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Reduction processing of technogenic microsilica with the use of a brown coal semi-coke

A E Anikin¹, G V Galevsky¹, V V Rudneva¹ and S G Galevsky²

¹Siberian State Industrial University, 42 Kirova street, Novokuznetsk, 654007, Russia

²St. Petersburg Mining University, V.O., 21 Line, 2, St. Petersburg, 199106, Russia

E-mail: kafcmet@sibsiu.ru

Abstract. Thermodynamics is investigated and optimal temperature-time regimes of carbidization of briquetted charge “microsilica – brown coal semi-coke” are determined. In Si-O-C and Si-O-C-H systems the carbide formation process is dominant: with the stoichiometric composition of the charge, the maximum content of silicon carbide reduction products is achieved at 1700 K. The complete carbidization of the charge in the conditions of heat treatment is achieved at a temperature of 1923 - 1973 K with a duration of 20 - 15 minutes. The technological expediency, conditions and chemical enrichment indices of carbidization products are established. The phase, chemical, granulometric compositions and morphology of silicon carbide particles are studied. It was found that carbidization forms a carbide of the cubic structure (β -SiC). The content of carbide after enrichment is more than 90%. Silicon carbide is obtained in the form of a micropowder with a specific surface area of 8000 - 9000 m²/kg from irregularly shaped particles with a size range of 0.2-1.0 μ m.

1. Introduction

The production of silicon carbide – one of the most important in the structure of modern metallurgy is about 800 thousand tonnes per year. The largest areas of silicon carbide application are metallurgy (about 45% of global demand), production of abrasives (up to 30%) and refractories (up to 25%). Specificity of thermomechanical, electrophysical, physical and chemical properties of silicon carbide predetermines the following directions of its traditional and perspective application: materials on bundles; structural and functional ceramics; composite materials and coatings; surface and volumetric modification of materials.

The current production of silicon carbide is almost entirely based on the carbon-thermal method of Acheson. According to this method the production of silicon carbide is carried out by a periodic block process in electric resistance furnaces with a capacity of 4.5 - 5.5 MVA at a temperature of 2500 - 2900 K. The obtained silicon carbide is crystals that have grown into so-called druses (pieces) which, after disassembling the electric furnace are subject to fragmentation, enrichment and sifting by fractions. The products of abrasive plants are carbide grains of various sizes: abrasive grit (size 2500 - 160 μ m), grinding powders (size 160 - 28 μ m), micropowders (size 63 - 10 μ m), fine micropowders (size 10 - 1 μ m). Currently there are three types of silicon carbide: black, green and electrotechnical.

For a long time the demands of metallurgy, refractory and ceramic production in silicon carbide were satisfied by abrasive grinding materials, which increased the cost of refractories and ceramics, and in metallurgy in some cases made the use of silicon carbide technologically and economically impractical. The situation was aggravated by the constant increase in electricity prices and requirement



strengthening of national environmental legislation. In this regard the main producers of silicon carbide – companies “Saint – Gobian” (France), “Exolon – ESK” (USA – Germany), “Carborundum Co” (USA), “H. Starck Co” (Germany), etc., in the 80’s developed and mastered the technological processes of the production of so-called non-grinded silicon carbide, obtained, as a rule, from highly dispersed batches by furnace synthesis in the form of micropowders with subsequent chemical enrichment. Research in this direction was carried out in Russia as well and ended with positive scientific and applied results: decrease in the synthesis temperature from 2500 - 2900 to 1900 K, i.e. by 600 – 1000°, duration of synthesis from 26 - 29 to 1 hour, electricity consumption in 2 - 4 times; achievement of silicon carbide content in synthesis products to 90.0% by weight; production of silicon carbide in the form of micropowders of fineness 1 - 5 μm ; possibility of application of non-commercial and technogenic raw materials for the production of silicon carbide, for example, low-quality sands, shungite rocks, microsilica, coke dusts and fines, semi-coke; possibility of realization of non-stop production of silicon carbide, for example, using tunnel, tubular rotating, shaft furnaces. In this regard, it was decided to perform implementation activities at a number of enterprises of the Ministry of Industry and Trade. However, the socio-economic changes that took place in the country at the turn of the 1980s-1990s did not allow the plans to be realized.

