product that is in demand, it also presents the risk of an occasional explosion, as has been experienced by the producers, when molten silicon comes in contact with water. Another advancement in silicon casting has been the development of technology whereby silicon is cast onto a cooled, vibrating copper table. The thickness of the resulting sheet of silicon can be controlled by the vibration of the casting table. This technology offers the advantage of fast cooling and reduced contamination of the silicon, since fines are not used as in traditional casting molds (22).

One of the most significant technology advances in recent years has been related to the production of low-cost solar-grade silicon. The demand for solar-grade silicon, has been growing at a rate of around 30% from the mid–1990s to 2005. Due to a projected shortage for solar-grade silicon, several companies have been aggressively pursuing alternative routes for producing solar silicon by upgrading metallurgical silicon. Boron and phosphorus are the two most important impurities in silicon that are most difficult to remove below the required level of less than 0.5 ppm. A typical approach for producing solar-grade silicon using the metallurgical route involves using high purity raw material in an arc furnace to produce a grade of silicon that is low in B and P. The resulting silicon is further refined by a combination of processes that effectively remove heavy metal impurities as well as lower the B and P levels down to the desired range. Solar cells produced from such processes have been reported to give solar cell efficiencies as high as 15% (23,24). Some of the listed publications (25–28) discuss approaches for upgrading metallurgical silicon to solar quality. Although processes to produce solar silicon by upgrading metallurgical silicon have been developed on a pilot scale, no production facility using such an approach currently exists, although plans to install new capacity have been announced.

2.4. Uses. The market for silicon can be broken down into chemical, dominated by silicones; secondary aluminum; primary aluminum, recovery; and electronics. The use of silicon for the silicones market is the fastest growing and largest segment of the silicon market. Silicones are remarkably versatile and can be produced in numerous forms. Examples range from fluids thinner than water to rigid plastics which can be clear or pigmented. These may be elastomeric compounds, heatcured rubber parts, sealants and adhesives, or free-flowing coatings. Silicones can be made to transmit almost no heat or be heat conductive; they can have excellent dielectric characteristics, but be made to conduct electricity. Silicone products are used in a vast number of industries, including aerospace, automotive, chemicals and petrochemicals, construction, electrical, electronics, food processing, paints and coatings, personal household care products, pharmaceuticals, plastics, pressure-sensitive adhesives, textiles, and leather. Some of the products and applications include pressure-sensitive labels for release coatings, drug delivery systems, room-temperature vulcanized (RTV) insulator coatings, hair care products, fabric softeners, foam control agents, optical fiber coating, silicone polyurethane roof system, touch-sensitive computer screens, automobile polishes, fuel-resistant silicones, silicone ink additives, etc.

The secondary aluminum market is the second largest consumer of silicon. The majority of the applications are in castings for the automotive industry. The most prominently used compositions in all casting processes are those of the aluminum–silicon family. The outstanding effect of silicon in aluminum alloys is the improvement of casting characteristics. Addition of silicon to pure aluminum dramatically improves fluidity, hot tear resistance, and feeding characteristics. It also reduces shrinkage and increases corrosion resistance, hardness, tensile strength, and wear resistance. One of the earliest and still one of the main automotive uses of aluminum alloys is to reduce vehicle weight in components such as radiators, cylinder blocks, cylinder heads, pistons, intake manifolds, crankcases, and compressor, fuel pump, and transmission housings. Another application of aluminum is in rotary air-conditioner compressors. These are made using powder metallurgy (PM) hypereutectic Al–Si alloys (see POWDER METALLURGY). The wear resistance of new PM aluminum alloys containing 18–29% Si is superior to the conventional die-cast aluminum alloys. Rapidly solidified aluminum alloys using PM to make near-net shapes are also replacing conventional materials in intake valves, connecting rods, and pistons. Aluminum is also being considered for structural components in automobiles with development of successful joining methods.

The third largest silicon consumer is the primary aluminum market. A small (1%) percentage of silicon is added to the virgin aluminum ingot to remove oxygen during casting. Relatively higher purity silicon is required for this application.

The electronics market uses silicon as trichlorosilane, which is decomposed with hydrogen at high temperatures to produce semiconductor-grade silicon and solar-grade silicon (see SILICON COMPOUNDS: ANTHROPOGENIC SILICAS AND SILICATES).

Silicon is also used in the copper (qv) industry for production of silicon bronzes. The addition of silicon improves fluidity, minimizes dross formation, and enhances corrosion resistance and strength.

Besides the chemical industry, silicon is used as a powder in the ceramics (qv) industry for the production of silicon carbide and silicon nitride parts (see ADVANCED CERAMICS, ELECTRONIC CERAMICS). Silicon powder is also used as an explosive for defense applications and in the refractory industry for plasma spraying with other oxide mixtures (see REFRACTORY COATINGS).

2.5. Supply and Demand. The demand for silicon metal is driven by consumption in the chemical and aluminum industries. Worldwide consumption of silicon metal grew at an average annualized rate of approximately 4.9% from 1989 to 2004. The growth in the chemical industry grew at a rate of 6.5%, whereas the growth in the aluminum industry was approximately 1.7%. In 1989, Western world consumption of silicon totaled just under 630,000 metric tons, of which approximately one-third was chemicals related, ie, for silicones, electronics, and fumed silica (qv). By 2004, Western silicon demand was 1,281,000 metric tons. Chemical-related demand more than doubled during this period to approximately 690,000 metric tons, whereas the aluminum-based consumption rose less than 30%. By 1996, over half of the Western world's consumption of silicon was chemicals related. By the year 2009, the global silicon demand is expected to exceed 1,800,000 metric tons (29). The relative growth in demand can be seen in Figure 4.

The main impetus for growth in the primary and secondary aluminum markets lies in the transportation sector, particularly in the automotive industry. In the Western world, transportation is the fastest growing aluminum market sector. Western aluminum consumption totaled 8,400,000 metric tons in 2000. Silicon is present in some quantity in virtually all aluminum alloys, but primarily in the foundry alloys where it can range from 5% to 20%. The silicon content typically constitutes 7% of the metal used in cast aluminum products (30).

The demand for silicon since the 1990s has exceeded the installed Western world capacity. In 2001, the share of Western demand met by non-Western producers rose to nearly 30%. As a result of improvements in refining practices and product quality, Chinese and Russian silicon continues to gain market share outside the secondary aluminum industry. By all indications, the increase in worldwide consumption of Chinese and Russian chemical-grade silicon is likely to exceed that of Western material in years to come (31). The trend in silicon production by geographic region is shown in Figure 5.

Growth in silicon consumption has not been limited to the Western world. Growth in China has been particularly strong and has been driven primarily by the domestic silicones industry. This demand has been growing at about 40% a year and overall consumption exceeded 100,000 metric tonnes in 2004. Several new silicones projects have been announced in China that will rely on Chinese silicon supply, so the domestic demand is expected to continue at a high growth rate over the next ten years (32). Relative silicon consumption in selected countries in 2004 is shown in Figure 6.

2.6. Economic Aspects. The location of a silicon metal plant is determined by balancing market costs against processing ones. Principal elements in the cost of silicon production, which are site-dependent, are the delivered cost of the raw materials, energy cost, and labor. Typical costs for production of silicon are given in Table 3.

Silicon prices tend to be cyclical. The average annual import price of silicon metal based on U.S. dealer import price is shown in Figure 7 (33–35). Beginning in 1992, prices began a gradual increase. This was followed by a sharp gain in 1996, reaching a record high of $1.98/kg, a 35% increase over the 1995 average price. Prices then showed a gradual decline until 2002. This decline was followed by a sharp rise in prices between 2002 and 2004.

