

Use of Technogenic Silica Fume and Brown Coal Semi-Coke in the Technology of Silicon Carbide

A E Anikin^a, G V Galevskiy^a, V V Rudneva^a, S G Galevskiy^a,
D P Il'yaschenko^b

^aSiberian State Industrial University, Novokuznetsk
654007, Novokuznetsk, ul. Kirova, 42

^bYurga Institute of Technology (Affiliate) National Research Tomsk Polytechnic
University
652055, Kemerovo obl., Yurga, ul. Leningradskaya, 26, tel.+7 384 51 777 66

E-mail: mita8@rambler.ru

Abstract. The paper describes thermodynamic experiments to determine the optimal temperature and time modes for the carbide production process from the briquette charge comprising silica fume and brown coal semi-coke, conditions for chemical enriching of silicon carbide, its phase, chemical and granulometric compositions and particle morphology.

1. Introduction

Production of silicon carbide is one of the most important in the structure of modern metallurgy. About 800 thousand tons are made annually. Silicon carbide is commonly used in steelmaking (about 45% of global demand), abrasive (up 30%) and refractory materials (25%) production. Depending on thermo-mechanical, electro-physical, physicochemical properties, silicon carbide is targeted for the following applications in both traditional and potential fields [1-4]: bonded refractory, structural and functional ceramics, composite materials and coatings, surface and volume modification of materials.

In manufacturing today, silicon carbide is mostly synthesized with using the Acheson method. According to this method, silicon carbide is produced by the carbothermic reduction process in electric furnaces with a capacity of 4.5 - 5.5 MVA at a temperature of 2500 - 2900 K. The silicon carbide material resulting from such process has a crystal structure, where the crystals grow together to form the so-called druses (pieces); after electric furnaces dismantling, the material goes through crushing [5], chemical enriching and size grading. The commercial product of abrasive manufacturers is the carbides in granular forms ranging in size: abrasive grit (2500 - 160 microns), microgrit (160 - 28 microns), micropowders (63 - 10 microns), super thin powder (10 - 1 microns). There are three types of silicon carbide made today: black, green and electro technical.

For quite a long time, the demands of metal making, refractory and ceramic industries for silicon carbide were met by using grinding materials intended for abrasive applications, causing an unnecessary increase in the cost of refractory materials and ceramics; in some cases, the use of silicon carbide was technologically and economically unfeasible in the



metallurgical industry. The situation was aggravated by constantly rising energy prices and tightening control to follow ecology regulative requirements of nations. In this connection, in the 80s, the major manufacturers of silicon carbide: Saint - Gobian (France), Exolon - ESK (US - Germany), Carborundum Co. (USA), H. Starck Co. (Germany) and other companies developed and introduced the technology of making the so-called non-ground silicon carbide by synthesis from finely dispersed charges in a furnace usually in the form of micro powders, followed by its chemical enrichment. In the same period, a number of activities were carried out in this field in Russia that demonstrated positive science-based and application-oriented results: a decrease in the temperature of synthesis within 2500 - 2900 by 600 - 1000 ° down to 1900 K, the time required for the synthesis from 26 - 29 hours to 1h, and electricity consumed by a factor of 2 - 4; the content of silicon carbide reached as high as 90.0% by mass in the synthesized products; silicon carbide was made in the form of micro powders of 1 - 5 microns in size; non-commercial and technology-related by-product materials were proved as available for the production of silicon carbide, such as low-quality sand, schungite rock, silica fume, coke fines and dust, and semi-coke; a continuous process for manufacturing silicon carbide was demonstrated as possible, using e.g., tunnel-type, tubular rotary, and shaft-type furnaces. In this regard, it was decided to introduce the developed technologies in a number of enterprises of Minstankoprom. But the socio-economic changes taking place at the turn of the 80 - 90s in the country did not allow these plans to be implemented.

Therefore, providing a scientific background and technological justification for the non-ground silicon carbide production remains an urgent task, which is of great practical importance. In this regard, the aim of this work was to study the processes of carbidizing technogenic silica fume with using semi-coke from brown coal mined at the Berezovsky deposit at the Kansk-Achinsk Coal Basin.

