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## Study on the conditions and composition of the plasma treatment products of silicon carbide micropowder

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**Abstract.** The conditions of plasma processing of silicon carbide microgrit, phase and chemical compositions, nanolevel and the mechanism of nanocrystalline silicon carbide formation are investigated.

### 1. Introduction

The modern production of silicon carbide is almost entirely based on Acheson's method. The process of carbon-thermal synthesis of silicon carbide is carried out by a periodic block process in electric resistance furnaces with a capacity 4.5-5.5 MVA at temperatures 2500-2900 K [1, 2]. A coke core serves as a heater, laid in the center of the furnace around which the charge of quartz sand and oil coke is placed.

The use of small, sufficiently pure and thoroughly mixed materials, slow heating (6-7 hours) and long aging (20-22 hours) cause the reactions to proceed, including solid-phase type, in regimes close to equilibrium. The process develops in a practically immobile mass of solid reagents with a slow movement of the reaction front from the core to the outer surface of the working space of the furnace. During the electrothermal process the crystalline silicon carbide is formed as a result of chemical reactions, as well as products of incomplete reduction: amorph, intergrowths and siloxicon. A significant part of the charge plays the role of thermal insulation and does not undergo a noticeable change in the composition. The chemical composition of the grain of technical silicon carbide is given in table 1 [3].

**Table 1.** Chemical composition of technical silicon carbide in the grain.

Type of silicon carbide	Content of components, % mass								
	SiC	Si	SiO <sub>2</sub>	C	Fe	Al	Ca	Mg	Ti
Green	98.0-99.5	0.1-1.0	0.1-0.2	0.1-0.3	0.05-0.2	0.01-0.08	0.01-0.1	0.01-0.05	0.01-0.05
Black	98.0-99.0	0.1-1.5	0.1-0.5	0.1-0.3	0.1-0.3	0.1-0.2	0.05-0.2	0.01-0.1	0.01-0.1

The sorted piece of silicon carbide with a size less than 400 μm is forwarded to the production of grinding materials (grinded grain and microgrit), representing a multi-stage redistribution [2]. The grain fineness of very fine microgrits is denoted by the upper limit of the grain size of the main fraction in accordance with table 2 [4]. The chemical composition of ultra-fine microgrits of silicon



carbide must meet the requirements of table 3.

## 2. Methodology of research

The nonpowders of silicon carbide can be obtained by plasma processing of microgrinding powders.

**Table 2.** Grain fineness of ultra-fine micro microgrits.

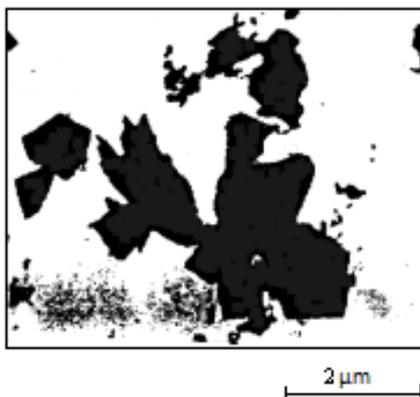
Grain fineness	M3	M2	M1
Grain size of the main fraction, $\mu\text{m}$	3.0 – 2.0	2.0 – 1.0	1.0 – 0.5

**Table 3.** Chemical composition of ultra-fine microgrits from green silicon carbide.

Make	Grain fineness	Chemical composition, % mass		
		SiC not less	Fe not more	C <sub>free</sub>
64C	M2	92.0	0.4	0.4
63C		90.0	0.6	0.7

For plasma processing, a microgrit K3 64S M5 with a specific surface 4500 m<sup>2</sup>/kg, containing impurities of nitrogen, oxygen and iron in the amount of 0.7; 3.3 and 0.5 wt%, respectively. A microphotograph of the microgrit of silicon carbide is shown in figure 1, and the X-ray diffraction pattern is shown in figure 2. The X-ray diffraction pattern contains all the main reflexes of  $\alpha$ -SiC<sub>II</sub> and  $\beta$ -SiC, which agrees well with the data on the polytype composition of technical silicon carbide given in [5].