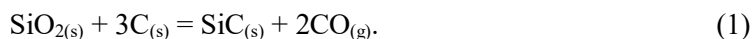
Consequently, the scientific and technological justification and implementation of the production of domestic non-grinded silicon carbide remains an urgent task of great practical importance. In connection with this, the purpose of this work was to study the processes of carbidization of technogenic microsilica by a semi-coke from brown coals of the Berezovsky deposit of the Kansk-Achinsk basin, the technological properties of which were investigated earlier by the authors and described in detail in [1, 2]. The technological and economic feasibility of using semi-coke as a carbon reducing agent was confirmed in [3 - 6].

2. Thermodynamic modeling of carbide formation in Si-O-C, Si-O-C-H systems

Thermodynamic modeling was carried out to predict the optimal parameters for the production of silicon carbide (the ratio of components, temperature and pressure in the system), to determine the equilibrium parameters of the process (the degree of conversion of the raw material into carbide, the compositions of gaseous and condensed products), to estimate the contribution to the carbide formation of individual reactions providing conditions under investigation, efficient processing of raw materials. In connection with the use of a brown coal semi-coke with a volatile content up to 10% as a reducing agent and carbidizer in the process, the objects of investigation were Si-O-C, Si-O-C-H systems.

The equilibrium compositions of the Si-O-C and Si-O-C-H systems were calculated by the “constant” method. Calculations were carried out using the computer simulation software for high-temperature complex chemical equilibria “PLASMA” (IHTTiM SB RAS), which has a built-in database of interaction products for oxide, boride, carbide, and nitride-forming systems. In the calculations, the temperature range 800-2000 K was considered at different pressures in the system: from 0.1 to 0.0001 MPa. The calculations were carried out at intervals of 100°. The initial data were the reaction equilibrium constants of compounds formation from the elements. The calculations took into account the possibility of formation in the gas phase in the Si-O-C system of Si, Si⁺, Si⁻, Si₂, Si₃, O, O₂, C, C⁺, C₂, C₃, C₄, C₅, SiO, SiC, SiC₂, Si₃C, CO, CO₂, in the system Si-O-C-H of 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 condensed phase in both systems – Si, SiO₂, C, SiC systems. The choice in the investigated systems of the ratios of the initial components was determined by the stoichiometry of the formation reaction of silicon carbide and the composition of the charge materials. The fruitfulness of this approach in studying the processes of carbide formation was confirmed earlier in [7, 8].

The results of calculations of the equilibrium compositions of the Si-O-C and Si-O-C-H systems for the total pressure 0.1 MPa are given in figures 1 and 2, and for pressure 0.01 and 0.0001 MPa – in tables 1 and 2. It can be seen that in both systems the carbide formation process is dominant



With the stoichiometric composition of the charge, the maximum content of silicon carbide in products is achieved at 1700 K, and with 10% shortage of carbon at 1900 K. Introduction of hydrogen into the system does not actually affect the carbide formation process, which is caused by an extremely low content (less than 0.001 mole) of hydrocarbons and hydrocarbon radicals in the temperature range of the carbide formation. In the Si-O-C system the equilibrium degree of silicon conversion to carbide does not exceed 0.97%, which corresponds to a content of silicon monoxide in the gas phase of 0.02 mol. As a consequence, it is impossible to obtain a single-phase silicon carbide with no free carbon from the charge of the stoichiometric composition ($\text{SiO}_2 + 3\text{C}$) (table 2).

