Chapter 14
Silicon

14.1 Introduction

The history of silicon (Si) began shortly after 1800 when Davy concluded that silica was a compound, not an element. Silicon is second only to oxygen in occurrence in nature. It constitutes 27.6% of the Earth's crust. Man knows more than 200 different varieties of silicon: quartz, quartzite, chalcedony, rock crystal, opal, sand and many others. Silicon is a strong deoxidizer; this property determines basically its use in metallurgy. Commercially, pure silicon is used for the production of semiconductor, silicon bronzes, etc. It is used as a deoxidizer, in the forms of ferroalloy, in the production of all kind of steels. High amounts of ferrosilicon in the form of powder are used as a slag deoxidizer; it is also used for the reduction of various oxides in ferroalloy production.

14.2 Sources

Silicon occurs widely over the Earth's surface; minerals having a high content in silica, such as quartz, quartzite and chalcedony. Quartz is a compact mineral with crystal structure, specific gravity of 2.59–2.65, hardness 7, mostly colourless, white, grey or reddish, depending on impurities. Quartz is a relatively costly mineral and is used for the manufacture of crystalline silicon. SiO_2 content in quartz is 98% and over. Iron oxide in quartz should not exceed 0.3%.

Quartzite is a rock composed of quartz grains, cemented by a substance mainly containing silicon. Quartzites are widely distributed and their reserves are inexhaustible. Good grades of quartzite contain 96–97% SiO_2, 1% Al_2O_3, roughly 1% CaO and MgO, and not more than 0.02% P_2O_5. They do not require upgrading, and are readily available.

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Chalcedony is a thin fibrous, sometimes porous, mineral, of various colours. Its behaviour in metallurgical processes is somewhat worse than that of quartz and quartzite as it contains a lesser amount of SiO_2 (about 95%); its use is limited.

14.3 Extraction

14.3.1 Metallic Silicon

The quartzite is reduced by charcoal in an electric furnace to produce silicon.

$$SiO_2 + 2C = 2Si + 2CO \tag{14.1}$$

$$SiO_2 + 3C = SiC + 2CO \tag{14.2}$$

Any SiC formed is removed by secondary smelting with quartzite:

$$2SiC + SiO_2 = 3Si + 2CO \tag{14.3}$$

In the production of silicon or ferrosilicon, it appears that the major gaseous reagent is silicon monoxide (SiO), which can form through the reaction of silicon or silicon carbide with SiO_2 in the high-temperature region of the furnace. The silicon monoxide (SiO) product rises through the furnace and reacts with the reductant in the upper part of the furnace, to yield silicon carbide and carbon monoxide as products:

$$Si + SiO_2 = 2SiO \tag{14.4}$$

or

$$SiC + 2SiO_2 = 3SiO + CO \tag{14.5}$$

By production of SiO gas in the higher temperature (1650 °C) region, the reduction of SiO to silicon or silicon carbide is higher in the furnace:

$$SiO + C = Si + CO \tag{14.6}$$

or

$$SiO + 2C = SiC + CO \tag{14.7}$$

This silicon is suitable for metallurgical applications. However, silicon of a very high purity is required for semiconductor applications. Pure silicon is produced by first obtaining $SiCl_4$ gas through the chlorination of silicon, then purifying the $SiCl_4$

gas by distillation, which is followed by reduction with either zinc vapour or hydrogen gas at 1000 °C.

$$Si + 2Cl_2 = SiCl_4 \quad (14.8)$$

$$SiCl_4 + 2Zn = Si + 2ZnCl_2 \quad (14.9)$$

$$SiCl_4 + 2H_2 = Si + 4HCl \quad (14.10)$$

If the reduction is carried out in the presence of a heated silicon rod, the diameter of the rod gradually increases. This silicon rod is zone refined and used to grow single crystals, which are widely used in semiconductor applications.

14.3.2 Ferro-Silicon

The ore components of the charge for making ferro-silicon are minerals having a high content in silica, such as quartz and quartzite. Good grade of quartzite should have the lower content of alumina; the smaller would be the volume of slag, and therefore the lower the loss of electrical energy. Quartzite with a high content in alumina should be washed after grinding. The optimum size of quartzite lumps is 20–80 mm. Quartzite used in the production of ferro-silicon should meet the following requirements:

(1) Silicon content should be minimum 96%, desirably 97–99%.
(2) Amount of slag forming gangue materials (i.e. alumina [1%], magnesium oxide and calcium oxide [1%]) should be minimum.
(3) P_2O_5 content should not exceed 0.02%.
(4) Its moisture absorption should not exceed 5%.
(5) It should have no clay content.

