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# Microsilica in the production of silicon carbide: the results of testing and evaluation of technological challenges

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**Abstract.** The world production and consumption of silicon carbide is estimated. The expediency of using technogenic microsilica for the production of silicon carbide by the methods of furnace synthesis and plasma-metallurgical technology is shown. Schemes of mechanisms of carbon-thermal synthesis and plasma-metallurgical production of silicon carbide are proposed.

## 1. Introduction

The world consumption of silicon carbide is 600 – 700 thousand tonnes per year and is estimated at 670 million US dollars. The largest areas of silicon carbide applications are metallurgy (about 45% of the global demand), the production of abrasives (up to 30%) and refractories (up to 25%). The sales markets for silicon carbide powder materials are small-scale in terms of actual volume (less than 1%) but intensively developing and having a high cost estimate: powder with a particle size of less than 1 µm (so-called micronized carbide) for ceramics and nanopowder with particle size less than 100 nm (so-called “nanocarbide”) for high-quality structural ceramics and electroplating. Silicon carbide in the form of nanocarbide opens up new directions for its application.

World production facilities for the production of silicon carbide of all types are estimated at 1.1 million tonnes per year. Geographical structure of their distribution is characterized by the following data (thousand tons per year): China – 400-500, Norway – 85, Russia – 70, Japan – 59, USA – 42, Venezuela – 41, Canada – 40, Ukraine – 32.5, Brazil – 30, Spain – 20, Poland – 20, Mexico – 20.

The leader in the world market for the production of silicon carbide is the French giant company Saint-Gobian. On the second place are the merged companies Exolon-ESK (USA) and Electroschmelzwerk Kempten GmbH (ESK) (Germany). In Russia the main producer of silicon carbide is the Volzhsky Abrazivny Zavod OJSC (Volzhsky city in Volgograd Region), which produces black, green and electrotechnical silicon carbide, abrasive grit, microgrits and abrasive ceramic and resinoid bond tools. The contribution of Russia to the world production of silicon carbide is about 70 thousand tonnes per year.

The prices for grain and silicon carbide powders in the last few years remain stable and amount to (US \$ per tonne):

Black, with purity approx. 99 %	
Grade 1	1400 – 1500
Grade 2	1150 – 1300
Green, with purity approx. 99.5 %	1650 – 1850
Refractory	



Grade 1, with purity approx. 98 %	1300 – 1400
Grade 2, with purity approx. 95 %	1050 – 1250
Micronized with purity approx 98 %	13000 – 15000
Nanocarbide with purity approx. 98 %	200000 – 250000
In the near future the increase in prices for silicon nanocarbide is predicted.	

## 2. Purpose and statement of the problem

A new direction in the technology of silicon carbide, which allows the necessary characteristics of the product to be achieved and the requirements of resource-saving to be met, is the use of fine silica-containing materials of anthropogenic and natural origin as raw materials that have no value and are accumulated in great amounts. For example, over the course of twenty-five years the attention of researchers and technologists was focused on microsilica of various origins (technogenic, natural, artificially synthesized), its production conditions and properties were described in [1-5]. A common property of microsilica is its extremely high dispersity, which is 4-10 nm in artificially synthesized silica-carbon compositions, 100-200 nm in microsilica of technogenic origin, formed during silicon electrofusion and high-silicon ferroalloys, 1000-5000 nm in silica-containing natural schungites. The use of microsilica promotes the development of nanotechnologies in the production of silicon carbide and the creation of nanomaterials based on it.

To date, three directions of using microsilica in technological processes have been formed: the synthesis of organic-silicon compounds; secondary use in production cycles (for silicon smelting and ferrosilicon); synthesis of high-dispersed silicon carbide (figure 1).