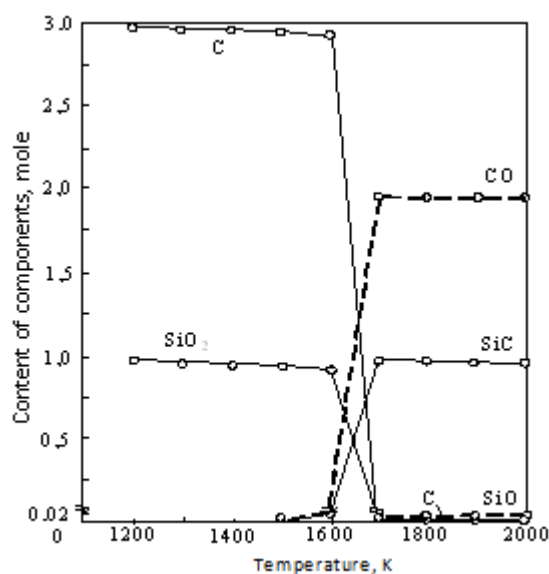


Figure 1. Dependence of the equilibrium composition of the Si-O-C system on the temperature with ratio Si:O:C = 1:2:3 and pressure $P = 0.1$ MPa (— condensed, — — — gaseous products).

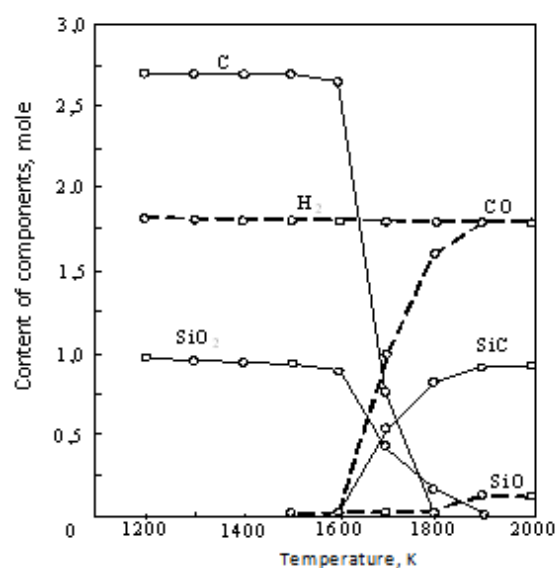
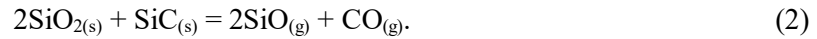


Figure 2. Dependence of the equilibrium compositions of the Si-O-C-H system on the temperature with ratio Si:O:C:H = 1:2:2.7:3.6 and pressure $P = 0.1$ MPa (— condensed, — — — gaseous products).

This can be avoided by using the charge with some (~ 10%) shortage of carbon – a reducing agent (table 2). In this case, the area of coexistence of silicon carbide and excessive silica appears in the system. And the temperature range of coexistence of these phases is wider the higher the pressure in the system. Above these temperatures, silicon carbide itself is a reducing agent for silica, i.e. the following reaction becomes possible



As a result of this reaction, silicon carbide is purified from excessive silica. It can be particularly effective to conduct it in the vacuum.

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

T, K	P = 0.01 MPa			P = 0.0001 MPa		
	SiO ₂	C	SiC	SiO ₂	C	SiC
800	62.5	37.5	0	62.5	37.5	0
900	62.5	37.5	0	62.5	37.5	0.02
1000	62.5	37.5	0.01	62.2	37.3	0.52
1100	62.4	37.4	0.2	0	0.3	99.71
1200	61.0	36.7	2.3	0	0.4	99.60
1300	0	0.2	99.8	0	0.6	99.40
1400	0	0.2	99.8	0	1.0	99.0
1500	0	0.3	99.7	0	1.3	98.7
1600	0	0.4	99.6	0	2.0	98.0
1700	0	0.6	99.4	0	2.8	97.2
1800	0	0.9	99.1	0	3.7	96.3

Table 2. Equilibrium concentrations (in %) of the condensed reaction products in the Si-O-C-H system with the components ratio Si:O:C:H 1:2:2.7:3.6.