3. Silicon Alloys and Silicides

Silicides are compounds of silicon and a metal. More than half the elements in the Periodic Table react with silicon to form one or more silicides. Figure 8 gives the known silicides, arranged according to their position in the Periodic Table (36). The silicides of Groups 4–6 (IVA, VA, VIA), the refractory metal silicides, and of Groups 8–10 (VIII), the near-noble metal silicides, are of importance for very large-scale integration (VLSI) electronic applications (see INTEGRATED CIRCUITS). Metal silicides form well-defined crystals with a bright metallic luster. These are usually hard and high melting. Metals that do not form silicides are Al, Sb, As, Bi, Ca, Au, Hg, Ru, Ag, Na, Th, and Zn (4).

3.1. Ferrosilicon and Alloys. Ferrosilicon is a grayish ferroalloy consisting mainly of the elements silicon and iron. Ferrosilicons for steelmaking and foundry uses have a silicon content of 14–95 wt %. The Fe–Si phase diagram (Figure 9) shows the existence of four compounds: Fe_2Si, Fe_5Si_3, Fe–Si, and $FeSi_2$. Silicon is an essential element in cast iron. The silicon level is often the controlling factor in whether cast iron solidifies as gray iron having its accompanying mechanical properties or as white iron or iron carbide, which has little engineering significance because of its brittle nature.

Ferrosilicon Production. Ferrosilicon is produced in a three-phase submerged arc furnace by the carbothermic reduction of quartz in the presence of high quality iron ore or scrap steel. The smelting process for ferrosilicon is quite similar to silicon, with the exception of the amount of silicon carbide that is formed as an intermediate. As the iron content of ferrosilicon increases, the stability of the silicon carbide phase is known to decrease. In grades of ferrosilicon containing less than 22% Si, silicon carbide is not formed as an intermediate and quartz is directly reduced by carbon in the presence of iron. The presence of iron during the carbothermic reduction of quartz lowers the partial pressure of SiO required for reduction to silicon. Thus the losses of SiO from the furnace top decrease as the iron content of ferrosilicon increases. Because of this thermodynamic consideration, it is typical to have silicon recovery of greater than 90% for 50% and lower grades of ferrosilicon. Another significant difference in ferrosilicon production is the widespread use of Søderberg electrodes, which utilize a carbon paste that is baked *in situ*. Ferrosilicon production also utilizes larger furnaces having a power rating of up to 70 MW.

Ferrosilicon production is a nearly slag-free process. Most of the impurities introduced into the furnace via the raw materials and any other sources are transferred to the product. In order to produce high purity grades of ferrosilicon, the tapped alloy is refined by treating with gas mixtures and slag additions. The principle of ferrosilicon refining is quite similar to that of silicon. Details on the thermochemistry of ferrosilicon refining and practical examples are available (37).

Processes for casting ferrosilicon are quite similar to those used for silicon. During solidification of the standard grade of 75% ferrosilicon, silicon crystallizes initially, followed by solidification of the ϵ-phase. The transformation of the ϵ-phase to stable $FeSi_2$ is accompanied by an increase in volume, which can lead to disintegration of the alloy in the range of 45–65% silicon. The transformation and thus the disintegration can be suppressed by casting ferrosilicon in shallow molds. Ferrosilicon may be granulated by pouring a controlled molten stream of alloy in a tank of water. The range of resulting granule size is 0.32–1.92 cm (1/8–3/4 in.). Alloys of silicon are of significant commercial importance and are typically produced by post-taphole ladle additions.

Silvery pig iron containing $<25\%$ Si is magnetic, which is an advantage in handling. It is used primarily as a furnace block and is added in the form of controlled-weight piglets for initial deoxidization (38,39). It is also furnished in powder form for ore beneficiation (39). The low silicon content of silvery pig iron makes it unsuitable for ladle addition, because the large quantity normally required would cause excessive chilling.

3.2. Specialty Silicon Alloy Uses. In the iron and steel industry, silicon alloys or silicides are used for alloying, deoxidizing, and reducing other elements such as manganese, chromium, tungsten, and molybdenum. Silicon in the form of 75% ferrosilicon is used as a reducing agent in magnesium manufacture by the Pidgeon process. Ferrosilicons containing 14–95% silicon are used extensively by the iron and steel industry, and silicon is present in most commercial grades of steel and cast iron. Ternary and quarternary ferroalloys, often proprietary, are also available for the simultaneous addition of silicon and other alloying elements, usually manganese and iron. Other elements added in this way include aluminum, boron, barium, calcium, chromium, magnesium, strontium, titanium, vanadium, zirconium, and the rare earths. These combinations are widely used in the iron foundry and steel industries.

As an effective and economical deoxidizer, silicon is used to refine most grades of carbon and alloy steels. In importance to steelmaking, it is second only to manganese. As an alloying element in steels, it increases tensile strength and elastic limits, improves resistance to corrosion and high temperature oxidation, improves electrical characteristics, and decreases yield point. As a reducing agent, it reduces metal oxides from slag, thereby permitting the desired element, such as chromium, to sink and be recovered as an alloying agent. Silicon in cast iron reduces the stability of iron carbide and promotes the formation of graphitic carbon. As an effective graphitizer in cast iron, silicon softens the iron and improves its fluidity and machinability. For wear resistance, silicon in gray iron ranges from 0.50 to 1.50%. In ductile iron, silicon ranges from 1.50 to

3.00%. Increased percentages of silicon improve the corrosion and oxidation resistance of gray and ductile cast irons.

3.3. Regular Ferrosilicon.

Regular 50% ferrosilicon is a widely used, economical source of silicon for both iron and steel. Unlike steel scrap, 50% ferrosilicon provides a known source of high quality iron. This ferrosilicon is used as a deoxidizer and alloying agent in the production of killed and semikilled steels. Killed steels are those that have been made free from bubbling, while molten, by the addition of a deoxidizer. This process minimizes reaction of carbon and oxygen during solidification. The melting point of 50% ferrosilicon at 1220°C is the lowest of the iron−silicon alloys, except for the 1200°C eutectic for silvery pig iron containing about 22% Si (see Figure 9). Iron foundries add 50% ferrosilicon to the cupola and subsequently to the ladle for the purpose of inoculation. Inoculation may be defined as a change in the physical properties of iron that are not explainable by a change in chemistry. In practice, inoculation consists of withholding from the base iron some portion of the desired silicon and adding it to the ladle. The calcium and aluminum levels in these alloys effectively combine with other elements such as sulfur and oxygen in liquid iron to form oxy−sulfide nucleation sites. The nucleation sites assist in the formation of graphite and allow the iron to solidify without undercooling or the formation of chill or carbides without appreciable effect on pearlitic stability, increased randomness of graphite flakes and decrease in flake size (decreased section sensitivity), increased ratio of tensile strength to hardness, and improved machinability at all strength levels. Regular 50% ferrosilicon containing 0.04−0.1% boron is used in the production of malleable castings, where small amounts of boron accelerates the annealing cycle.

Regular 75% ferrosilicon is widely used for deoxidizing and alloying additions to iron and steel that do not require tight control of residuals. This ferrosilicon is ideal for ladle additions because its higher silicon content permits smaller additions in order to reach desired silicon levels. The slight exothermic nature of 75% ferrosilicon is also desirable from the standpoint of ladle heat balance. Regular 75% ferrosilicon and 90% ferrosilicon grades are used mainly for high alloy cast steels that require large additions of silicon. Regular 75% ferrosilicon can also be used to reduce the chromium oxide in the slag of stainless steel produced by the argon oxygen decarburization (AOD) process. Because 75% ferrosilicon is not quite as dense as steelmaking slags, additions are best added to the ladle during tapping or refining.

