

Conference Paper

The Production of Silicon Carbide and Achievements in the Field of Furnace Gases Collection and Purification

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Abstract

Silicon carbide is obtained in ore-thermal furnaces by reduction of silica (quartzite) with carbon. The use of silicon carbide in the production of technical silicon as a carrier of the target element and as a reducing agent can significantly improve the technical and economic performance (TEP) melting. The process of reducing silicon melting in electric furnaces takes place in two stages. First, silicon carbide is formed as a pseudomorphosis over the carbon of the reducing agent, then silicon carbide interacts with silicon oxide to form elementary silicon. Physical and chemical properties of silicon carbides obtained with the use of various reducing agents were studied. The reducing potential and reaction ability of carbides depends on how their surface is developed. Carbide volume and density characteristics are obtained on the matrices of charcoal and petroleum coke. For comparison, data for carbide obtained in the Acheson furnace are presented. Measurements of relative electrical resistivity of the reducing agent were performed and obtained on the carbides basis with temperature in the range of 700–1700°C. For comparison, the RER values of silicon carbide obtained in the Acheson furnace are given, the resistance of carbides is several times higher than the RER of the corresponding reducing agents, which favorably affects the furnaces smelting silicon electric mode. As a result of the silicon carbide addition to the charge, the power of the arc discharge increases and the intensity of the reduction process increases.

Keywords: silicon carbide, gas cleaning dust, gas capture system

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Published: 31 December 2020

Publishing services provided by
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Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

1. Introduction

In recent years, silicon carbide has been increasingly used in the production of non-ferrous, ferrous metals and silicon-based alloys [1]. This material is refractory (decomposes at a temperature of 2880°C), has a high hardness (33400 Mn/m²), second only to boron carbide and diamond. It is stable in different chemical environments and at high temperatures.

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Silicon carbide is obtained in ore-thermal furnaces by reduction of silica (quartzite) with carbon by reaction:



At the same time, the dependence of Gibbs energy on temperature has the form: $\Delta G_0 = 555615 - 322,11 \cdot T$. Equality $\Delta G_0 = 0$, at $p = 100$ kPa, observed at a temperature of 1452°C . Figure 1 shows the section of the furnace and the type of melting product after the completion of the electrothermal process.

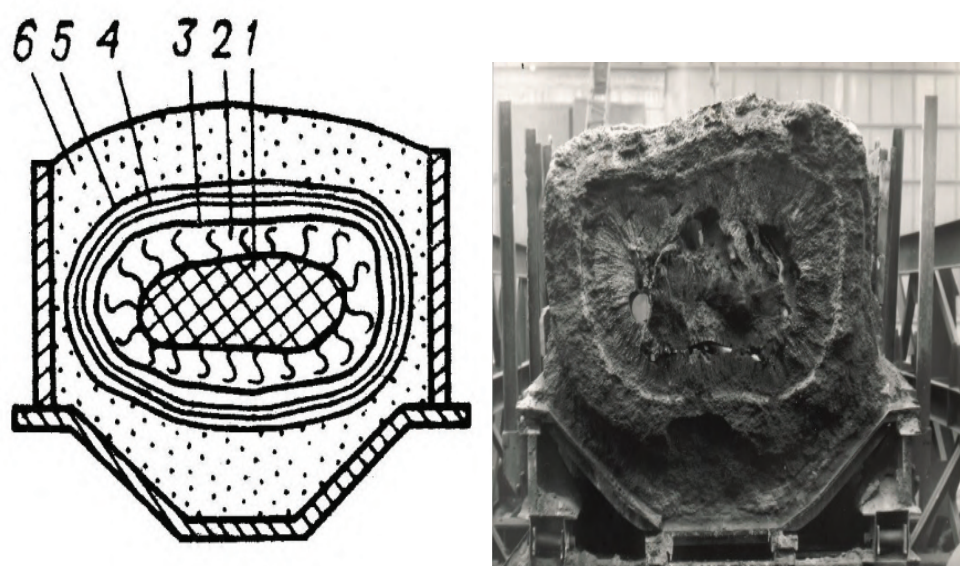


Figure 1: Section of the furnace for the production of silicon carbide after completion of the electrothermal process: 1 – core, 2 – silicon carbide (target product), 3 – amorphous, 4 – joints, 5 – siloxane, 6 – return charge.