For the research nitrogen of technical purity was used as a coolant and a carrier gas. The initial temperature of the nitrogen plasma flow, depending on the power supplied to the plasmatrons, was 3300, 5000, 5400 and 5600 K. The quenching of the condensed products of processing was carried out at a temperature of 2800 K by adiabatic expansion of the gas stream at the reactor outlet.



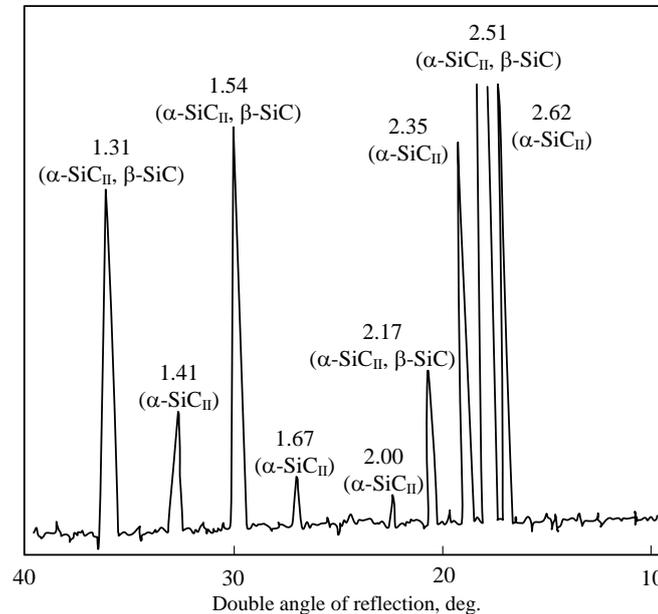
**Figure 1.** Micrograph of microgrit of silicon carbide K3 64S M5.

## 3. Research of conditions and results of plasma processing

The influence of the plasma flow and the mass flow rate of silicon carbide on the initial temperature process was studied. The physical and chemical evaluation of plasma treatment products was carried out using the methods of investigation of nanocrystalline materials described in [6 - 11]. The results are given in table 4 and in figure 3.

At a mass flow rate of silicon carbide 0.06 kg SiC/nm<sup>3</sup> N<sub>2</sub>, the main product is  $\beta$ -SiC, the higher the initial temperature of the plasma flow, the greater the specific surface area, and hence the dispersion of the powder particles. At a higher mass flow rate of silicon carbide the structural conversion of  $\alpha$ -SiC<sub>II</sub>

→  $\beta$ -SiC does not occur. In this case the dispersion of the plasma treatment products varies insignificantly with the increase in the initial temperature of the flow.



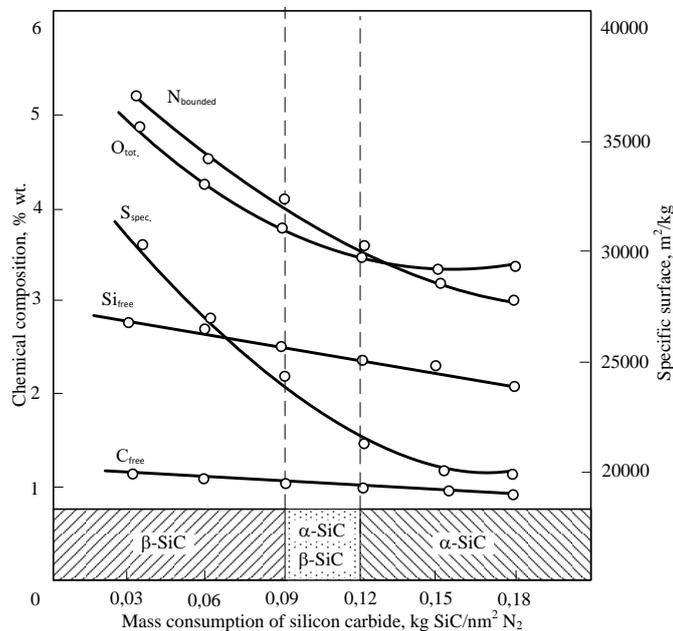
**Figure 2.** X-ray diffraction pattern of microgrit of silicon carbide K3 64S M5.