In the production of cast irons, 50% and 75% ferrosilicon can both be used in either cupola charges or electric furnace melting. If density is a consideration in electric furnace melting, 50% ferrosilicon has a slight advantage, because 50% ferrosilicon tends to sink deeper and penetrate the slag layer, owing to its higher density (Table 4). In cupola applications, 75% ferrosilicon is preferred because it dissolves exothermically at a faster rate (Table 4) than 50% ferrosilicon and consequently penetrates further into the melt zone, resulting in slightly higher recoveries.

High aluminum grade of 75% ferrosilicon containing 3−5% Al is used for the production of spheroidal iron. In gray iron applications, this inoculant is used to control and minimize the formation of carbides and decrease section sensitivity by refining graphite size and distribution. In ductile iron it is also effective in minimizing carbide formation while increasing nodule count.

High purity 50% ferrosilicon containing <0.1% Al and C is used for production of stainless steel and corded wire for tires, where residual aluminum can cause harmful alumina-type inclusions. These are also useful in continuous cast heats, where control of aluminum is necessary. High purity grades of 50% and 75% ferrosilicon containing low levels of aluminum, calcium, and titanium are used for silicon additions to grain-oriented electrical steels, where low residual aluminum content contributes to the attainment of desired electrical properties, eg, significant reduction of eddy currents.

High purity 75% ferrosilicon containing low aluminum and calcium can be used in continuously cast heats where nozzle blockage is a problem. In iron melting, this alloy is desirable to minimize buildup on refractory faces in the furnace or on stopper rods or nozzles. Low aluminum ferrosilicons can also help reduce hydrogen pin holes in castings poured in green-sand molds.

3.4. Ferrosilicon Supply and Demand. The demand for ferrosilicon is driven primarily by consumption in the steel industry. Worldwide production of ferrosilicon amounted to 4,900,000 metric tons in 2003, based on gross weight. Worldwide production of ferrosilicon grew at an average annualized rate of 4.7% from 1998 to 2003. Western world production of ferrosilicon amounted to 1,240,000 metric tons in 2003. The Western world production has fallen by 18% during the period from 1998 to 2003. The United States imported 58% of the ferrosilicon it consumed in 2003, up from 39% in 1998. The reduction in ferrosilicon produced in the Western world has been more than offset by the rise in ferrosilicon production in China, Eastern Europe, Russia, and other CIS countries. Production in these countries has increased by over 50% during the same period. Recent growth in China has been especially strong, with ferrosilicon production increasing by over 40% in a single year from 2002 to 2003. China is now estimated to be the world's largest producer of ferrosilicon, with production almost twice that of the next two largest producing countries combined, Norway and Russia (40). Ferrosilicon production trends by geographic region are shown in Figure 10.

3.5. Economic Aspects. The prices of 50% and 75% grade ferrosilicon are shown in Figure 7. The prices are given on a contained silicon basis (33–35). The price of ferrosilicon follows the same general trend as the price of silicon metal. Beginning in 1992, ferrosilicon prices have gradually increased, posting significant gains in 1995 and 1996 owing to increased demand in both 50% and 75% grades of ferrosilicon. Prices then showed a gradual decline until 2002, at which time they began to rise sharply again.

4. Specialty Silicon Alloys

4.1. Magnesium Ferrosilicons. Of the miscellaneous silicon alloys consumed in the United States, magnesium ferrosilicon is the most significant. Magnesium ferrosilicon alloys have a light gray to silvery crystalline appearance and are primarily used in the production of ductile iron. Magnesium ferrosilicon alloys are produced by post-taphole ladle additions of magnesium and at times rare earths to the ferrosilicon production process. In order to improve magnesium recovery and uniformity, the alloys are produced using thin casting techniques in chill molds. The rare-earth-free grades typically contain 44–45% Si, 3–9% Mg, 0.8–1.5% Ca, and 1.25% (max) Al. The cerium -bearing grades contain 0.2–2% Ce in addition. The content of rare earths range from 0.2–2.5%. Rare-earth-containing magnesium ferrosilicons are also available with high calcium contents of up to 3.4%. The presence of calcium slows down the dissolution rate of magnesium ferrosilicon, providing uniform magnesium recoveries.

Magnesium ferrosilicon alloys react vigorously when added to molten iron. As the magnesium vaporizes and cools, it reacts with residual surface tension modifiers such as sulfur and oxygen and greatly increases the surface tension of the molten iron. The dissolved graphite in the molten iron nucleates and grows into a spheroidal shape because of the increased surface tension of the molten iron.

High quality ductile iron can be produced by closely controlling impurities in base irons without adding rare earth. Rare-earth-free grades of magnesium ferrosilicons are used for heavy section ductile iron castings where high quality scrap or pig iron is used in large quantities. Presence of cerium improves nucleation, neutralizes the harmful contaminants in base iron, and reduces chill in this section of iron castings.

Ductile cast iron is made by converting the flakes of graphite in gray iron into tiny balls or spherulites by the addition of one or more elements to the molten metal. Magnesium, calcium, cerium, barium, or other elements produce spherulitic graphite structures (41); magnesium and cerium (rare earth) are commercially important. The addition of 1.50–1.95% nickel to nodular iron significantly increases the strength of the pearlitic matrix. Conversion of graphite flakes into spherulites increases tensile strength and notch hardness of cast iron; subsequent heat treatment produces desirable mechanical properties that cannot be obtained with iron-containing graphite in flakes.

4.2. Rare-Earth Silicides.

Rare-earth silicides, in the form of a ferroalloy that contain up to 33% rare earths, are used increasingly by the iron and steel industries. Whereas the term silicides is no longer used for alloys of this type, it is still in common usage for these materials. For nodular iron, addition of rare earths gives spheroidal rather than flaky graphite. Rare earths desulfurize and, combined with silicon, deoxidize and alloy steels. They may be substituted for mischmetal.

4.3. Manganese–Silicon Alloys.

Manganese–silicon alloys usually contain various amounts of iron and carbon. They are made by carbon reduction of manganese ore or manganese slag in the presence of silica in an electric furnace. The lower silicon grades, referred to as silicomanganese, contain ca 1.5–3% carbon, 18–20% silicon, and 65–68% manganese. The remainder is mainly iron. Silicomanganese is widely used in steelmaking furnaces and ladles for alloying and deoxidization. The use of silicomanganese is often preferred to separate additions of manganese and silicon because it introduces less aluminum, carbon, nitrogen, and phosphorus. It also provides stronger deoxidization and produces higher purity steel. A low carbon grade of silicomanganese containing about 30% silicon and 0.6% carbon (max) is made by a two-stage process. It is used extensively in the production of the 200 and 300 stainless steel series.

Barium- and calcium-bearing manganese silicon is used as an inoculant in gray and ductile iron. The alloy contains 60–65% Si, 9–11% Mn, 4–6% Ba, 1–3% Ca, and 1–1.5% Al. The combination of barium, calcium, and manganese provides excellent chill reduction, improves the graphite structure, and minimizes section sensitivity in castings having thin and thick sections.

The zirconium-bearing manganese silicon, having a composition of 60–65% Si, 5–7% Mn, 5–7% Zr, 0.75–1.25% Al, and 0.6–0.9% Ba and Ca, is also used as an inoculant for gray and ductile iron castings. This alloy minimizes chill tendency while improving the mechanical properties of cast iron. Manganese in the alloy enhances its dissolution rate, strengthens the matrix, and improves tensile strength without impairing machinability. Calcium and barium help reduce chill and increase cell or nodule count. Zirconium acts as an effective nitrogen stabilizer, and the presence of barium and zirconium has a synergistic effect on minimizing the rate of inoculation fade.