T, K	P = 0.01 MPa			P = 0.0001 MPa		
	SiO ₂	C	SiC	SiO ₂	C	SiC
900	64.94	35.06	0	64.94	35.06	0
1000	64.94	35.06	0	64.94	35.06	0.001
1100	64.94	35.06	0.002	64.84	35.00	0.16
1200	64.74	36.04	0.04	62.54	33.86	3.60
1300	64.54	35.94	0.30	12.47	0	87.53
1400	62.84	34.53	2.63	8.95	0	91.05
1500	51.27	26.61	22.12	0	0	100.00
1600	11.35	0	88.65	0	0	100.00
1700	0	0	100.00	0	0	100.00
1800	0	0	100.00	0	0	100.00
1900	0	0	100.00	0	0	100.00

3. Method for studying microsilica carbidization

The study of microsilica carbidization was carried out by the discrete method, including the thermal treatment of the briquetted charge at the given temperatures and durations and hardening of the carbidization products followed by their chemical analysis.

For studies microsilica formed in the production of silicon (MC-Cr) and high-silica ferrosilicon (MK-FS) were used. They contain 93.92 and 93.00 wt% of silicon dioxide, respectively, with a specific surface area of 25,000 m²/kg, as well as a semi-coke of brown coal (BSC) from the

Berezovsky deposit of the Kansk-Achinsk basin, containing %: carbon – 81.9; volatile – 9.5; ash – 8.6, with a specific surface area of 264000 m²/kg. In all cases, the stoichiometric charge was used to produce the carbide composition.

Examination of the temperature and time conditions of carbidization of briquettes with microsilica of MC-Cr, MC-FS-BSC was carried out at temperatures 1883, 1923, 1973 K with a heat treatment time of 5, 10, 15, 20, 25, 30 min.

Heat treatment of the charge was carried out in the electric resistance furnace with a cylindrical graphite heater with an internal diameter of 0.075 m (Tamman furnace). Temperature control in the working space of the furnace was carried out using a tungsten-rhenium thermocouple BP 5/20. Cylindrical briquettes weighing approximately $2.5 \cdot 10^{-3}$ kg and an outer diameter of 0.015 m were placed in graphite crucibles. Three crucibles were simultaneously installed in the working space of the heated electric furnace, were heated in it for 3 – 4 minutes to the required temperature, and then kept in it for a specified time period – from 5 to 90 minutes. At the end of the specified time, the graphite crucibles were removed from the electric furnace, installed in corundum glasses, which were tightly closed with stoppers and placed for 10 minutes in the cold water for rapid cooling of the carbidization products. This made it possible to prevent the oxidation of carbidisation products by oxygen and atmospheric moisture. After cooling, the products of carbidization were extracted without losses from crucibles, weighed, placed in platinum tanks, poured with a solution of a mixture of nitric acid with a concentration of 7.5 – 12.5 M and hydrofluoric concentration 2.0 – 3 M, taken in a volume ratio of 1: (3 ÷ 5), and boiled for 2.5 - 3.0 hours.

The treatment of 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 silicon carbide powders of fineness from 5 to 200 µm. In the presence of nitric acid, metal impurities and their oxides form soluble nitrate complexes, while when treated with hydrofluoric acid, insoluble fluorides can be formed. After cooling, the insoluble residue, which is silicon carbide with an admixture of free carbon, was filtered out on a paper filter, washed on a filter with distilled water and acetone, dried to constant weight and weighed. After that, the undissolved residue was subjected to oxidative firing for refining from free carbon at a temperature of 1073 - 1123 K for 1.5-2.0 h. After the loss of mass, the content of free carbon and silicon carbide was calculated in the carbidization products. According to the average content of silicon carbide for three crucibles, its yield was calculated as the ratio of the mass of the practically obtained carbide to the theoretically possible ratio.