Thermodynamic modeling of the carbide forming processes in Si – O – C and Si – O – C – H systems

Thermodynamic modeling was performed in order to forecast the optimal parameters for making silicon carbide (a ratio of compounds, temperature and pressure in the system), determine equilibrium constants parameters of the reaction (a conversion degree of reactants in carbide, compositions of gaseous and condensed products), and evaluate how independent reactions contributed to the carbide forming processes, with these reactions ensuring the effective processing of raw materials in the course of experiments. The targets of research were the Si - O – C and Si - O - C - H systems, where brown coal semi-coke with a content of volatile products up to 10% was used as a reducing and carbide forming agent.

Values of equilibrium constants were calculated to determine the balanced composition of the Si – O – C and Si – O – C – H systems. The computer simulation software "PLASMA" (Institute of Solid State Chemistry and Mechanochemistry SB RAS), with an in-built database of interaction products for oxide-, boride-, carbide- and nitride-forming systems and designed for modeling high-temperature complex chemical equilibria, was used for calculations. For making calculations, the range of temperature was 800 - 2000 K at a pressure varying within 0.1 to 0.0001 MPa in the systems. The calculations were performed in increments of 100°. The equilibrium constants for reactions to form compounds from the given elements were taken as initial data. In modeling, it was taken into account the possibility of forming gaseous Si, Si⁺, Si⁻, Si₂, Si₃, O, O₂, C, C⁺, C₂, C₃,

C₄, C₅, SiO, SiC, SiC₂, Si₃C, CO, CO₂ in the Si - O - C system and Si, Si⁺, Si⁻, Si₂, Si₃, O, O₂, C, C⁺, C₂, C₃, C₄, C₅, H, H⁺, H₂, CH₂, CH₃, CH₄, C₂H, C₃H, C₄H, C₂H₂, C₂H₄, SiO, SiC, SiC₂, Si₃C, CO, CO₂ in the Si - O - C - H, and condensed Si, SiO₂, C, SiC in both systems. The amount of reacting substances and their ratios in the systems under study were determined by using stoichiometry on the basis of the silicon carbide forming reaction and compositions of charged materials. The relevance of this approach to the study of carbide-forming processes was confirmed earlier in works in reference [3-6].

The calculated equilibrium compositions of the Si - O - C and Si - O - C - H systems are shown in Figures 1 and 2 and Tables 1 and 2.

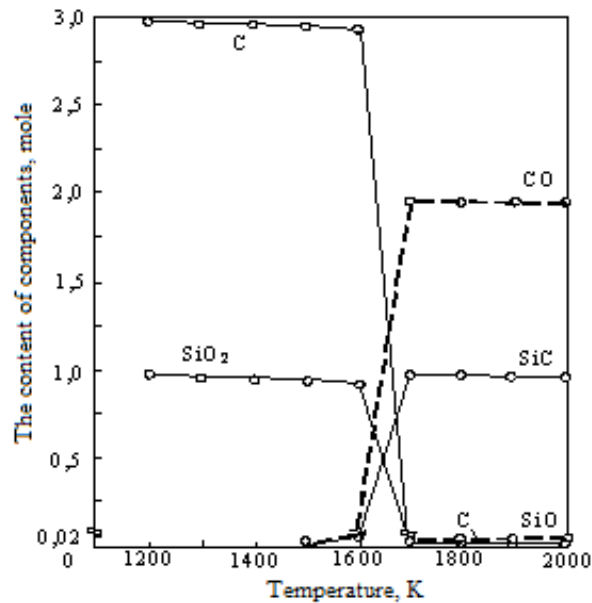


Figure 1 – The temperature dependence of the equilibrium composition of the Si - O - C system at a ratio of Si: O: C = 1: 2: 3 and a pressure P = 0.1 MPa (— condensed and - - - gaseous products)