**Table 4.** Influence of the initial temperature of the plasma flow on the phase composition and dispersity of silicon carbide powders.

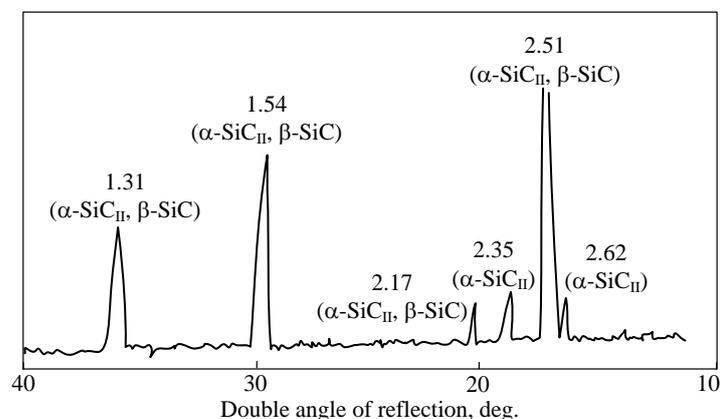
Initial temperature of the plasma flow, K	Mass flow rate, $\text{kg SiC}/\text{m}^3 \text{N}_2$	Phase composition, wt%		Specific surface, $\text{m}^2/\text{kg}$
		$\beta$ -SiC	$\alpha$ -SiC <sub>II</sub>	
5600	0.06	95.0	5.0	30000
5400	the same	95.0	5.0	28000
5000	– " –	89.0	11.0	24000
3300	– " –	19.0	81.0	12000
5600	0.15	25.0	79.0	19000
5400	the same	23.0	77.0	18000
5000	– " –	22.0	78.0	17000
3300	– " –	15.0	85.0	13000

The influence of the mass flow of silicon carbide on the crystal structure, the specific surface and the chemical composition of the plasma treatment products was investigated at the initial flow temperature 5600 K and a hardening temperature 2800 K. As it can be seen from figure 3, the specific surface area of the resulting silicon carbide decreases with the increase in the mass flow of the initial microgrit. The oxygen content of the powder varies from 4.9 to 3.4 wt% (in all cases more than in the initial one, amounting to 3.0 wt%). The nitrogen content of the plasma treatment products with a minimum mass flow of silicon carbide reaches 5.2 wt%. However, X-ray phase analysis of the nitride and oxynitride phases did not detect silicon. This suggests that the nitrogen in the carbide-containing products of plasma treatment is in the form of a solid solution of substitution. The structure of the formed silicon carbide depends significantly on the mass flow of the initial microgrit and, consequently, the capacity of the plasma flow to homogenize the process, i.e. to transfer the initial powdered raw material into the vapour phase.

At a low mass flow rate (0.06-0.09 kg SiC/nm<sup>3</sup> N<sub>2</sub>), during the heating silicon carbide is disproportionated, silicon is evaporated followed by carbidization, which is confirmed by the obtained specific surface values typical for powders of plasma-metallurgical synthesis. The natural result of the processes taking place in these conditions in the plasma flow is the formation of silicon carbide in the form of  $\beta$ -modification according to the mechanism “vapour-crystal”. A X-ray diffraction pattern of the nanodispersed silicon carbide powder obtained by plasma processing at a mass flow rate 0.06 kg of SiC/nm<sup>3</sup> N<sub>2</sub> is shown in figure 4. It can be seen that, as a result of plasma processing,  $\alpha$ -SiC<sub>II</sub> reflections (2.62, 2.35 Å) decreased significantly; other reflexes  $\alpha$ -SiC<sub>II</sub> (2.00, 1.67, 1.41 Å) disappeared. At the same time, the height of joint reflections of  $\alpha$ -SiC<sub>II</sub> and  $\beta$ -SiC (2.51, 2.17, 1.54, 1.31 Å) remained almost the same. A significant decrease and disappearance of  $\alpha$ -SiC<sub>II</sub> reflections (2.62, 2.35, 2.00, 1.67, 1.41 Å) indicates a decrease in the content of this polytype in the nanopowder, which is confirmed by a quantitative determination of the phase content. Therefore, the nanopowder is basically  $\beta$ -SiC with an insignificant  $\alpha$ -SiC<sub>II</sub> content.