## 3. Study of microsilica properties

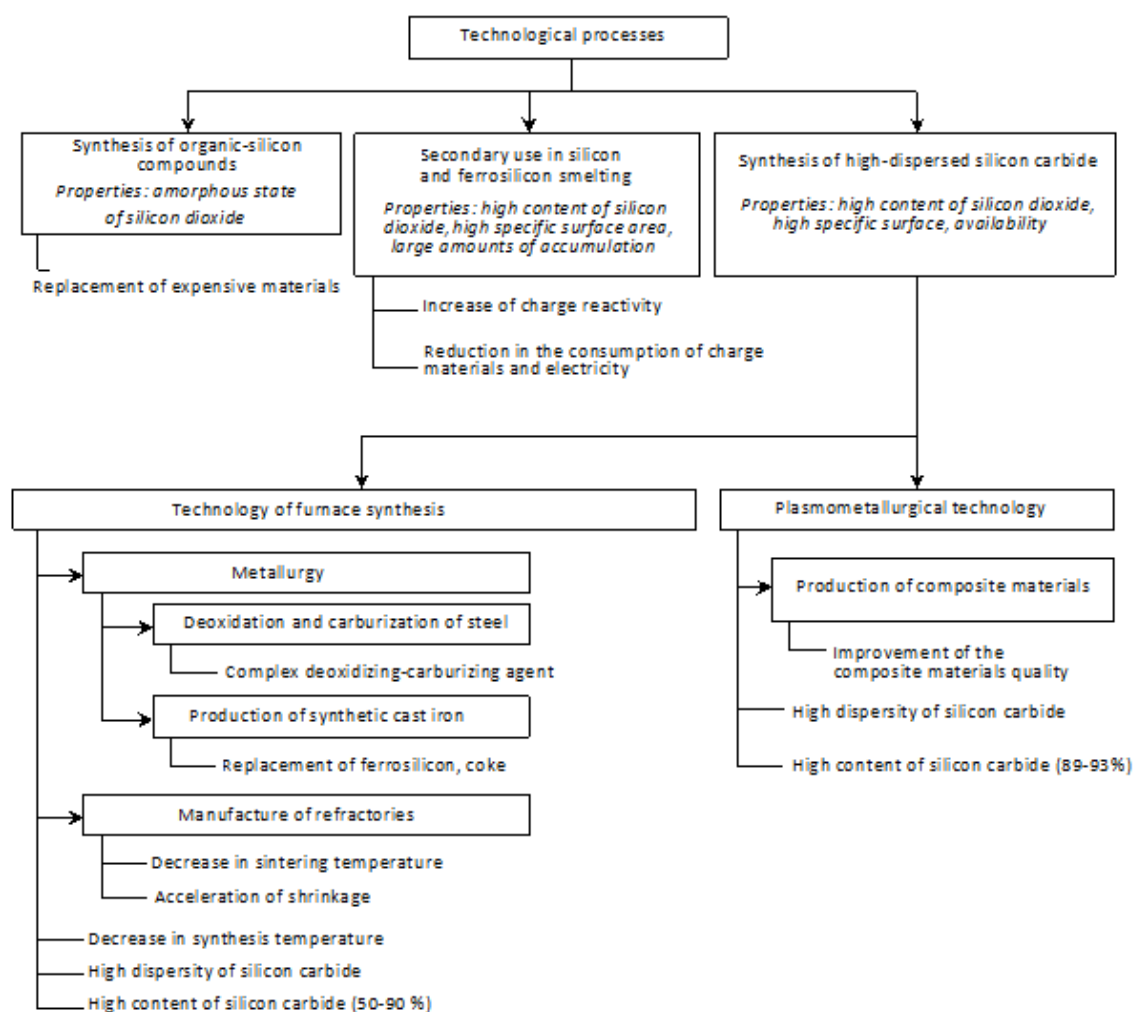
Due to the inconsistency of the existing data on the characteristics of microsilica, its complex physical and chemical study was carried out, which included the determination of phase and chemical compositions, specific surface area, particle size and morphology. The microsilica obtained in the production of crystalline silicon Kr1 at RUSAL-Irkutsk JSC (MS-Si) and ferrosilicon of grade FS75 at Kuznetsk Ferroalloys JSC (MS-FS) were studied.