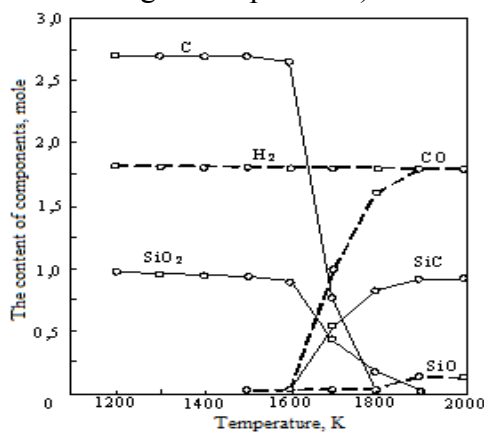


Figure 2 – The temperature dependence of the equilibrium compositions of the Si - O - C - H system at a ratio of Si:O:C:H = 1: 2: 2.7: 3.6 and a pressure P = 0.1 MPa (— condensed and - - - gaseous products)

Table 1 - Equilibrium concentrations (%) of the condensed reaction products in the Si - O - C system for a ratio of Si:O:C = 1:2:3

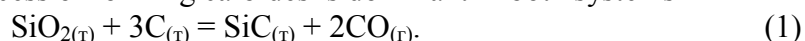
T, K	P = 0,1 MPa	P = 0,01 MPa	P = 0,0001 MPa
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	SiO ₂	C	SiC	SiO ₂	C	SiC	SiO ₂	C	SiC
800	62,5	37,5	0	62,5	37,5	0	62,5	37,5	0
900	62,5	37,5	0	62,5	37,5	0	62,5	37,5	0,02
1000	62,5	37,5	0	62,5	37,5	0,01	62,2	37,3	0,52
1100	62,5	37,5	0	62,4	37,4	0,2	0	0,3	99,71
1200	62,5	37,5	0	61,0	36,7	2,3	0	0,4	99,60
1300	62,5	37,5	0	0	0,2	99,8	0	0,6	99,40
1400	61,8	37,1	1,1	0	0,2	99,8	0	1,0	99,0
1500	61,0	36,8	2,2	0	0,3	99,7	0	1,3	98,7
1600	53,7	32,5	13,8	0	0,4	99,6	0	2,0	98,0
1700	0	0,6	99,4	0	0,6	99,4	0	2,8	97,2
1800	0	0,8	99,2	0	0,9	99,1	0	3,7	96,3

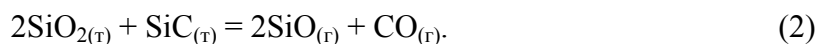
Table 2 - Equilibrium concentrations (%) of the condensed reaction products in the Si - O - C - H system for a ratio of Si:O:C:H = 1:2:2,7:3,6

T, K	P = 0,1 MPa			P = 0,01 MPa			P = 0,0001 MPa		
	SiO ₂	C	SiC	SiO ₂	C	SiC	SiO ₂	C	SiC
900	64,94	35,06	0	64,94	35,06	0	64,94	35,06	0
1000	64,94	35,06	0	64,94	35,06	0	64,94	35,06	0,001
1100	64,94	35,06	0	64,94	35,06	0,002	64,84	35,00	0,16
1200	64,94	35,06	0	64,74	36,04	0,04	62,54	33,86	3,60
1300	64,94	35,06	0	64,54	35,94	0,30	12,47	0	87,53
1400	64,92	35,06	0,03	62,84	34,53	2,63	8,95	0	91,05
1500	63,97	34,51	1,52	51,27	26,61	22,12	0	0	100,00
1600	60,75	32,15	7,10	11,35	0	88,65	0	0	100,00
1700	25,57	8,89	65,54	0	0	100,00	0	0	100,00
1800	9,33	0	90,67	0	0	100,00	0	0	100,00
1900	0	0	100,00	0	0	100,00	0	0	100,00

It can be seen that the process of forming carbides is dominant in both systems



With a stoichiometric ratio of reactants in the charge, the maximum content of silicon carbide in the products is achieved at 1700 K, and at 1900 K when there is a 10% deficiency of carbon. In fact, hydrogen adding to the systems has no influence on the carbide forming process due to the extremely low (less than 0.001 mol) content of hydrocarbons and hydrocarbon radicals within the temperature range of carbide formation. With the Si - O - C system, the equilibrium degree of silicon conversion into carbide does not exceed 0.97% that corresponds to the content of gaseous silicon monoxide in an amount of 0,02mol. As a consequence, it is impossible to obtain homogeneous silicon carbide without free carbon when using the charge (SiO₂ + 3C) of the stoichiometric composition (Table 2). This can be avoided by using a charge with a certain deficiency of carbon (~10%), acting as a reducing agent (see Table 2). In this case, there is a temperature range where both silicon carbide and excessive silica co-exist in the system. And the higher the pressure in the system, the wider this temperature range of both compounds' occurrence. Above these temperatures, silicon carbide is a reducing agent for silica, i.e. the following reaction is possible



In this reaction, silicon carbide is purified and excessive silica is removed. This reaction has a greater effect when takes place in vacuum.