**Figure 3.** Dependence of phase and chemical compositions, the specific surface area of plasma processing products on the mass flow of silicon carbide.



**Figure 4.** X-ray diffraction pattern of plasma-processed silicon carbide.

With a higher reactor load (0.15-0.18 kg SiC/nm<sup>3</sup> N<sub>2</sub>) the heat content of the plasma flow is insufficient to vaporize the microgrit of silicon carbide and, consequently, to perform the structural transformation of  $\alpha$ -SiC<sub>II</sub>  $\rightarrow$   $\beta$ -SiC. In this case, the most likely mechanism for dispersing is the thermal cracking and destruction of particles of silicon carbide microgrit.

Thus, it is established that the products of plasma treatment are characterized by high dispersity (20000-30000 m<sup>2</sup>/kg) corresponding to the nanolevel. However, the silicon carbide obtained by this method contains a significant (5-10 wt%) amount of SiO<sub>2</sub> due to the oxidation of products by oxygen and water vapour introduced by the plasma-forming gas. In connection with this, further experimental studies of plasma processing of silicon carbide microgrit were carried out in the following two directions:

- 1) Plasma processing in the drained and purified process gases.
- 2) Plasma processing of microgrit in process gases containing hydrocarbon additives to prevent oxidation of initial materials and synthesis products.

In experimental studies the initial temperature of plasma flow was 5600 K. Quenching of the synthesis products was carried out at a temperature 2800 K. In all experiments the mass flow of microgrit was 0.12 kg of SiC per 1 nm<sup>3</sup> N<sub>2</sub>. Drying and cleaning of the plasma-forming gas was carried out in a column-type unit with a chromium-nickel filler and electric heating to a temperature of 750-850 K.

Additives of hydrocarbon – technical propane were introduced together with the initial powder into the zone of impact of plasma jets in amounts varying from half of the required by stoichiometry to bind oxygen in CO up to a fourfold excess. The results of the studies are given in table 5. For comparison, the table also includes the data obtained by plasma processing of microgrit in the untreated process gases.

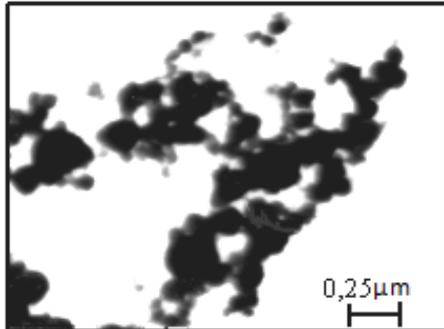
**Table 5.** Influence of the composition of process gases on the characteristics of the products of plasma processing of microgrit.

No.	Composition of process gases	Phase composition, wt%		Chemical composition, wt%				S <sub>sp</sub> , m <sup>2</sup> /kg
		$\beta$ -SiC	$\alpha$ -SiC <sub>II</sub>	Si <sub>free</sub>	C <sub>free</sub>	SiO <sub>2</sub>	Fe	
1	N <sub>2</sub> +0.5% vol. O <sub>2</sub>	57.0	43.0	2.25	1.07	6.6	0.32	21500
2	N <sub>2</sub> +0.007% vol. O <sub>2</sub>	56.0	44.0	3.00	0.88	2.7	0.37	26000
3	N <sub>2</sub> +0.5% vol. O <sub>2</sub> + 0.1% vol. C <sub>3</sub> H <sub>8</sub>	55.0	45.0	2.05	0.82	3.8	0.29	23000
4	N <sub>2</sub> +0.5% vol. O <sub>2</sub> + 0.44% vol. C <sub>3</sub> H <sub>8</sub>	52.0	48.0	1.05	0.78	2.5	0.31	21000
5	N <sub>2</sub> +0.5% vol. O <sub>2</sub> + 0.84% vol. C <sub>3</sub> H <sub>8</sub>	59.0	41.0	1.01	0.91	2.5	0.27	19000
6	N <sub>2</sub> +0.5% vol. O <sub>2</sub> + 1.4% vol. C <sub>3</sub> H <sub>8</sub>	56.0	44.0	1.12	1.1	2.3	0.29	22000