The technogenic microsilica of both species is represented by the following phases:  $\beta$ -cristobalite,  $\alpha$ -quartz, iron oxides, silicates. In microsilica MS-FS there is magnetite, and in microsilica MS-Si – spinel  $\text{FeO} \cdot \text{Al}_2\text{O}_3$ . Both kinds of calcium oxides, oxides of phosphorus, magnesium, manganese, titanium, free carbon and silicon are present in microsilica. Quantitative differences in the chemical composition of microsilica refer mainly to the content of silica, iron compounds and free carbon (table 1). The specific surface of microsilica of both types is 20000-22000  $\text{m}^2/\text{kg}$ . The study of photomicrographs obtained by scanning electron microscopy (SEM) shows that both types of microsilica in the state of delivery are represented by aggregates of spherical shape of various sizes, varying in a wide range – from 100 to 600 nm. Individual aggregates are formed by spherical particles predominantly 50-80 nm in size, the number of which in the aggregate depends on its size (figures 2, 3).

## 4. Carbidization of microsilica

Two technologies have been developed for the production of high-dispersed silicon carbide based on microsilica: plasma-metallurgical and furnace synthesis, the results of which are presented in table 2, and micrographs of micro- and nano-powder of silicon carbide – in figures 4, 5.

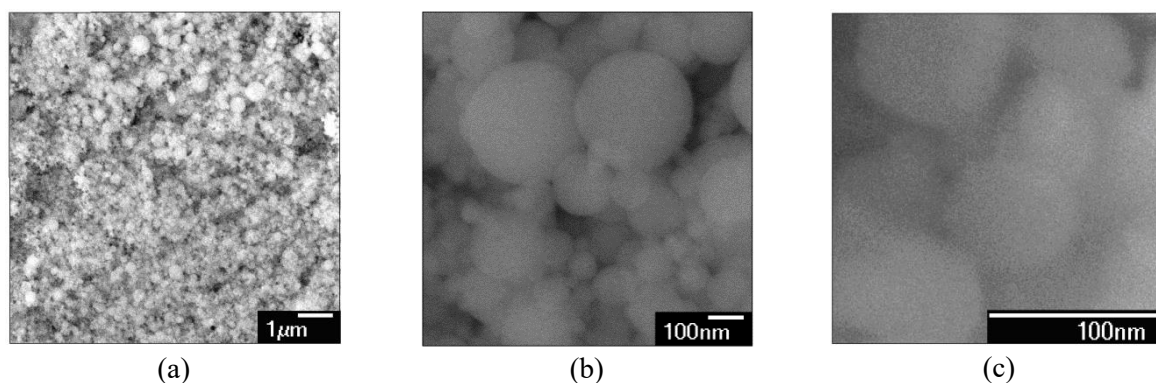
According to the existing thermodynamic concepts, the process of carbothermal reduction of silica occurs with the active participation of gaseous silicon oxides. The size effect arising in the one-component system “gas-dispersed crystalline phase” consists in changing the saturated vapor pressure above the surface of crystalline particles depending on the degree of solid phase dispersion. It is supposed that the speed of interaction can be increased by increasing the evaporation surface of  $\text{SiO}_2$  and using a carbonaceous reductant with a high adsorption capacity and a developed surface.



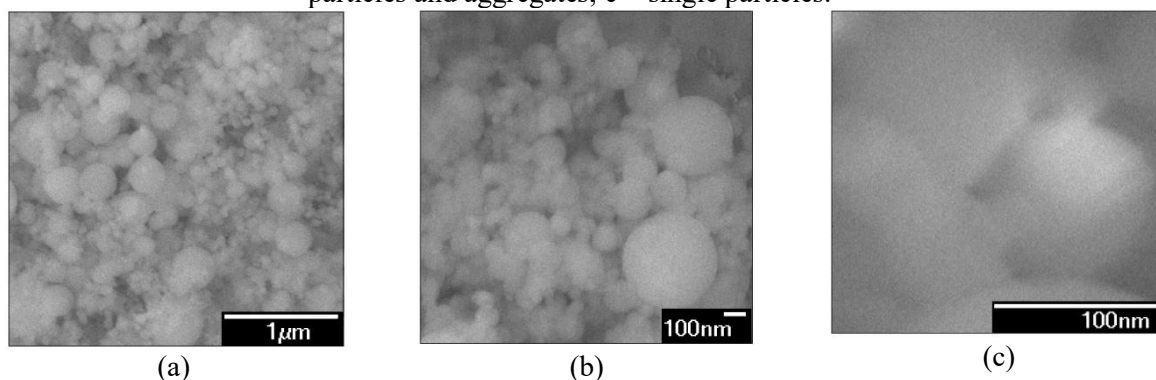
**Figure 1.** The use of microsilica in technological processes.