2. The experimental technique for carbidizing silica fume

The process for carbidizing silica fume was analyzed using the discrete method, including heat treatment of the charge in briquettes at specified temperatures and time, quenching of carbidized products with subsequent chemical analyzes.

The charges were heated in a graphite electric resistance furnace with an internal diameter of 0.075 m (the Tamman type furnace). The temperature inside the furnace was controlled using a tungsten-rhenium thermocouple BP 5/20. Cylindrical briquettes with a mass of about $2,5 \cdot 10^{-3}$ kg and an outside diameter of 0.015m were placed in graphite crucibles. Three crucibles were loaded simultaneously inside the working chamber of the heated electric furnace, then heated for 3 - 4 min to a specified temperature, and held therein during a specified period of time within 5 to 90 minutes. After holding at the specified time, the graphite crucibles were removed from the electric furnace and placed in corundum containers, which were tightly plugged, and put for 10 minutes in cold water for rapid cooling of the products formed. This enabled us to prevent oxidation of the products with oxygen and atmospheric moisture. After cooling, the products formed in the reaction were extracted from the crucibles without losses in their amount, then weighed and placed in platinum containers for their subsequent filling with a solution of nitric acid, with a concentration of 7, 5 - 12, 5M, mixed with hydrofluoric acid, with a concentration of 2,0 - 3M, taken at a ratio of 1: (3 ÷ 5), and boiled during a period of 2.5 - 3.0 hours. Treating silicon carbide with a mixture of nitric and hydrofluoric acids ensures the removal of impurities of aluminum, magnesium, calcium, iron, manganese, nickel, chromium, copper, sodium, potassium, silicon and their oxides, and is recommended for the silicon carbide powder of a grain size from 5 to 200 microns [5]. In the presence of nitric acid, metallic impurities and their oxides form soluble nitrate compounds, while using hydrofluoric acid only may cause the formation of insoluble fluorides. After cooling, the insoluble residue in the form of silicon carbide admixed with free carbon was collected with using a paper filter, then the collected on the filter residue was washed with distilled water and acetone, dried to obtain a constant mass, and weighed. Following that, according to the recommendations in [1-4], the insoluble residue was heat treated at a temperature of 1073 - 1123 K for 1.5 - 2.0 hours to remove free carbon by oxidation. The content of free carbon and silicon carbide in the products of carbidization was calculated in the context of their loss in mass. The percentage yield of silicon carbide was calculated as the ratio of actual yield, being the average amount of silicon carbide produced with the three crucibles, to theoretically possible yield.

3. Experimental carbidization of silica fume - brown coal semi-coke, measurement and discussion of results

The following materials were used to carry out the laboratory works: (i) silica fume, collected as a by-product in the production of silicon (MK-Kr) and high-silica ferrosilicon (MK-FS), with a content of silicon dioxide equal to 93.92 and 93.00 % by mass respectively and a specific surface of 25000 m²/kg [6-10], and (ii) brown coal semi-coke (BPK), produced at the Berezovsky deposit at the Kansk-Achinsk Coal Basin, containing, %: carbon - 81.9, volatile matter - 9.5, ash - 8.6, a specific surface of 264000 m²/kg [1-5]. In all cases, the charges had a stoichiometric composition to obtain carbides.

In terms of time and temperature conditions for the carbidization process, the single-component briquette charge comprising silica fume MK-Kr, MK-FS-BPK were investigated at temperatures of 1883, 1923, 1973 K and during a period of time of 5, 10, 15, 20, 25, 30 min. The results of experiments are shown in Figures 3 and 4.