4.4. Calcium–Silicon. Calcium–silicon and calcium–barium-silicon are made in the submerged-arc electric furnace by carbon reduction of lime, silica rock, and barites. Commercial calcium–silicon contains 28–32% calcium, 60–65% silicon, and 3% iron (max). Barium-bearing alloys contains 16–20% calcium, 9–12% barium, and 53–59% silicon. Calcium can also be added as an alloy containing 10–13% calcium, 14–18% barium, 19–21% aluminum, and 38–40% silicon. These alloys are used to deoxidize and degasify steel. They produce complex calcium silicate inclusions that are minimally harmful to physical properties and prevent the formation of alumina-type inclusions, a principal source of fatigue failure in highly stressed alloy steels. As a sulfide former, they promote random distribution of sulfides, thereby minimizing chain-type inclusions. In cast iron, they are used as an inoculant.

4.5. Barium–Silicon. Barium–silicon alloy, containing 70–77% Si, 1.5–2.5% Ba, 1.7–3% Ca, and 0.8–1.5% Al, is used as an inoculant in both gray and ductile iron. The combined effect of barium and calcium provides extremely potent nucleation and is very effective in minimizing carbide precipitation and decreasing section sensitivity by refining graphite size and distribution in gray iron applications. In ductile irons, it is also effective in minimizing carbide formation while increasing nodule count.

4.6. Strontium–Silicon. The strontium–silicon alloy contains 30–40% strontium and 45–55% silicon; 0.9% Ca, 1% Al, and 5% Fe. It is made in an electric furnace by carbon reduction of silica- and strontium-bearing ore. In cast irons, this alloy effectively reduces chill. It dissolves rapidly, produces little dross, and minimizes shrinkage defects. This alloy is also used to make a master alloy containing 9–11% Sr, 12–16% Si, and the remainder aluminum. This master alloy is used for additions to aluminum to improve machinability. Strontium is an alternative to sodium in this application. Strontium–silicon can also be used as a strontium source to produce an alloy having either 50 or 75% ferrosilicon and a strontium level in the range of 0.6–1%. This alloy is very effective in controlling graphite structure by providing an excellent nucleating effect and reducing chill in gray iron. It also helps avoid casting shrinkage and pinhole defects.

4.7. Titanium–Silicon. The titanium–silicon alloy is made by adding titanium scrap to molten metallurgical silicon or silicon alloys. It is also made by carbon reduction of titanium ore, limestone, and quartz in a submerged arc furnace. Titanium–silicon alloy is an efficient graphitizing inoculant for chill reduction in gray cast iron. It is also a supplementary deoxidizer for wrought and cast steels. The high calcium-based titanium silicon alloy contains 50–60% Si, 9–12% Ti, 5–8% Ca, and 0.9–1.4% Al and is used primarily for steel deoxidization. The high calcium level permits deoxidization to occur with reduced aluminum additions. The titanium readily combines with dissolved nitrogen in liquid steels eliminating subsurface porosity. The low calcium grade containing 50–55% Si, 10–12% Ti, 0.5–1.5% Ca, 0.9–1.2% Al, and 1.2% Ba (max) is used primarily for inoculation of gray iron castings to eliminate nitrogen porosity.

The high barium grade, titanium-bearing, 75% ferrosilicon is used as an inoculant aimed at reducing nitrogen porosity, while simultaneously providing superior inoculating effects for controlling graphite structures and reducing chill. Typical composition consists of 65–70% Si, 8–10% Ti, 5% Mn (max), 2–2.5% Ba, 1–1.5% Ca, and 1.5% Al. The manganese in the alloy produces a mild pearlite stabilizing effect. Pearlitic matrix structures in gray irons enhance tensile properties.

An alloy of titanium containing 40–50% Ti and 45–50% Si is used as an additive in cast iron to shorten the graphite flakes. The effect is to provide a smooth casting surface. The resulting casting is then used to produce glass bottle molds.

4.8. Vanadium–Silicon. Vanadium–silicon alloy is made by the reduction of vanadium oxides with silicon in an electric furnace. Application is essentially the same as that of the titanium alloys. Vanadium alloys sometimes offer the most economical way of introducing vanadium into molten steel.

4.9. Zirconium–Silicon. Zirconium–silicon alloy is made in an electric furnace by carbon reduction of the oxides. It is used by the iron and steel industries as a deoxidizer and scavenger. Zirconium combines readily with oxygen, nitrogen, and sulfur, forming nonmetallic inclusions that either float out of the molten bath or are rendered minimally harmful. The principal alloy contains a typical level of 35–40% Zr, 49% Si, and 10% Fe. A lower zirconium product containing about 14% Zr, 42% Si, and 42% Fe has also been produced. Zirconium–silicon alloy is mainly added to steel as a grain refiner, but can also be used for oxygen and nitrogen removal. When added to high strength low alloy steels, it serves as a sulfide inclusion modifier.

Zirconium-bearing 75% ferrosilicon is used as an inoculant in both gray and ductile iron. The alloy contains 70–80% Si, 0.4–1.5% Ca, 1–1.8% Al, and 0.25–3.5% Zr. Because of its high dissolution rate, it can be added in the ladle or in-stream inoculant. This alloy gives excellent chill reduction.

5. Health, Safety, and Environmental Factors

The off-gas from the production of silicon and ferrosilicon alloys contains large amounts of dust having approximately 90% silica fume. This nonhazardous silica fume is amorphous and more of a nuisance than hazardous. The amount of fume generated from a furnace is a function of its efficiency. Since the early 1980s, furnace performance has improved considerably and consequently the amount of fume produced from a furnace has been reduced by a factor of two. In the late 1970s, the silica fume collected as a by-product presented a significant disposal problem. As of the mid-1990s, the silica fume is used as an additive for the production of cement and is in such demand that a silicon plant is known to operate for maximizing fume production and for silicon as a by-product.

A 75% ferrosilicon furnace operating at 90% silicon recovery would give 0.24 kg of by-product silica fume per kg of silicon produced. A silicon metal furnace operating at 85% recovery (typical of the industry) would give 0.38 kg of fume silica per kg silicon produced.

The principal health hazard that may be associated with silicon and silicon alloys is caused by the crystalline form of the oxide, ie, quartz, used as a raw material. Silica in its crystalline form is the chief cause of disabling pulmonary fibrosis, such as silicosis. Over a period of years, the breathing of air containing excessive amounts of crystalline silica can cause shortness of breath (42).

In the United States, amendments to the Clean Air Act limited the amount of sulfur dioxide emissions that coal-based power utilities could produce. The cost of compliance incurred by the utilities would be passed along to the power consumers. The U.S. Bureau of Mines estimated that the requirements to limit sulfur dioxide emissions would increase the operational cost of certain silicon producers by up to $0.02/kg (43).

As silicon production is energy intensive, silicon smelters can have a large greenhouse gas footprint. The net amount of CO_2 emitted as a result of silicon production can vary widely from one facility to another. This is influenced heavily by two factors—the source of energy used to generate electricity used at the smelter (typically either coal or hydroelectric power) and the reductant used (typically either coal or charcoal) (44,45). Using charcoal that is produced from renewable forestry practices as a “carbon−neutral” reductant can significantly reduce net CO_2 generation.

Silicon and ferrosilicons by themselves are nontoxic. Some ferrosilicons may produce phosphorus hydride on coming in contact with water.

