Development of scientific and technological bases for application of brown coal semi coke in the technology of non-milled silicon carbide

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Abstract. Thermodynamics is investigated, and the optimum temperature and time modes of carbonization of a briquetted silica fume batch–brown coal semi coke are defined. The complete carbonization of the batch in the conditions of heat treatment is achieved at a temperature of 1923 – 1973 K within 15 – 20 minutes. The conditions and indicators of the chemical enrichment of carbonization products are established. After enrichment, the carbide content is more than 90%. Silicon carbide micro-powder is obtained with a specific surface area 8000 – 9000 m\textsuperscript{2}/kg.

1. Introduction
Production of silicon carbide is one of the most important in the structure of modern metallurgy; its annual output is about 800 thousand tonnes. The major fields of use are metallurgy industry (about 45 \% of the world demand), production of abrasives (up to 30 \%) and refractory materials (25 \%). Specific nature of thermo-mechanical, electro-physical, physical-chemical properties of silicon carbide determines the following areas of its traditional and advanced application: bonded materials; structural and functional ceramics; composite materials and coatings; surface and volume modification of materials. Scientific and technological substantiation and development of production of domestic non-milled silicon carbide is a task of great practical importance. In this regard, the aim of the present work was to study the processes of carbonization of technogenous silica fume by semi coke from brown coal mined in Berezovsky deposit of the Kansk-Achinsk Basin, technological properties of which are described in detail in [1-6].

2. Thermodynamic process modelling of carbide formation in Si–O–C, Si–O–C–H systems
Thermodynamic modeling was carried out in order to predict the optimal parameters of silicon carbide production (ratio of the components, temperature and pressure in the system), to define the equilibrium parameters of the process (conversion degree of raw materials to carbide, composition of gaseous and condensed products), to evaluate the contribution of individual reactions providing an effective processing of raw materials in the investigated conditions to the processes of carbide formation.
Taking into account use of brown coal semi coke with content of volatiles up to 10% in the process as a reducing agent, the objects for research were systems Si–O–C, Si–O–C–H. Calculation of equilibrium compositions of Si–O–C and Si–O–C–H systems was made by the “constant” method.

The calculations were carried out using the software for simulation of high-temperature complex chemical equilibria “PLASMA” with a built-in database for reaction products of oxide-, boride-, carbide- and nitride-forming systems. In the calculations we considered the temperature range from 800 to 2000 K at different pressures in the system: from 0.1 to 0.0001 MPa. The calculations were carried out in increments of 100°. The equilibrium constants of reactions of compounds formation from the elements served as initial data. During the calculations the possibility of formation was taken into account in the gas phase in the system Si, SiO, SiC, SiC₂, Si₃C, CO, CO₂, in the system Si–O–C–H 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 Si, Si⁺, Si₂, Si₃, O, O₂, C, C⁺, C₂, C₃, C₄, C₅, H, H⁺, H₂, CH₂, CH₃, CH₄, C₂H, C₃H, C₄H, C₅H₂, C₆H₆, SiO, SiC, SiC₂, Si₃C, CO, CO₂, in the condensed phase in two systems of Si, SiO₂, C, SiC. The choice of the ratio of initial elements in the investigated systems was determined by the stoichiometry of reaction of silicon carbide formation and composition of the batches.

The calculation results of the equilibrium compositions of systems Si–O–C and Si–O–C–H are given in Figures 1, 2 and in Tables 1, 2.

It can be seen that in both systems the process of carbide formation is dominant:

$$\text{SiO}_2(s) + 3C(s) = SiC(s) + 2CO(g)$$  \hspace{1cm} (1)

In the batch of stoichiometric composition the maximum content in the silicon carbide products is achieved at 1700 K, and with 10% of carbon deficiency – at 1900 K.

Introduction of hydrogen into the system practically does not affect the process of carbide formation due to the extremely low (less than 0.001 mol) content of hydrocarbons and hydrocarbon radicals in the temperature range of carbide formation.