Various carbon-bearing materials may be used as reducing agents in ferro-silicon production: carcoal, petroleum and pitch cokes, metallurgical coke, and coal. The main requirements to be met by a reducer are a low ash, low volatiles content, high strength of lumps, high electric resistance and cheapness. The best reducers are charcoal and petroleum coke; they contain little ash (1–2%), but are rather expensive. The ash of coke is the main source of aluminium in alloys. Therefore, low ash coke is needed as reducer in order to make 75% ferro-silicon with a low content in aluminium, as required. A large content of fines in coke breeze can hamper the evolution of gases and disturb the normal operation of the furnace. The presence of large lumps is likewise undesirable, since this can increase the electrical conductivity of the charge, which will necessitate rising of the electrodes and thus reduce the furnace productivity.

Ferro-silicon is commonly produced in the electric arc furnace from quartzite, coke and steel scrap (turnings of carbon steel having a low content of phosphorus).

The physical state of the charge is of prime importance for successful operation of a furnace. The charge materials must have constant moisture and lumps of coke breeze and quartzite should have only slightly varying size. A typical charge for the production of 75% grade of ferro-silicon is 2000 kg of quartz, 1000 kg of coke and 225 kg of steel turnings. Power consumption is about 10,000 kWh per tonne of ferro-silicon.

The reduction reaction of silicon from quartzite occurs with solid carbon:

$$SiO_2(1) + 2C(s) = Si(1) + 2CO(g) \tag{14.11}$$

With high temperature reduction which is typical of the process of smelting ferro-silicon, the process of reduction of silica into silicon at atmospheric pressure is most likely to occur in two stages:

$$SiO_2(1) + Si(1) = 2SiO(g) \tag{14.12}$$

$$SiO(g) + C(s) = Si(1) + CO(g) \tag{14.13}$$

Samples taken from lower levels in the furnace usually contain much silicon carbide (SiC). The formation of silicon carbide from the elements can only occur with large kinetic difficulties and requires a high mobility of atoms, which can only be achieved at a temperature above 1700 °C. On the other hand, the reaction is probable occur as:

$$SiO(g) + 2C(s) = SiC(g) + CO(g) \tag{14.14}$$

Solid inclusions of silicon carbide, if present, in the slag, can impair the fluidity of already tough siliceous slag. At corresponding temperatures, silicon carbide can be destroyed by metals and oxides, its destruction by iron following the reaction:

$$SiC(s) + Fe(1) = FeSi(1) + C(s) \tag{14.15}$$

At high temperature and in the presence of a solvent (iron with silicon) the aluminium oxide and calcium oxide, if present in the charge, are reduced by carbon and silicon:

$$Al_2O_3(s) + C/Si \rightarrow Al(1) + CO(g)/SiO_2(s) \tag{14.16}$$

$$CaO(s) + C/Si \rightarrow Ca(1) + CO(g)/SiO_2(s) \tag{14.17}$$

Industrial grade of ferro-silicon can thus contain up to 2% Al and up to 1.5% Ca.

14.4 Properties

Pure silicon obtained is a brown highly hygroscopic powder. Macro-crystalline silicon is obtained when silicon is melted and cooled; its colour is grey steel with metallic lustre. It is hard and brittle. Silicon is a metalloid with an atomic mass of 28.09, and specific gravity of 2.37. Melting and boiling points of silicon are 1414 °C and 2287 °C respectively. In its electric properties, silicon is a semiconductor material.

An addition of 1.3–2.0% Si to steel increases its hardness, ultimate strength, elastic and yield point and oxidation resistance of steel, but lowers the ductility.

Silicon can fuse together with iron in any proportion and forms a series of iron silicides. A number of chemical compounds are formed: ε-FeSi (33.3% Si), η-Fe_3Si_2 (25.1% Si), and ζ-Fe_2Si_5 (55.68% Si). The specific gravity of iron-silicon alloys varies with their silicon content. The melting point of standard grades of ferro-silicon does not exceed 1370 °C, 40–47% silicon alloy melts at 1260–1370 °C, while a 74–80% silicon alloy melts at 1320–1340 °C.

Silicon is a strong deoxidizer. Silicon reacts with oxygen to form silica (SiO_2), whose melting point is 1710 °C. Silicon and carbon form silicon carbide (carborundum, SiC), having a melting point above 2700 °C.

14.5 Applications

Metallic silicon is used mainly for alloying with copper, aluminium, magnesium and iron. Silicon is also used as a reductant in metallo-thermic reduction. Pure silicon (98–99%) is used for semiconductor applications and as silicon chips in the electronic industry.

Ferro-silicon is used for deoxidation and alloying of steel. Siliceous steels are widely used for making springs and like parts. Siliceous transformer iron (with 4% Si) is known to have relatively low power losses. The content of silicon may be up to 0.35% in tool steels, up to 0.37% in structural steels, and up to 5% in alloys grades. Ferro-silicon is used as a slag deoxidizer and for the reduction of various oxides in ferro-alloy production; e.g. in the production of Fe–Mo, Fe–V etc.