In both cases, the process of forming carbides begins from the first minute, and at the beginning of the fifth minute the yield of carbide produced reaches 5.23 - 7.21% at a temperature of 1873 K, 17.06 - 22.30 % at a temperature of 1923 K, and 20.20 - 23, 51 % at a temperature of 1973 K.

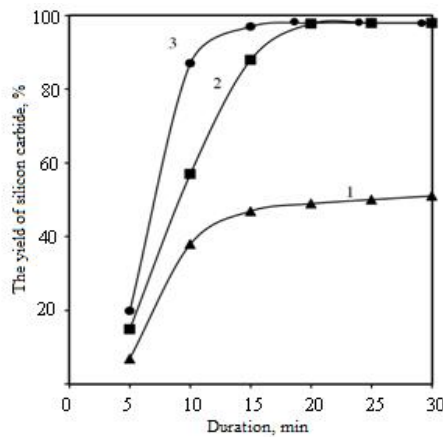


Figure 3 – Relationship between the percentage yield of silicon carbide, temperature and duration of heat treatment for the MK-FS-BPK charging mixture

- (1 – 1873 K (Δ) = (7,21 ÷ 53,13) ± (0,20 ÷ 1,13);
- 2 – 1923 K (□) = (17,06 ÷ 96,82) ± (0,55 ÷ 1,35);
- 3 – 1973 K (○) = (20,20 ÷ 97,01) ± (0,61 ÷ 1,45))

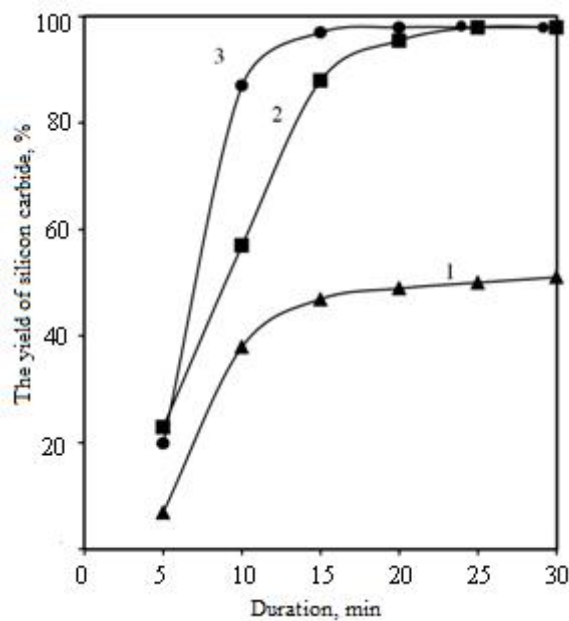


Figure 4 - Relationship between the percentage yield of silicon carbide, temperature and duration of heat treatment for the MK-Kr-BPK charging mixture

- (1 – 1873 K : (Δ) = (5,23 ÷ 46,26) ± (0,19 ÷ 1,11);

$$2 - 1923 \text{ K} : (\square) = (22,30 \div 96,78) \pm (0,59 \div 1,33);$$

$$3 - 1973 \text{ K} : (\circ) = (23,51 \div 97,62) \pm (0,67 \div 1,38)$$

The carbidization process ends at a temperature of 1973 at the beginning of the fifteenth minute and 1923 K at the twentieth minute. The mass percentage of carbide is 92.50 for the MK-FS charge and 94.90 for the MK-Kr charge in the products after heat treatment. These time and temperature conditions for forming carbide are confirmed by the study of phase compositions of products after heat treatment. Thus, it was established that, in both cases, the cubic crystal structure (β -SiC) of silicon carbide prevailed by the start of the tenth minute, and partially modified to form the hexagonal structure (α -SiC_{II}), when heated to a temperature of 1923 to 1973 K and held for 50 - 90 minutes. Alpha ferrite accompanied the process of forming carbide in silica fume of the MC-FS-BPK mixture. There was a glassy phase present in all test samples, which were formed, presumably, by silicates of calcium, magnesium and iron.

As a result of chemical processing, the SiC content exceeded 90% in carbide, i.e. the rate specified for abrasive micro powders of a grain size of 1 - 2 microns. The rate of enrichment was sufficiently high, standing for 87 - 95% in the presence of impurities: oxides and iron. Silicon carbide was characterized by a high content of silicon dioxide that amounted to more than 7%, and this allowed us to consider it as a promising material for the production of silica-bonded silicon carbide refractories, normally containing 84 - 89 % of SiC and 6 - 12% of SiO₂.