In the system Si–O–C the equilibrium degree of silicon conversion to carbide is not more than 0.97%, which corresponds to the content of silicon monoxide in the gas phase 0.02 mol. Thus, it is impossible to obtain a single phase silicon carbide with no free carbon (Table 2) from the batch of stoichiometric composition (SiO₂+3C). Use of a batch with some (~ 10 %) carbon deficiency – reducing agent can help to avoid it (Table 2).
In this case, the area of coexistence of silicon carbide and excessive silica fume appears in the system. And the wider the temperature range of these phases coexistence, the higher the pressure in the system. Above these temperatures the silicon carbide itself is a reducing agent for silica fume, i.e. the following interaction becomes possible:

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

**Figure 2.** Dependence of equilibrium compositions of Si–O–C–H system on temperature with the ratio of Si:O:C:H = 1:2:2.7:3.6 and the pressure $P = 0.1$ MPa (—condensed, — gaseous products).
2 SiO\(_2\) + SiC \(\xrightarrow{\text{g}}\) 2 SiO(g) + CO(g)

Table 1. Equilibrium concentration (in%) of the condensed reaction products in the system Si–O–C with the ratio of components Si:O:C = 1:2:3.

| T, K | \(P = 0.1\) MPa | \(P = 0.01\) MPa | \(P = 0.0001\) MPa |
|------|-----------------|-----------------|-----------------|
| SiO\(_2\) | C | SiC | C | SiO\(_2\) | C | SiC | C | 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 | 0.02 | 62.5 | 37.5 | 0.02 |
| 1000 | 62.5 | 37.5 | 0 | 62.5 | 37.5 | 0.01 | 62.5 | 37.5 | 0.01 |
| 1100 | 62.5 | 37.5 | 0 | 62.5 | 37.5 | 0.2 | 62.5 | 37.5 | 0.2 |
| 1200 | 62.5 | 37.5 | 0 | 61.0 | 36.7 | 2.3 | 62.5 | 37.5 | 2.3 |
| 1300 | 62.5 | 37.5 | 0 | 0 | 0.2 | 99.8 | 0 | 0.2 | 99.8 |
| 1400 | 61.8 | 37.1 | 1.1 | 0 | 0.2 | 99.8 | 0 | 0.2 | 99.8 |
| 1500 | 61.0 | 36.8 | 2.2 | 0 | 0.3 | 99.7 | 0 | 0.3 | 99.7 |
| 1600 | 53.7 | 32.5 | 13.8 | 0 | 0.4 | 99.6 | 0 | 0.4 | 99.6 |
| 1700 | 0 | 0.6 | 99.4 | 0 | 0.6 | 99.4 | 0 | 0.6 | 99.4 |
| 1800 | 0 | 0.8 | 99.2 | 0 | 0.9 | 99.1 | 0 | 0.9 | 99.1 |

Table 2. Equilibrium concentration (in %) of the condensed reaction products in the system Si–O–C–H with the ratio of components 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 | C | SiO\(_2\) | C | SiC | C | 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 | 0.002 | 64.94 | 35.06 | 0.002 |
| 1100 | 64.94 | 35.06 | 0 | 64.94 | 35.06 | 0.04 | 64.94 | 35.06 | 0.04 |
| 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 |

As a result of this reaction silicon carbide is cleaned from the excessive silica fume. It might be particularly effective in the vacuum.

3. Research methodology of silica fume carbonization

The study of silica fume carbonization was conducted by the discrete method that includes heat treatment of the briquetted batch at given temperatures and duration and quenching of carbonization products with their subsequent chemical analysis.