BIBLIOGRAPHY

“Silicon and Silicon Alloys” in *ECT* 1st ed., Vol. 12, pp. 360−365, by J. C. Vignos, Ohio Ferro-Alloys Corp.; “Metallurgical Silicon and Silicides” in *ECT* 2nd ed., Vol. 18, pp. 125−132, by E. G. Simms, Ohio Ferro-Alloys Corp.; “Silicon and Silicon Alloys−Metallurgical” in *ECT* 3rd ed., Vol. 20, pp. 846−854, by R. F. Silver, Elkem Metals Co.; “Silicon and Silicon Alloys, Chemical and Metallurgical” in *ECT* 4th ed., Vol. 21, pp. 1104−1122, by V. Dosaj, Dow Corning Corp.; “Silicon and Silicon Alloys, Chemical and Metallurgical” in *ECT* (online), posting date: December 4, 2000, by V. Dosaj, Dow Corning Corp.

CITED PUBLICATIONS

1. H. Moissan, *The Electric Furnace*, 2nd ed., trans. by V. Lenker, Chemical Publishing Co., Easton, Pa., 1920.
2. C. L. Yaws and co-authors, Solid State Technology, (Jan. 1981).

3. B. M. Turovskii and A. P. Lubinov. Invest. Vyzov (Russian) Chem. Met. No. 1, 24 (1960).
4. M. Hansen, *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill Book Co., Inc., New York, 1958.
5. F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl., McGraw-Hill Book Co., Inc., New York, 1969.
6. A. Schei, J. K. Tuset, and H. Tveit, *Production of High Silicon Alloys*, Tapir Forlag, Trondheim, 1998.
7. B. Skei, in *Electric Furnace Conference Proceedings*, Vol. 48, New Orleans, La., 1990, p. 225.
8. U.S. Provisional Patent Application Serial No. 60/560,532 (April 8, 2004), V. D. Dosaj, M. G. Kroupa, and P. J. Marion.
9. J. Kr. Tuset, Principles of Silicon Refining, International Seminar on Refining and Alloying of Liquid Aluminum and Ferro-Alloys, Trondheim, Norway, Aug. 26, 1985.
10. J. Kr. Tuset, Principles of Silicon Refining, Silicon for Chemical Industry, Geiranger, Norway, June 1992, p. 1.
11. U.S. Pat. 4,575,856 (Mar. 11, 1986), J. A. Persson.
12. U.S. Pat. 6,590,926 (July 8, 2003), H. C. L. Albuquerque.
13. R. F. Silver, in *Electric Furnace Conference Proceedings*, Vol. 41, Detroit, Mich., 1983, p. 175.
14. R. F. Silver, in *Electric Furnace Conference Proceedings*, Vol. 52, Nashville, Tenn., 1994, p. 361.
15. M. D. Young and R. F. Silver, in *Electric Furnace Conference Proceedings*, Vol. 51, Washington, D.C., 1993, p. 165.
16. U.S. Pat. 4,798,659 (Jan. 17, 1989), V. D. Dosaj, D. H. Filsinger, and J. E. Trunzo.
17. V. D. Dosaj, J. B. May, and A. N. Arvidson, *Direct Current, Closed Furnace Silicon Technology*, Silicon for Chemical Industry II, Loen, Norway, June 1994, p. 9.
18. D. W. Ksinsik, Silicon Metal Production in an Open DC Arc Furnace, Silicon for Chemical Industry II, p. 25.
19. H. R. Larson and J. H. Welborn, Revitalize the U.S. Silicon/Ferrosilicon Industry Through Energy Efficient Technology, DOE Final Report No. DOE/AL/94598-1 (DE95010689), U.S. Dept. of Energy, Washington, D.C., Feb. 1995.
20. L. Nygaard and H. Brekken, Production of Water Granulated Silicon, Silicon for Chemical Industry II, p. 61.
21. B. Pachaly, Process Development in the MCS-Production: For Example Water Granulated Silicon, Silicon for Chemical Industry II, p. 55.
22. J. B. Camarasa and A. More, *Experiences at Ferroatlantica using the New Casting Machine*, Silicon for Chemical Industry VI, Loen, Norway, June 2002, pp. 47–53.
23. C. Dethloff, *Update on Elkem's Solar-grade Silicon Development–The Metallurgical Route*, 2nd Solar Silicon Conference, Munich, Germany, April 11, 2005.
24. E. Fourmond and co-workers, *Refining of Mettalurgical Silicon for Crystalline Solar Cells*, 19th European Photovoltaic Conference, Paris, France, June 7–11, 2004.
25. L. J. Geerligs and co-workers, *Solar-grade Silicon by a Direct Route based on Carbothermic Reduction of Silica: Requirements and Production Technology*, 12th NREL Workshop on Crystalline Silicon Solar Cells, Materials and Processes, Breckenridge, Colo., USA, August 11–14, 2002.
26. A. I. Nepomnyaschikh and co-workers, Direct Production of Multicrystalline Solar Silicon from High Purity Metallurgical Silicon, Silicon for the Chemical Industry VII, Tromso–Bergen, Norway, with MS Trollfjord, September 21–24, 2004, pp. 299–306.
27. A. Schei, High Purity Silicon Production, Proceedings of the International Seminar on Refining and Alloying of Liquid Aluminum and Ferro-Alloys, Trondheim, Norway, August, 1985, pp. 73–89.

28. V. Dosaj and L. Hunt, Solar Silicon via the Dow Corning Process. Final Report 1979, DOE/JPL-954 559-78/7.
29. J. De Linde, Silicon Metal Industry Analysis, CRU Analysis, February 2005 (selected data used with permission).
30. D. W. Macmillan, *Aluminum-Based Solutions for the Automotive Industry*, 9th International Ferroalloys Congress, Quebec City, Canada, June 2001.
31. J. deLinde, Silicon: Changing Market Fundamentals?, Silicon for Chemical Industry VI, Loen, Norway, June 2002, pp. 377–383.
32. J. B. May, P. Sun, and W. M. Buck, China Silicon Industry, Silicon for Chemical Industry VII, Tromso–Bergen, Norway, September 2004, pp. 357–364.
33. L. D. Cunningham, *Silicon Commodity Summary*, U.S. Dept. of Interior, U.S. Geological Survey, Reston, Va., 1996.
34. T. S. Jones, *Silicon Commodity Summary*, U.S. Dept. of Interior, U.S. Geological Survey, Reston, Va., 2000.
35. L. A. Corathers, *Silicon Commodity Summary*, U.S. Dept. of Interior, U.S. Geological Survey, Reston, Va., 2005.
36. R. Keiffer and F. Benesovsky, *Hartstoffe*, Springer-Verlag, Vienna, Austria, 1963, p. 455.
37. V. Dosaj, J. K. Tuset, and H. Holta, *Silicon and Ferrosilicon Refining Lecture Notes*, Iron and Steel Society Continuing Education Course, Nov. 1994.
38. D. N. Matter, *Silicon: Its Alloys and Their Use*, Ohio Ferro-Alloys Corp., Canton, Ohio, 1961.
39. *Pulverized Silvery Pig Iron*, Foote Mineral Co., Exton, Pa., 1980.
40. J. D. Jorgenson, *Ferroalloys Commodity Summary*, U.S. Dept. of Interior, U.S. Geological Survey, Reston, Va., 2003.
41. *Metals Handbook*, Vol. 1, 8th ed., American Society for Metals, Metals Park, Ohio, 1961.
42. N. I. Sax, *Dangerous Properties of Industrial Minerals*, 3rd ed., Reinhold Book Corp., New York, 1968.
43. L. D. Cunningham, *Silicon Annual Review*, U.S. Dept. of Interior, Bureau of Mines, Washington, D.C., 1990.
44. H. Tveit, M. Storset, and I. J. Eikeland, *The Silicon Process–Improved Environmental Standards*, Silicon for Chemical Industry VII, Tromso–Bergen, Norway, September 2004, pp. 55–66.
45. L. J. Kurin, *An Overview of Factors Impacting Global Energy Availability and Price*, Silicon for Chemical Industry VII, Tromso–Bergen, Norway, September 2004, pp. 345–355.