4. Experimental studies of carbidization of MC – BSC charges and discussion of the results

The results of the studies are presented in figures 3 and 4. In both cases the carbide formation process starts from the first minutes and by the 5th minute the carbide yield at the carbidization temperatures of 1873, 1923, 1973 K is 5.23 – 7.21, 17.06 – 22 , 30, 20.20 – 23.51%. The process of carbidization is completed at a temperature of 1973 K by the 15th minute, 1923 K – by the 20th minute. The content of carbide in the products of thermal treatment of charge is 92.50 for MC-FS and 94.90% for MC-Cr. Such temperature-time conditions for carbide formation are confirmed by the results of a study of the phase composition of heat treatment products. Thus, it was found that in both cases by the 10th minute the dominant phase is silicon carbide of cubic structure (β-SiC), partially changing to hexagonal one (α-SiCII) at a temperature of 1923 – 1973 K and a heat treatment time of 50 – 90 min. During the carbidization of the charge microsilica MC-FS-BSC, α-iron accompanies it. In all the samples studied, there is also a vitreous phase, formed, apparently, by silicates of calcium, magnesium and iron.

As a result of chemical enrichment, content of SiC in carbide exceeds 90%, i.e. level, regulated for abrasive micropowders with a grain size of 1 – 2 µm [9]. The efficiency of enrichment from impurities of oxides and iron is rather high and amounts to 87 – 95%. Silicon carbide is characterized by an increased silica content of more than 7%, which makes it possible to consider it as a promising material for the production of silicon carbide refractories based on silica, containing usually, %: SiC – 84 – 89, SiO₂ – 6 – 12 [10].

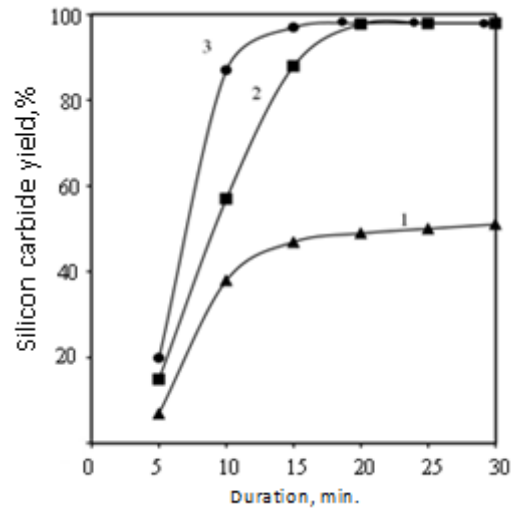


Figure 3. Dependence of the yield of silicon carbide on the temperature and duration of heat treatment for the charge of microsilica MK-FS-BOD (1 – 1873 K (Δ) = $(7.21 \div 53.13) \pm (0.20 \div 1.13)$, 2 – 1923 K ($\square$) = $(17.06 \div 96.82) \pm (0.55 \div 1.35)$, 3 – 1973 K ($\circ$) = $(20.20 \div 97.01) \pm (0.61 \div 1.45)$).

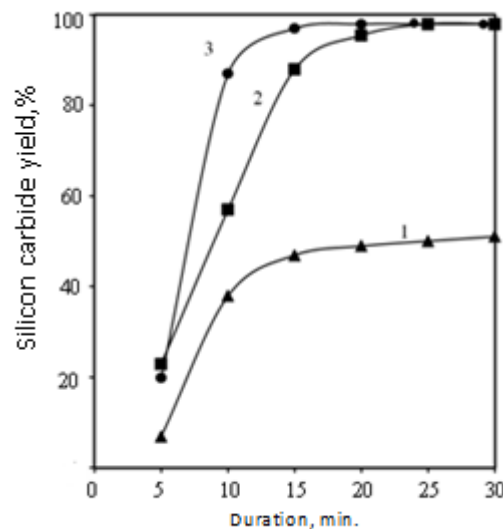


Figure 4. Dependence of the yield of silicon carbide on the temperature and duration of heat treatment for the charge of microsilica MC-Cr-BSC (1 – 1873 K: (Δ) = $(5.23 \div 46.26) \pm (0.19 \div 1.11)$; 2 – 1923 K: ($\square$) = $(22.30 \div 96.78) \pm 0.59 \div 1.33$; 3 – 1973 K: ($\circ$) = $(23.51 \div 97.62) \pm (0.67 \div 1.38)$).