Basic characteristics with their ranges and optimal conditions for obtaining and processing silicon carbide are given in Table 3 for a series of five parallel experiments. It can be seen that the examined technology options enable us to produce silicon carbide with reproducible phase, chemical and granulometric composition, and they can be regarded as a technological basis for developing an industrial production of non-ground silicon carbide from briquette finely dispersed mixtures of silica fume - brown coal semi-coke.

Table 3 - Optimal conditions for producing and enriching silicon carbide and its properties

Conditions for producing and enriching silicon carbide and its main properties	SiC (MK-FS+BPK)	SiC (MK-Kr + BPK)
Charge mixture, %:		
- silica fume (MK)	58,80	58,04
- brown coal semi-coke (BPK)	42,20	41,96
Specific surface of mixed components, m ² /kg		
- silica fume	20000 - 22000	
- brown coal semi-coke	255000 - 265000	
Temperature of carbidization, K	1923 - 1973	
Duration of carbidization, min	25 - 20	
Chemical enrichment of products		
- Concentration of hydrochloric acid, %	35	
- Solid-to-Liquid Ratio	1:2	
- Temperature, K	383	
- Duration, h	3	
Phase composition	β - SiC	
Chemical composition, %:		
SiC	90,42 - 90,86	90,94 - 91,18

Al ₂ O ₃	0,10 - 0,25	0,10 - 0,15
CaO	0,32 - 0,53	0,37 - 0,49
MgO	0,12 - 0,18	0,03 - 0,10
Fe	0,08 - 0,12	0,05 - 0,11
SiO ₂	7,32 - 7,94	6,97 - 7,13
free C	0,41 - 0,54	0,63 - 0,81
free Si	0,13 - 0,17	0,23 - 0,27
Yield of silicon carbide, %	96,84 - 97,12	97,31 - 97,63
Fineness and morphology of silicon carbide particles: - Specific surface, m ² /kg - Range in size, micron - Shape	8000 - 9000 0,2 - 1,0 Irregular	

4. Conclusions

Experimental works were performed to study and analyze the thermodynamic processes of deoxidizing industrial silica fume with brown coal semi-coke to produce silicon carbide.

It is established that the process of forming carbide is dominant in both Si - O - C and Si - O - C - H systems chosen for the thermodynamic analysis. With a stoichiometric ratio of reactants in the charges, the maximum content of silicon carbide in the products after the reduction reaction is achieved at 1700 K, and when there is a 10% deficiency of carbon - at 1900 K. The second charge composition is more technically advantageous due to obtaining carbide without impurities.

The single-component briquette charges of silica fume (MK-FS and MK-Cr) and brown coal semi-coke were processed at temperatures of 1883, 1923, and 1973 K with a range of time from 5 to 30 min to produce carbide. The following time-temperature conditions were determined as the optimal: a temperature of 1923 - 1973 K during a period of 20 - 15 minutes.

The feasibility, optimal conditions and parameters for the chemical enrichment of the formed products were defined as follows: when hydrochloric acid treating with a concentration of minimum 35% at a temperature of 353 K and a S:L ratio = 1: 2, and duration of 3 hours, the carbide content in the products is higher than 90%, impurities of iron and oxides are removed by 87 - 95%.

The particle size distribution, the morphology of particles, the phase and chemical properties were studied relating to both processing techniques employed to produce silicon carbide. It is established that the cubic crystal structure (β -SiC) of silicon carbide is formed in the process, which is partially modified to form the hexagonal structure (α -SiC_{II}) when heated to a temperature ranging from 1923 to 1973 K and maintained for a period of time between 50 and 90 minutes. The content of carbide after enrichment is 90, 42 - 90, 86 % when using the MK-FS silica fume and 90, 94 - 91,18 % when using the MK-Kr silica fume. In both cases, the silicon carbide produced is in the form of micro powders with a specific surface of 8000 - 9000 m²/kg, and the particles have an irregular shape and a size of 0.2 - 1.0 microns.

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