GENERAL REFERENCES

Product data literature, Elkem Metals Co., Pittsburgh, Pa., 1996.
Product data literature, Globe Metallurgical Sales Inc., Cleveland, Ohio, 1996.
Product profile literature, Hickman, Williams and Company, Lakewood, Ohio, 1996.

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Table 1. **Properties of Silicon**[a]

Property	Value	Reference
symbol	Si	
atomic weight	28.09	
boiling point, °C	2,878	2
density, g/cm^3	2.33	2
hardness, Moh	7	2
heat capacity, cal/g.mol °C	4.78	2
heat of fusion at mp, cal/g	264	2
heat of sublimation at mp, cal/g	4,075	2
heat of vaporization at mp, cal/g	3,812	2
liquid density at mp, g/cm^3	2.533	2
liquid heat capacity at mp, cal/g.mol °C	6.755	2
liquid thermal capacity at mp, cal/sec.cm.°C	1.025×10^{-3}	2
liquid viscosity at mp, centipoises	0.88	2
melting point, °C	1,412 ± 2	2
percent expansion on freezing at mp	10%	2
poisson's ratio	0.27	2
refractive index	3.4	2
shear modulus, dynes/cm^2	7.55×10^{11}	2
surface tension at mp, dynes/cm	736	2
thermal conductivity cal/sec.cm., °C	0.353	2
torsion modulus, dynes/cm^2	3.97×10^{11}	2
vapor pressure at mp, mm Hg	2.8×10^{-4}	2
resistivity at mp, ohm.cm	7.6×10^{-5}	3

[a] Refs. 2, 3.

Table 2. **Specifications for Various Grades of Silicon, %**

Component	Chemical-grade	Primary aluminum	Secondary aluminum	Metallurgical-grade
Si	99	99	98.5	98.5
Fe	<0.4	<0.35	<0.4	<1.0
Ca	<0.1	<0.5	<0.07	<0.4
Al	<0.2			
Ti	<0.05			
P	<0.01	<0.06		

Table 3. **Silicon Production Costs in 2004**[a]

Operating cost	Cost, $/kg Si	Cost contribution, %
quartz	0.08	7
carbon	0.24	21
electrodes	0.13	11
electricity	0.31	28
labor	0.12	10
supplies and equipment	0.24	22
working capital	0.01	1
Net operation cost	*1.12*	*100*

[a] Costs assume pre-baked electrodes.

Table 4. **Ferroalloy Density and Thermal Effects on Steel Baths**

Alloy	Apparent density, g/mL	Temperature change from adding 0.2% silicon, °C
silicon	2.3	2.78
ferrosilicon		
75%	2.9	0.56
50%	4.9	-4.44
iron	6.9	
steel	7.2	
slag	3.3	

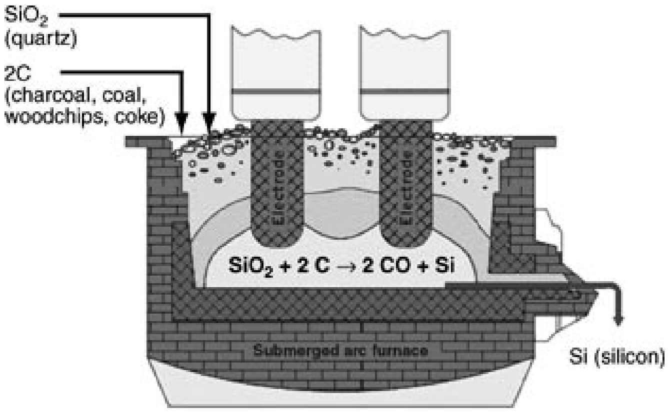

Fig. 1. Simplified silicon furnace diagram.

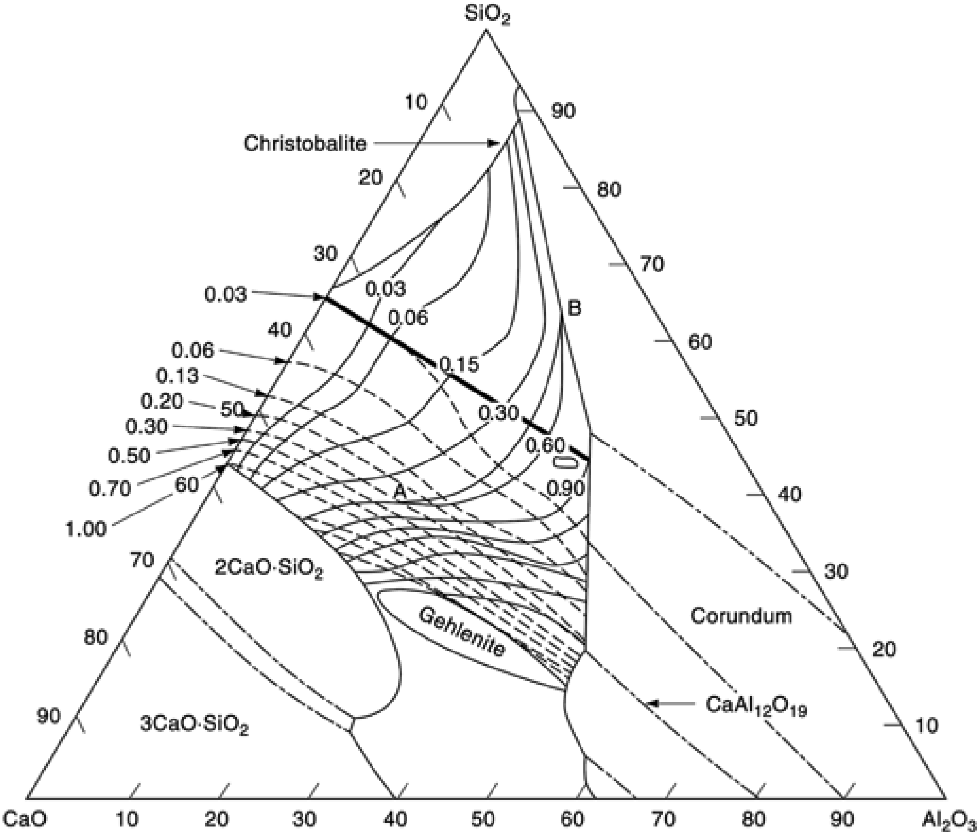

Fig. 2. Equilibrium between SiO_2–CaO–Al_2O_3 slag and Si–Ca–Al alloy at 1550°C (10), where (–) and (—) represent isoconcentration lines for Ca and Al, respectively, and (- - -) represent phase transitions in the silicon in equilibrium with the SiO_2–CaO–Al_2O_3 slag. The numbers represent values in wt %. The path designated by A–B represents the change in the slag composition when silicon having 0.6% Al and 0.2% Ca reacts to equilibrium with oxygen; (——) corresponds to a slag density of 2.5 g/mL.

Fig. 3. Photograph of a typical casting operation.