Optimal conditions for obtaining and enriching silicon carbide and the range of variation of its main characteristics for a series of five parallel experiments are given in Table 3. It can be seen that the investigated technological options provide silicon carbide with reproducible phase, chemical and granulometric compositions and can be considered as a technological basis for the design of industrial production of silicon-free silicon carbide from the briquetted highly dispersed charge “microsilica – brown coal semi-coke”.

Table 3. Optimal conditions for obtaining and enriching silicon carbide and its characteristics.

Conditions for obtaining and enriching silicon carbide and its main characteristics	SiC (MC–FS+BSC)	SiC (MC–Cr + BSC)
Charge composition,%:		
Microsilica (MC)	58.80	58.04
Brown coal semi-coke (BSC)	42.20	41.96
Specific surface area of charge components, m ² /kg		
microsilica	20000 – 22000	
brown coal semi-coke	255000 – 265000	
The temperature of charge carbidization, K	1923 – 1973	
Duration of charge carbidization, min	25 – 20	
Chemical enrichment of carbidization products		
concentration of hydrochloric acid solution,%	35	
the ratio S:F	1:2	
temperature, K	383	
duration, hour	3	
Phase composition	β - SiC	

Continuation of Table 3.

Conditions for obtaining and enriching silicon carbide and its main characteristics	SiC (MC–FS+BSC)	SiC (MC–Cr + BSC)
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
C free	0.41 - 0.54	0,63 - 0,81
Si free	0.13 - 0.17	0,23 - 0,27
The yield of silicon carbide, %	96.84 - 97.12	97,31 - 97,63
The size and morphology of silicon carbide particles:		
specific surface area, m ² /kg	8000 - 9000	
size range, μm	0.2 - 1.0	
form	irregular	

5. Conclusion

Thermodynamic and experimental studies of the processes of reducing processing of technogenic microsilica on silicon carbide with the use of brown coal semi-coal were carried out.

It was established that in both Si-O-C and Si-O-C-H systems chosen for thermodynamic analysis, the carbide formation process is dominant. With the stoichiometric composition of the charge the maximum content in the reduction products of silicon carbide is reached at 1700 K, and with 10% shortage of carbon – 1900 K. The second composition of the charge is technologically more preferable, since it ensures the production of carbide that does not contain impurities.

The carbidization of the briquetted charges with microsilica (MC-FS and MC-Cr) – brown coal semi-coke was carried out at temperatures 1883, 1923, 1973 K and duration 5 – 30 min. Optimum temperature and time conditions of carbidization are determined: temperature 1923 – 1973 K at a duration of 20 – 15 minutes.

The expediency and the optimal conditions and indices of chemical enrichment of carbidization products were determined: exposure to hydrochloric acid with the concentration at least 35% at the temperature 353 K, ratio of S:F = 1:2, duration of 3 hours, carbide content in enrichment products of more than 90%, removal of oxides and iron impurities by 87 – 95%.

The phase, chemical, granulometric compositions and morphology of silicon carbide particles of both technological production variants were studied. It was found that during the carbidisation the carbide of the cubic structure (β -SiC) is formed, partially resrtuctured at a temperature of 1923 – 1973 K and the heat treatment time 50 – 90 min into a hexagonal one (α -SiC_{II}). The content of carbide after enrichment is 90.42 – 90.86% with the use of microsilica MC-FS and 90.94 – 91.18% using microsilica MC-Cr. In both cases, silicon carbide is obtained in the form of a micropowder with a specific surface of 8000 – 9000 m²/kg, particle size range 0.2 – 1.0 μ m, having an irregular shape.

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