**Table 1.** Chemical composition of microsilica.

Element (compound)	Content,% wt.	
	Microsilica MS-Si	Микрокремнезём Microsilica MS-FS
SiO <sub>2</sub>	93.41-95.33	91.72-93.63
C <sub>free</sub>	1.96-3.28	0.56-1.18
Si <sub>free</sub>	0.30-0.34	0.18-0.20
Ca(CaO)	0.30	0.52
Al(Al <sub>2</sub> O <sub>3</sub> )	0.40	0.68
Fe(Fe <sub>2</sub> O <sub>3</sub> )	0.36	0.6-1.4
P(P <sub>2</sub> O <sub>5</sub> )	0.18	0.20
Mn(MnO)	0.05	0.30
Mg(MgO)	traces	1.08
Ti(TiO <sub>2</sub> )	0.01	traces



**Figure 2.** Microphotographs (SEM) of microsilica MS-Si: a – in the state of delivery; b – ensemble of particles and aggregates; c – single particles.



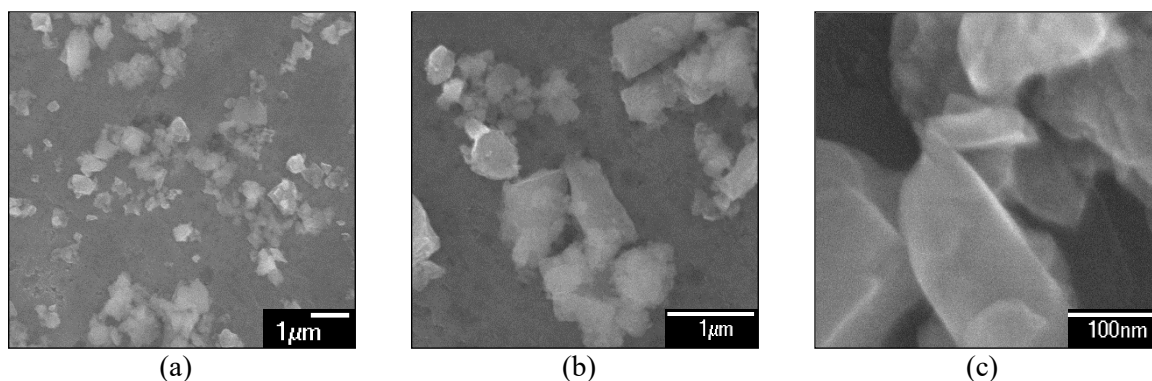
**Figure 3.** Microphotographs (SEM) of microsilica MK-FS: a – in the state of delivery; b – ensemble of particles and aggregates; c – single particles.