In the center is positioned a graphite core material. In the immediate vicinity of the core is a layer of graphite, which appears due to the decomposition of silicon carbide, formed at the initial stages of the process. Next is a layer of crystalline silicon carbide with 25–35 cm thickness. Silicon carbide is surrounded by a layer of "amorphous". "Amorphous" is an undeveloped product, which is represented by a fine-grained silicon carbide of two modifications (about 80 %) with impurities of carbon, silicon and SiO_2 .

On "amorphous" is formed a small layer of joints, which are represented by densely sintered material, characterized by high strength, lower SiC content (about 60 %) and a significant impurities content, especially Al_2O_3 (up to 8 %). Next is a layer of siloxane with a thickness of 3-5 cm. In the area of siloxane formation temperature is quite low and insufficient for the silicon carbide formation. The SiC content in this zone is only 20–30 %. In this region during the melting process of the oxides condensation, warded off from the hot furnace zones, in fact, the area of siloxane is a basic impurities collection that settle in it and form a fine amorphous phase.

On the periphery of the furnace, where the temperature in the melting process is less than 1400°C, the charge components do not enter into chemical reactions at all, so the reaction zone is surrounded by a layer of unreacted 35–50 cm thick charge. This layer plays the thermal insulation role, and this material is returned to the process (return charge).

2. Theoretical Basis

The use of silicon carbide in the production of technical silicon as a carrier of the target element and as a reducing agent can significantly improve the technical and economic performance (TEP) melting. The process of reducing silicon melting in electric furnaces takes place in two stages. First, silicon carbide is formed as a pseudomorphosis over the carbon of the reducing agent, then silicon carbide interacts with silicon oxide to form elementary silicon.

The first stage of the silicon reduction process



explored in details and the main researchers conclusions are that the completeness and effectiveness of the transition of silicon from oxides to carbide is mainly determined by the physico-chemical properties of carbon reducing agents.

The first stage of the silicon reduction process



depends on the properties of the carbide phase.

The effect of the carbon reducing agent type on the properties of silicon carbide has not been fully studied. In this respect, the practical interest are represented by the properties of intermediate phases formed as a result of carbon conversion and, above all, their chemical activity relative to silica.

Physical and chemical properties of silicon carbides obtained with the use of various reducing agents were studied. The reducing potential and reaction ability of carbides depends on how their surface is developed. Carbides volume and density characteristics are obtained on the matrices of charcoal and petroleum coke are given in table 1. For comparison, data for carbide obtained in the Acheson furnace are presented.

3. Practical Relevance of the Technology

It should be noted that the volume of open pores and the specific surface area of the charcoal carbide obtained on the matrix is higher than similar parameters for carbide obtained from oil coke. That is, the reducing ability of the source material determines the properties of carbides derived from them. The transition degree of carbon reducing agents to silicon carbide in the silicon reduction melting process depends on the carbon materials physical and chemical properties and, first of all, on the degree of surface development. The carbon conversion to carbide is accompanied by an increase in relative electrical resistivity (RER).

TABLE 1: Porosity and specific surface area of pseudomorphosis SiC – C.

Indicators	Silicon carbide obtained on the matrix		Carbide obtained in the Acheson furnace
	wood charcoal	petroleum coke	
Open pore volume, m ³ gr ⁻¹ / %	48.8 / 86.0	20.4 / 71.0	– / 18.0
Specific surface, m ² gr ⁻¹ / %	140.0 / 12.0	1.4 / 0.92	– / 0.20

Measurements of relative electrical resistivity of the reducing agent were performed and obtained on the carbides basis with temperature in the range of 700–1700°C. Their integral values are presented in table 2. For comparison, the RER values of silicon carbide obtained in the Acheson furnace are given, the resistance of carbides is several times higher than the RER of the corresponding reducing agents, which favorably affects the furnaces smelting silicon electric mode. As a result of the silicon carbide addition to the charge, the power of the arc discharge increases and the intensity of the reduction process increases.