As it can be seen from table 5 the purification of process gases from oxygen and water vapour and the introduction of hydrocarbon in an amount from a 2-fold excess by stoichiometry and more leads to a significant decrease in the oxidation of products (the content 2.7 and 2.5 wt% of SiO<sub>2</sub> in experiments No. 2 and No. 4-5, respectively) compared to silicon carbide treated in the unprepared process gases (6.6 wt% SiO<sub>2</sub> in experiment No. 1) with comparable phase composition and dispersity. A microphotograph of the silicon carbide NDP obtained in the conditions of test No. 6 is shown in figure 5.

It can be seen that the powder contains particles of fragmented and faceted forms, which indirectly confirms the two-channel mechanism for particles dispersing of the initial microgrit: thermal cracking

with retention of the  $\alpha$ -SiC<sub>II</sub> phase and evaporation followed by “vapour – crystal” condensation with formation of  $\beta$ -SiC.



**Figure 5.** Micrograph of plasma-processed silicon carbide.

The optimum values of technological factors and the main characteristics of the plasma processing product, obtained with a fivefold duplication of experiments, are given in table 6.

**Table 6.** Parameters of the process of microgrit plasma processing and the main characteristics of the obtained nanodispersed silicon carbide (reactor power 80 kW).

Parameters of plasma processing and characteristics	Values
Composition of the gas – coolant, % vol.	
- nitrogen	100
Raw material size, $\mu\text{m}$	
- microgrit	4-5
- boron	-1 <sup>a</sup>
Productivity by raw materials, kg/h	1.60
The amount of reducing agent, % vol. of the volume of the gas – coolant	0.44-0.84
The content of boron in the charge, % wt.	3.00 <sup>a</sup>
The initial temperature of the plasma flow, K	5600
Tempering temperature, K	2800
Phase composition	$\beta$ -SiC, $\alpha$ -SiC <sub>II</sub> , SiO <sub>2</sub> am.
Chemical composition, % mass	
- main phase	90.00-92.00
- associated impurities	
silicon	1.00-1.15
oxides	3.00-3.50
free carbon	0.90-1.0
common boron	2.45-2.63 <sup>a</sup>
volatile	2.12-2.72
Specific surface, m <sup>2</sup> /kg	19000-21000
Average particle size, nm	100-110
Shape of particles	faceted, fragmented
Productivity by target product, kg/h	1.45

<sup>a</sup>In the production of silicon carbide alloyed with boron

#### 4. Conclusion

The process of plasma processing of silicon carbide, including the introduction of its microgrit K3 64 M5 in the plasma nitrogen flow with the initial temperature of 5600 K, plasma treatment and

quenching at a temperature of 2800 K. It is established that the product of treatment is silicon carbide in the nanodispersed state, the phase composition of which depends on the mass flow of the initial micropowder:  $\beta$ -SiC at 0.03-0.12 kg/nm<sup>3</sup> N<sub>2</sub>,  $\beta$ -SiC +  $\alpha$ -SiC<sub>II</sub> at 0.12-0.15 kg/nm<sup>3</sup> N<sub>2</sub>,  $\alpha$ -SiC<sub>II</sub> at 0.15 and above kg/nm<sup>3</sup> N<sub>2</sub>. A two-channel mechanism for the dispersion of the initial carbide particles was revealed: thermal cracking with retention of the  $\alpha$ -SiC<sub>II</sub> phase and evaporation followed by “vapour – crystal” condensation with formation  $\beta$ -SiC. The possibility of increasing the oxidative stability of nanocrystalline silicon carbide with the addition of hydrocarbons (propane) in the amount of 0.44-0.84% vol. from the volume of the gas-coolant. The optimal values of technological factors and the main characteristics of nanocrystalline silicon carbide are determined: the content of the main phase is up to 92.00 wt%, silicon and free carbon is up to 1.00 wt%, oxides (calculated as SiO<sub>2</sub>) – up to 3.50 wt%; specific surface area 19000-21000 m<sup>2</sup>/kg; the average particle size is 100-110 nm.

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