**Table 2.** Conditions for silicon carbide production and its basic characteristics.

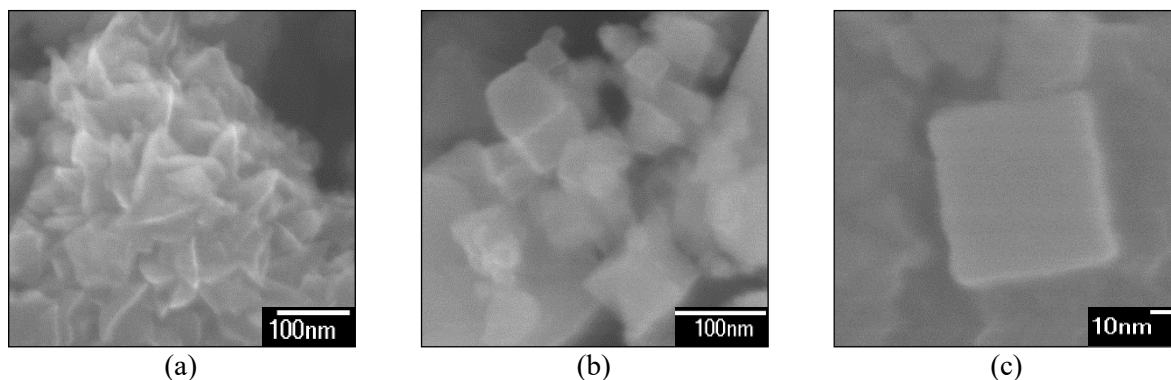
Conditions for silicon carbide production and its characteristics	Plasma-metallurgical technology	Technology of furnace synthesis
Equipment	plasma-metallurgical reactor	electric resistance furnace
Raw materials containing		
silica:	microsilica of silicon and ferrosilicon production	microsilica of silicon and ferrosilicon production
carbon:	natural gas (94.5% wt. CH <sub>4</sub> )	coke dust (82.69 % wt. C); carbon black
Process temperature, K	начальная температура плазменного потока 5400; температура закалки 2800-3000 initial temperature of the plasma flow is 5400; hardening temperature is 2800-3000	1843 – 1943
Duration of the process	25 · 10 <sup>-3</sup> sec	40-20 min
Phase composition	β-SiC, amorphous silica	α-SiC, mullite, silicate
Chemical composition, % wt.	carbide 90.87-93.23	carbide 89.77-92.02
Associated impurities, % mass	- silicon 0.61-1.04	- silicon 1.06-1.32



Conditions for silicon carbide production and its characteristics	Plasma-metallurgical technology	Technology of furnace synthesis
	- oxide 4.93-7.59 - carbon 0.61-0.95	- oxide 1.61-3.06 - carbon footprints
Specific surface area, m <sup>2</sup> /kg	36000-38000	3000-4000
Average particle size, nm	61-65	200-900
Shape of particles	faceted	irregular, fragmented



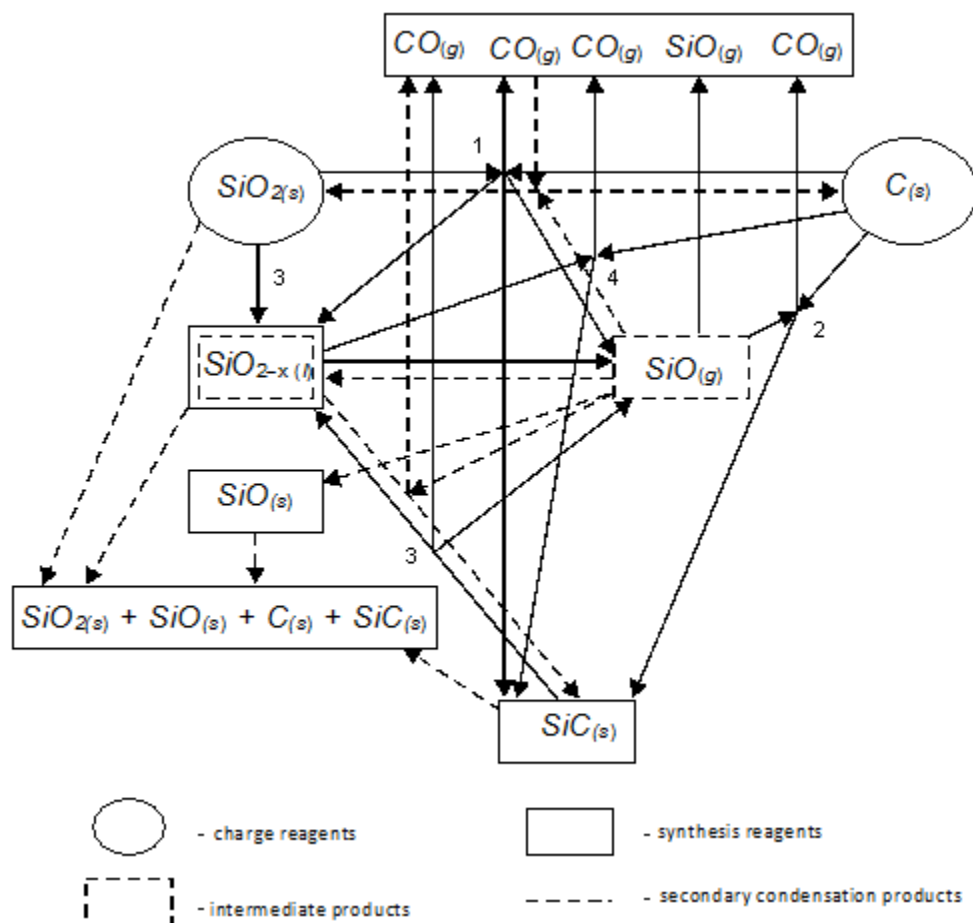
**Figure 4.** Microphotographs of silicon carbide micropowder – SEM: a – ensemble of particles; b – single particles; c – surface of a single particle.