TABLE 2: Specific electrical resistivity of the silicon carbides.

Source material	Integral RER, Ohm.cm	
	Reductant	SiC
Wood charcoal	1.48	7.04
Oil coke	0.81	6.17
Coal	1.86	–
Acheson furnace Carbide	–	7.84

High activity of silicon carbide also contributes to higher silicon production technical and economic indicators. The activity of reducing agents according to silica is repeated in the transition phases and in the carbide obtained on their basis. The chemical activity was determined by the interaction with silicon dioxide of intermediate phases and silicon carbides in the temperature range 1500–1900°C, and was estimated by the sample weight change rate. For all kinds of the reducing agent, the intermediate phases and

carbides were determined beginning temperature of interactions with silica. The results are shown in table 3.

TABLE 3: The silicon carbides reaction ability.

Reductant	reaction ability		reaction start temperature, °C	
	SiO ₂ +3C	SiC	SiO ₂ +3C	SiC
Wood charcoal	0.292	0.261	1515	1561
Coal	0.219	0.242	1566	1622
Petroleum coke	0.190	0.233	1625	1670
Acheson furnace Carbide	–	0.166	–	1690



Figure 2: Volga abrasive plant's self-propelled furnace.

It is important to emphasize that the use of small reducing agents classes (less than 5 mm), such as charcoal, petroleum coke and low-ash coal, adversely affects the technical and economic silicon reduction melting performance. Their use in the silicon carbide production makes it possible to obtain a material with higher technological properties, the use of which in the silicon allows reduction melting achieve a significant increase in the productivity of furnaces and reduce the specific energy consumption.

Silicon carbide is produced in resistance furnaces, which can be mobile and stationary. In Russia, silicon carbide is produced in mobile furnaces with a unit capacity up to 5 MVA (Fig. 2). Production is accompanied by the large number of gases formation,



Figure 3: Stationary furnace 12 MVA in Xinjiang province (China).



Figure 4: Stationary furnace of the open type with a system for collecting reaction gases at the plant ESK-SiC in Netherlands.

primarily CO, which is burned to CO₂ mainly in the upper layers of the charge and above the charge. Contained in the oil coke, the sulfur is oxidized to SO₂. Gas composition: CO –98.4–98.8%, SO₂ – up to 1.3 %, other sulfur compounds up to 0.4 %.



Figure 5: Gas treatment facilities of silicon carbide production in the company ESD-SiC (Holland).

1 ton of silicon carbide is formed from 30 to 45 kg of dust and gas emissions with an average solid content of 50 mg/m³. The amount of CO is 1350–1400 kg/t. Part of CO in the process of removing gases is oxidized to CO₂ up to 3.6–3.8 kg/t. Additionally, it is removed up to 3.8 kg/t of volatile substances, 14–18 kg/t of sulfur oxide (SO₂) and up to 58 kg/t of moisture. Products of recovery smelting, gases and fumes of charge materials from the shelter of the mobile furnace are evacuated and dispersed through the pipe in the atmosphere.

Stationary furnaces (Fig. 3 and 4) are made with the possibility of special shelters use, usually mobile for use in a nearby furnace. At the same time, the shelter is sealed to prevent air suction and fire under the reaction gases shelter. The shelter released gases are removed from the furnace by special tubular collectors and are sent to the cleaning plant. The gas purified from harmful impurities is sent for afterburning in special thermal units, or for further processing.

The most effective system of the existing plants for the silicon carbide production is the system of gas recovery and disposal at the ESK-SiC plant in the Netherlands, made by Dow Corning technology (USA) (Figure 5), the estimated cost of the system is 10–12 million USA dollars. As a result of deep processing of waste gases, elementary sulfur is formed, collected and sold on the market.

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