Heat treatment of the batches was carried out in the electric resistance furnace with a cylindrical graphite heater with the inner diameter of 0.075 m (Tamman furnace). Temperature control in the furnace was performed by the tungsten-rhenium thermocouple VR 5/20. Cylindrical briquettes weighing about 2.5 kg·10^{-3} and with an outer diameter 0.015 m were placed into the graphite crucibles. Three crucibles were simultaneously installed in the workspace of the heated electric furnace, were heated in it for 3 – 4 min up to the target temperature and kept for the specified time period – from 5 to 90 minutes. After the specified time the graphite crucibles were taken out of the
electric furnace, installed into the corundum crucibles that were tightly stoppered and placed for 10 minutes into the cold water to cool the carbonization product. This prevented oxidation of the carbonization product with oxygen and atmospheric moisture.

After cooling the carbonization products were quantitatively, i.e. lossless extracted from the crucibles, weighed, placed into the platinum containers filled with a solution of nitric acid (concentration 7.5 – 12.5M) and hydrofluoric acid (concentration 2.0 – 3M) taken in a volume ratio of 1:(3 – 5), and boiled for 2.5 – 3.0 hours. Treatment of silicon carbide with a mixture of nitric and hydrofluoric acids removes impurities of aluminum, magnesium, calcium, iron, manganese, nickel, chromium, copper, sodium, potassium, silicon and their oxides and is recommended for the silicon carbide powders with grain size from 5 to 200 µm [7, 8]. In the presence of nitric acid the metallic impurities and their oxides form soluble nitrate complexes, whereas treatment with hydrofluoric acid solely may cause formation of insoluble fluorides. After cooling the insoluble residue – silicon carbide with free carbon impurity was filtered through a paper filter, washed with distilled water and acetone, dried to a constant weight, and weighed. Further, the undissolved residue was subjected to oxidizing burning for refining from free carbon at a temperature of 1073 – 1123 K during 1.5 – 2.0 hours. In the carbonization products the content of free carbon and silicon carbide was calculated according to the mass loss. Based on the average content of silicon carbide in three crucibles its yield was calculated as the ratio of the obtained carbide mass to the theoretically possible mass.

4. Results and discussion

During the research silica fume was used, generated in the production of silicon (SF-S) and high-silicon ferrosilicon (SF-FS), containing silica dioxide 93.92 and 93.00 % by weight with a specific surface area of 25000 m2/kg [9-11], as well as semi coke from brown coal (BCSC) of Berezovsky deposit in the Kansk-Achinsk Basin containing, %: carbon – 81.9; volatiles – 9.5; ash – 8.6 with a specific surface area 264000 m2/kg. In all cases the batches of stoichiometric composition were used to produce carbide.

Investigation of time-temperature conditions for carbonization of the briquetted silica fume monobatches SF-S, SF-FS – BCSC was conducted at temperatures 1883, 1923 1973 K with the duration of heat treatment 5, 10, 15, 20, 25, 30 min. The research results are given in Figures 3 and 4.
In both cases the process of carbide formation begins from the first minute, and by the 5th minute the carbide yield at carbonization temperatures 1873, 1923, 1973 K is 5.23 – 7.21, 17.06 – 22.30, 20.20 – 23.51%. The carbonization process is completed at a temperature of 1973 K by the 15th minute, at 1923 K – by the 20th minute. Carbide content in the products of heat treatment of batches is 92.50 for SF-FS and 94.90% by weight for SF-S. Such time-temperature conditions of carbide formation are confirmed by the study results of the phase composition of these products.

Thus, it was found that in both cases by the 10th minute silicon carbide of cubic structure (β-SiC) becomes the prevailing phase, partially turning into a hexagonal one (α-SiCII) at a temperature 1923 – 1973 K and duration of heat treatment of 50-90 min. The carbonization process of the batch SF-FS – BCSC is accompanied by alpha iron. In all test samples the glassy phase is also present formed, presumably, by silicates of calcium, magnesium and iron.
As a result of chemical processing the content of SiC in carbide exceeds 90%, i.e. the level specified for abrasive micro-powders with grain size 1-2 µm. The efficiency of enrichment from iron and oxides impurities is sufficiently high 87–95%. Silicon carbide is characterized by high silica content – more than 7%, which allows us to consider it as a promising material for production of silicon carbide refractories with a silica bond, usually containing 84–89% of SiC, 6–12% of SiO$_2$ [7]. Optimal conditions for production and enrichment of silicon carbide and variation range of its basic characteristics for the series of five parallel experiments are provided in Table 3. It can be seen that the examined technological variants ensure production of silicon carbide with the reproducible phase, chemical and granulometric compositions and can be regarded as a technological basis for the design of industrial production of non-milled silicon carbide from briquetted high-dispersed batch of silica fume – brown coal semi coke.

**Table 3.** Optimal conditions for obtaining and enrichment of silicon carbide and its characteristics.

| The production conditions and enrichment of silicon carbide and its main characteristics | SiC (SF-FS + BCSC) | SiC (SF-S + BCSC) |
|---|---|---|
| Batch composition, %: | | |
| – silica fume (SF) | 58.80 | 58.04 |
| – brown coal semi coke (BCSC) | 41.20 | 41.96 |
| Specific surface area of the batch components, m$^2$/kg: | | |
| – silica fume (SF) | 20000 – 22000 | |
| – brown coal semi coke (BCSC) | 255000 – 265000 | |
| Temperature of the batch carbonization, K | 1923 – 1973 |
Duration of the batch carbonization, min 25 – 20

Chemical enrichment of the carbonization products:
– concentration of the hydrochloric acid solution, % 35
– ratio Solid : Liquid 1:2
– temperature, K 383
– duration, hour 3

Phase composition β-SiC

Chemical composition, %:
– SiC 90.42–90.86 90.94–91.18
– Al₂O₃ 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
– SiO₂ 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

Silicon carbide yield, % 96.84–97.12 97.31–97.63

Fineness and morphology of silicon carbide particles:
– specific surface area, m²/kg 8000 – 9000
– size range, µm 0.2 – 1.0
– shape irregular

5. Conclusions
Thermodynamic and experimental investigations of reductive processing of technogenious silica fume into silicon carbide using brown coal semi coke are carried out.

It is found that in both systems Si–O–C and Si–O–C–H chosen for the thermodynamic analysis the process of carbide formation is the dominant one. In the batch of stoichiometric composition the maximum content of silicon carbide in the reduction products is achieved at 1700 K and with 10% of carbon deficiency at 1900 K. The second composition of the batch is more technologically preferable since it allows carbide free of impurities to be obtained.

Carbonization of the briquetted mono-batches silica fume (SF-FS and SF-S) – brown coal semi coke is carried out at temperatures 1883, 1923, 1973 K with the duration of 5 – 30 minutes. The optimum time-temperature conditions of carbonization are defined: temperature 1923 – 1973 K with the duration of 15 – 20 minutes.

The expediency is established, and the optimal conditions and the parameters of chemical enrichment of carbonization products are found: the effect of hydrochloric acid with concentration not less than 35% at a temperature of 353 K; ratio S:L= 1:2; duration 3 hours, content of carbide in the enrichment products more than 90 %; removal of oxides and iron impurities by 87 – 95 %. The phase, chemical, granulometric compositions are investigated, and morphology of silicon carbide particles for both technological variants are received. It is found that during carbonization silicon carbide of cubic structure (β-SiC) is formed, partially turning into a hexagonal one (α-SiC₆) at a temperature 1923 – 1973 K and duration of heat treatment of 50-90 min. The content of carbide after enrichment when using SF-FS is 90.42 – 90.86 % and when using SF-S is 90.94 – 91.18 %. In both cases, silicon carbide as a micropowder with a specific surface area 8000 – 9000 m²/kg, particles of irregular shape within the size range 0.2 – 1.0 µm is obtained.

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