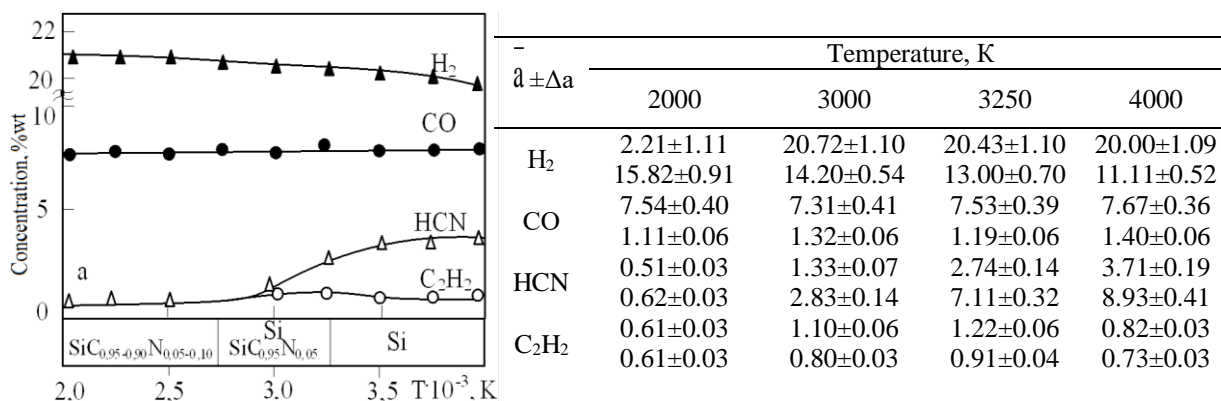
**Figure 5.** Microphotographs of silicon carbide nanopowder – SEM: a – morphological pattern of the aggregate; b – ensemble of nanoparticles; c – nanoparticles of a cubic shape.

According to the results of the research, a scheme of the mechanism of physical and chemical interactions in the carbon-thermal reduction of silicon oxide to carbide is proposed, which makes it possible to interpret the role of the size factor in the synthesis of silicon carbide (figure 6).

Using sufficiently small and well-mixed materials, the primary interaction is the solid-phase contact interaction of silicon dioxide with carbon  $\text{SiO}_{2(s)} + \text{C}_{(s)}$  “1”, which already produces gaseous monoxides of silicon and carbon at a temperature  $\approx 1500$  K, and at temperatures above 1800 K – silicon carbide and oxygen-deficient silicon-oxygen melt. The formation of silica with carbon films of silicon-oxygen melt in the contact zone increases the contact surface and intensifies the reduction process. