Conduct of reduction smelting of metallic silicon: theory and practice

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Abstract. Analysis of reduction smelting of silicon showed the formation of a secondary stable silicon carbide. The possibility of lading fresh charge to the lower horizons of the furnace tank was shown, which excludes the formation of stable silicon carbide. The initial temperatures of the interaction of silica and silicon carbide, obtained using various carbonaceous reducing agents, are determined.

1. Introduction

Complexity of the reduction of silicon by carbon is related to the fact that the conditions for the realization of both basic and accompanying reactions sharply differ from each other: some of the basic and concurrent reactions occur most intensively at high temperatures, while the other part – at low temperatures.

\[
\begin{align*}
SiO_2 + 3C & = SiC + 2CO \\
2SiO_2 + SiC & = 3 SiO + CO \\
SiC + SiO & = 2Si + CO
\end{align*}
\]

It means that the processes, described by the reactions mentioned above, can occur in different zones of the tank of the ore-thermal furnace. This leads to the fact that in the course of the reduction of silicon both stable condensed and gaseous intermediate products are formed, which move in the tank of the furnace towards each other: condensed substances, as they heat and spend in the lower horizons of the tank under the action of gravity, – from the top to the bottom, from the cold sections of the tank into the hot ones, gaseous, on the contrary, – from the bottom to the top, from the hot sections of the tank into the cold ones.

Silicon smelting reduction characteristics depend both on the completeness of the use of SiO (d) in the high-temperature zone, and on the completeness of trapping of its residues, which can, according to the considered scheme, occur with the participation of carbon by the reaction and only in the low-temperature zone of the furnace tank [1,2,3].
2. Loading the furnace with the charge

Loading the furnace top with the charge is carried out by charging pipes and with the help of loading machines. Loading is carried out uniformly in time, in small portions 2-3 times per hour, so that the level of the furnace top is constant.

A cone of charge should be maintained around each electrode. The cone disposition of the charge around the electrodes creates resistance to the escape of gases along the electrodes and improves the conditions for uniform gas release throughout the active surface of the furnace top, prevents the narrowing of the reaction crucibles. The height of the cones should be 400-500 mm.

Melting of silicon in ore-thermal furnaces is conducted in a continuous manner, with a constant loading of the proportioned charge on the surface of the furnace top. In the first stage of silicon reduction, silicon carbide is formed (table 1).

Since silicon carbide in the furnace tank can be in different polymorphic states (figure 1), it is important to obtain a primary silicon carbide of cubic syngony, since the hexagonal silicon carbide is more stable and its interaction with silicon monoxide to form silicon requires higher temperatures, which adversely affects the efficiency of the silicon production process [4].

| Reducing agent | Kind | Reacting capacity | Temperature of interaction start, K |
|----------------|------|-------------------|-----------------------------------|
|                | SiC  | SiO₂+3C | 50% SiC | 95% SiC | SiO₂+3C | 50% SiC | 95% SiC |
| Charcoal       | 3C   | 0.292   | 0.270   | 0.261   | 1788   | 1805   | 1834   |
| Petroleum coke | 2H   | 0.190   | 0.158   | 0.153   | 1898   | 1933   | 1943   |
| Black coal     | 3C   | 0.219   | 0.204   | 0.202   | 1839   | 1866   | –      |
| Silicon carbide| 6H   | –       | 0.166   | –       | –      | –      | 1963   |

Table 1. Reaction capacity of silicon carbides.

It is important, during the melting of silicon and siliceous ferroalloys, to use full section of the furnace tank without forming cavities, since in these places two gas phases interact by the reaction.

\[
\text{SiO} + \text{CO} = \text{SiC} + \text{SiO}_2
\] (4)

Uncontrolled consumption of SiO₂, which often leads to a reduction in the technical and economic performances of the reduction smelting.
In order to prevent the formation of stable hexagonal silicon carbide, it is necessary to have a supply of carbon to the surface and the deeper horizons of the furnace tank for trapping the gaseous intermediate products of SiO during melting. Continuity of mass transfer is supported by periodic processing of the furnace top (destruction of the crushed charge on separate sections of the surface of the furnace tank).

Equipment operation with certain functions for processing the furnace top, and for making the profile of the charge on the furnace top and in the furnace tank, necessary for maximum mass transfer is very important.

Rotation of the furnace tank about the vertical axis has an auxiliary function for loosening the furnace top. Possible variants of rotation: reversible or circular, where the circular rotation of the tank is preferred. Circular rotation gives a certain profile to the smelting products on the bottom of the tank, which facilitates the free escape of silicon from the furnace.

3. Processing of the furnace top
In the silicon smelting reduction process, intermediate reduction products are in the solid state (SiC) and gaseous state (SiO). With a continuous supply of reduction products to the high-temperature reaction zone, where the temperature is higher than 1817 °C, silicon carbide is consumed to form silicon by the reaction (4):

$$\text{SiC} + \text{SiO} = 2\text{Si} + \text{CO}$$  \hspace{1cm} (5)

When the supply of silicon carbide to the high-temperature zone of the tank slows down, heat of electric arcs is consumed to overheat the charge, part of silicon monoxide in the temperature range 1710-1940 °C disproportionates by the reaction (5):

$$2\text{SiO}_{\text{(g)}} = \text{Si} + \text{SiO}_2.$$  \hspace{1cm} (6)

This reaction is exothermic, which leads to further overheating of the furnace top. In addition, disproportionation products in this temperature range are: silicon in the liquid phase, silica in the plastic state (quartz glass), and this significantly reduces the gas permeability of the furnace top. These processes occur at a depth of 300-500 mm from the surface of the furnace top, so gases that were previously filtered through a loose charge, in this case tend to leave the reaction zone in the hottest places (along the electrodes), which leads to local gas release in the form of "fistulas" and losses of silicon.

High chemical activity of fresh charge leads to the formation of unstable silicon carbides with a high rate of interaction with other reaction products, prevents the formation of stable silicon carbide with low reactivity, maintains a constant rate of charge loss.

To prevent losses of silicon, simultaneously with the loading of fresh charge on the furnace top, this is processed by the machine for its processing. Basically, at the Russian smelters, processing is carried out by pneumatic machines. The periodicity of processing of the furnace top must be at least 2-3 times per hour.

The firm "Dango & Dienental" has developed a hydraulic loading-stirring machine for processing of the furnace top. The processing is carried out by immersing the pole of the machine in the charge, which makes it possible to move the charge during the processing of the furnace top, breaking the sintered sections of the furnace top. The processing of the top is conducted along the electrode, then between the electrodes in the center of the furnace. Charge is dragged forwards by the movement of the machine itself. The machine has removable devices (troughs) for loading separate components of the charge in the furnace pol in the form of additives which adjust the course of the furnace. The machines of the "Dango & Dienental" company occupy 65-70% of the market of this equipment (data of "Tekma" and "Dango & Dienental" companies).
Particular attention should be paid to the processing of the furnace top between the electrodes and the center of the furnace tank. In these places, level of the furnace top should be much lower than that of the electrodes, and this will lead to an increase in the active cross-sectional area of the furnace top.

4. Conclusion

Almost all of the reduced silicon accumulates in a circular trough and freely leaves the furnace through a tap-hole under the electrode in a place equipped for the release of silicon.

Correspondence of technological, energetic and geometric parameters of the entire furnace unit is important for high-performance operation of the furnace in the production of silicon.

5. References

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