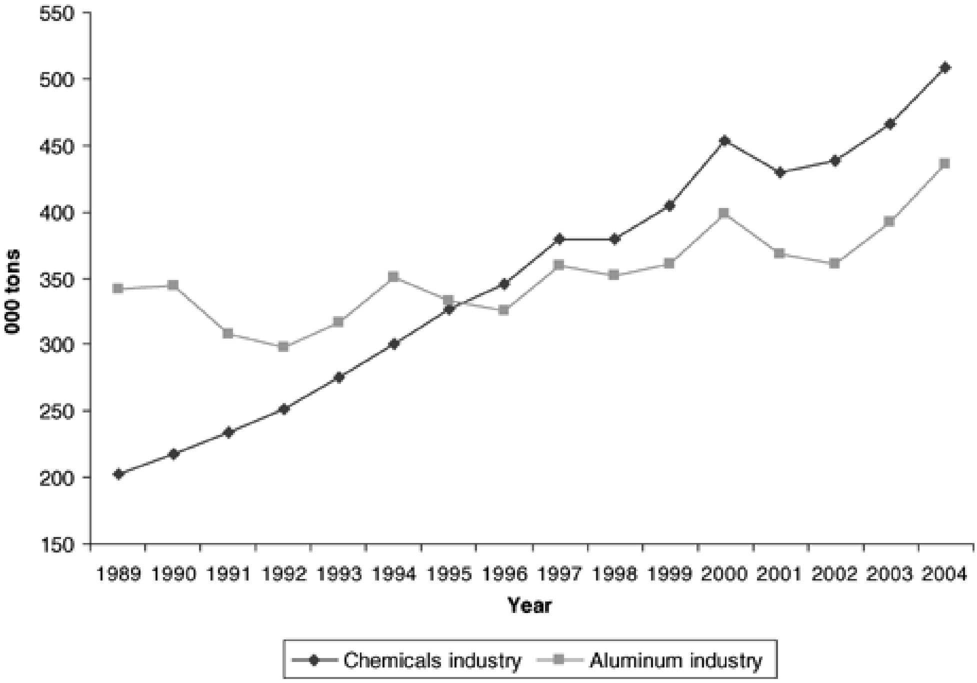

Fig. 4. Growth of Western-world silicon demand by major market (29).

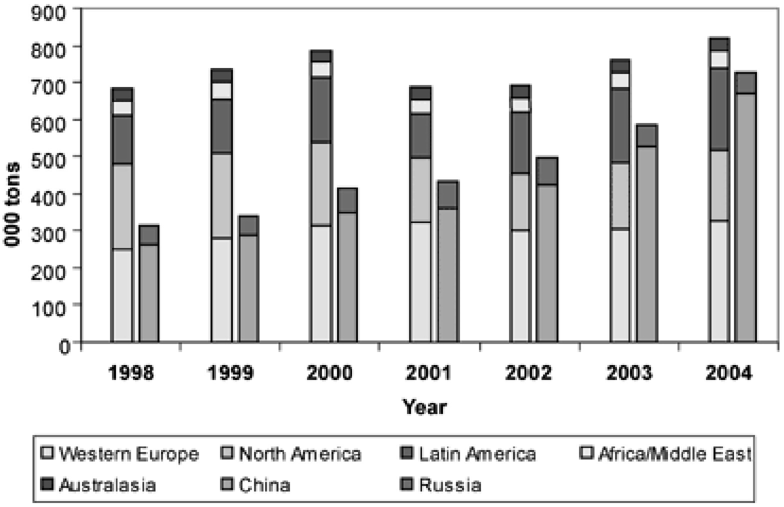

Fig. 5. Silicon production by geographic region (29).

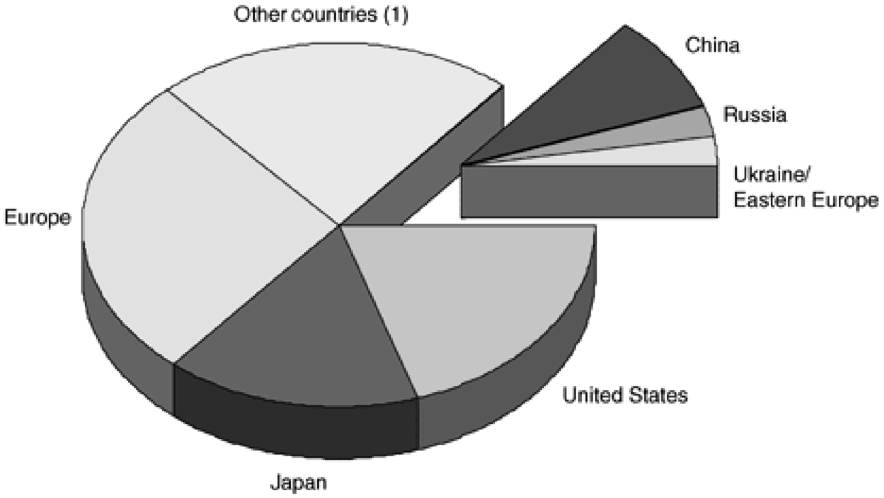

Fig. 6. Relative silicon consumption in selected countries in 2004 (29). The category "Other Countries" includes Thailand, Canada, South Korea, Norway, UAE, Brazil, Taiwan, India, Mexico, and Australia.

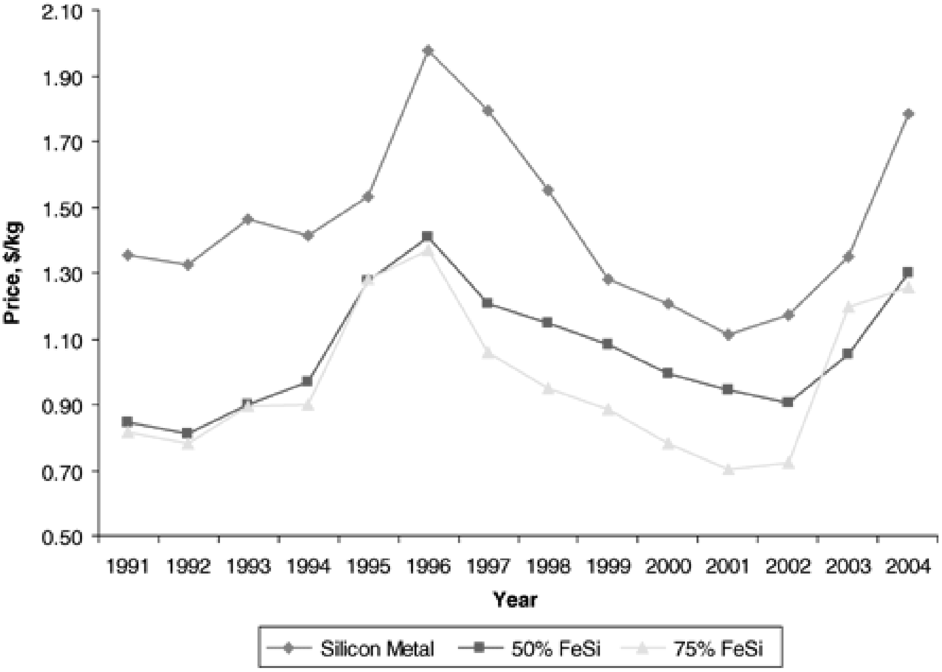

Fig. 7. Silicon product price trend (33–35).

1 (IA)	2 (IIA)	3 (IIIA)	4 (IVA)	5 (VA)	6 (VIA)	7 (VIIA)	8	9 (VIII)	10	11 (IB)	12 (IIB)	13 (IIIB)	14 (IVB)	15 (VB)	16 (VIB)	17 (VIIB)	18 (O)
H_4Si																	
$Li_{15}Si_4$ Li_2Si												B_6Si B_4Si B_3Si	CSi	N_4Si_3	OSi O_2Si	F_4Si	
NaSi	Mg_2Si		$TiSi_3$ Ti_5Si_3 TiSi $TiSi_2$	V_3Si V_5Si_3 VSi_2	Cr_3Si Cr_5Si_3 CrSi $CrSi_2$	Mn_3Si Mn_5Si_3 MnSi $MnSi_2$	Fe_3Si Fe_5Si_3 FeSi $FeSi_2$	Co_3Si Co_2Si CoSi $CoSi_2$	Ni_3Si Ni_2Si Ni_5Si_2 Ni_3Si_2 NiSi $NiSi_2$				Si	PSi	S_2Si	Cl_4Si	
KSi KSi_6	Ca_2Si CaSi $CaSi_2$	Sc_5Si_3 ScSi Sc_2Si_3 Sc_3Si_5	Zr_4Si Zr_2Si Zr_3Si_2 Zr_6Si_3 ZrSi $ZrSi_2$	Nb_4Si Nb_5Si_3 $NbSi_2$	Mo_3Si Mo_5Si_3 Mo_3Si_2 $MoSi_2$		Ru_2Si RuSi Ru_2Si_3	Rh_2Si Rh_5Si_3 Rh_3Si_2 RhSi Rh_2Si_3	Pd_3Si Pd_2Si PdSi	Cu_3Si				As_2Si AsSi	Se_2Si	Br_4Si	
RbSi $RbSi_6$	SrSi $SrSi_2$	Y_5Si_4 Y_5Si_3 YSi YSi_2													Te_2Si TeSi	J_4Si	
CaSi $CaSi_3$	BaSi $BaSi_2$	La_5Si_3 LaSi $LaSi_2$	Hf_2Si Hf_5Si_2 Hf_3Si_2 HfSi $HfSi_2$	$Ta_{4,5}Si$ Ta_2Si Ta_5Si_3 $TaSi_2$	W_3Si W_5Si_3 WSi_2	Re_3Si Re_5Si_3 ReSi $ReSi_2$	OsSi $OsSi_2$ $OsSi_3$	Ir_3Si Ir_2Si Ir_3Si_2 IrSi $IrSi_3$	Pt_3Si Pt_2Si PtSi								
				Ce_3Si Ce_2Si CeSi $CeSi_2$	$PrSi_2$	$NdSi_2$		$SmSi_2$		Gd_3Si_5 $GdSi_2$		Dy_3Si_5 $DySi_2$		Er_3Si_5		$YbSi_x$	Lu_2Si_5
				Th_3Si_2 ThSi $ThSi_2$		U_3Si_2 USi U_2Si_3 USi_2 USi_3	$NpSi_3$	PuSi $PuSi_2$									

Fig. 8. Silicides of elements in the Periodic Table 36.

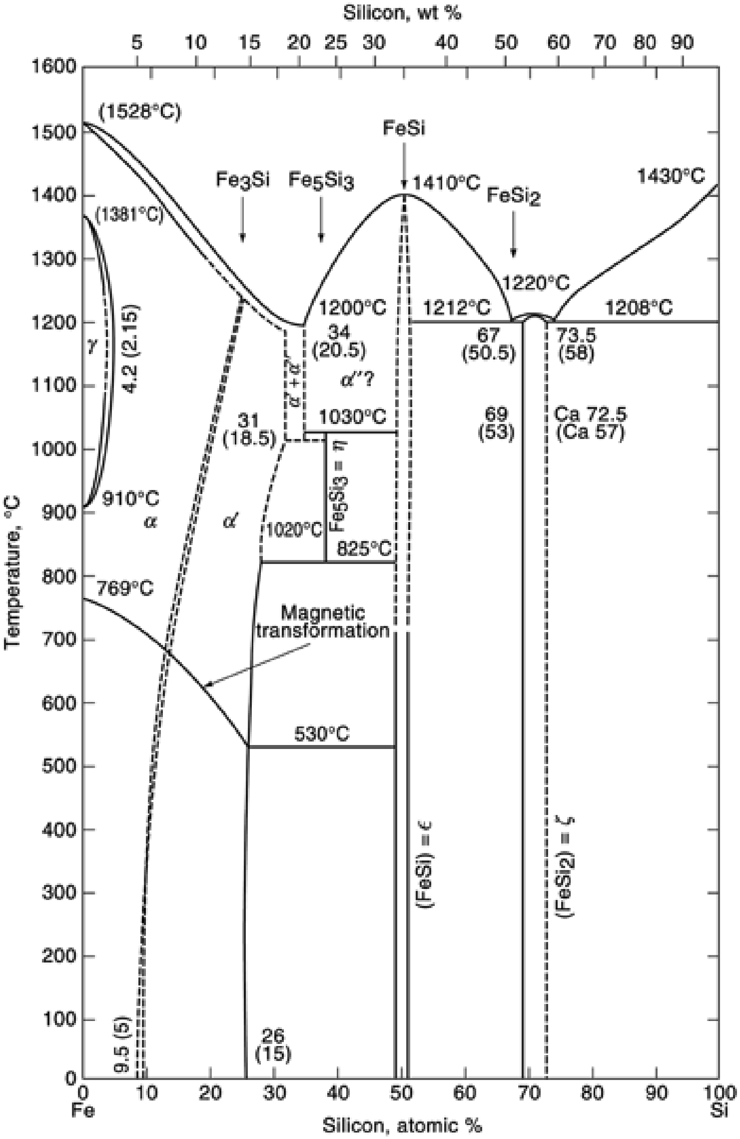

Fig. 9. Fe–Si phase diagram (4). Numbers in parentheses represent composition in wt%. Courtesy of McGraw-Hill Book Co., Inc.

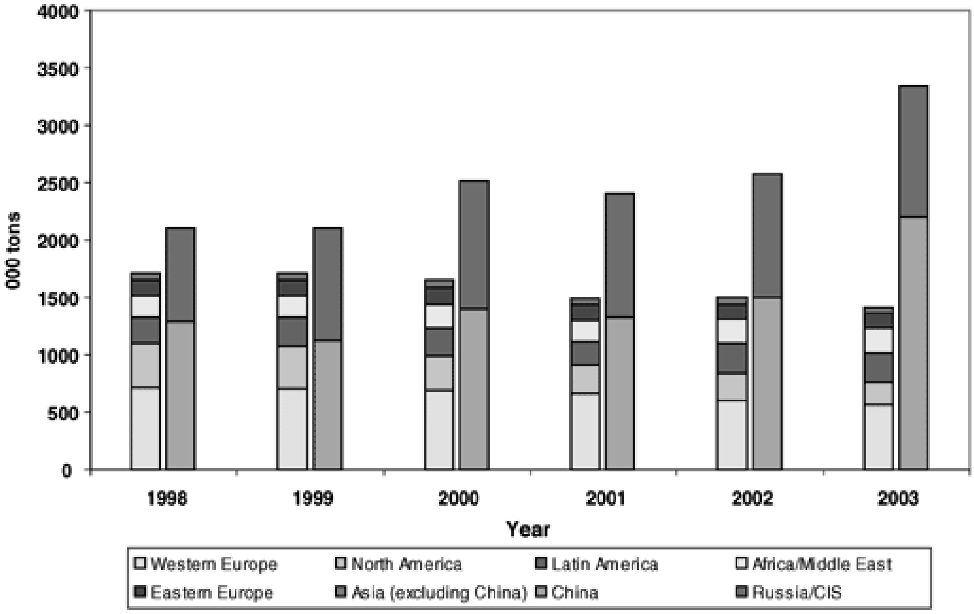

Fig. 10. Ferrosilicon production by geographic region (40).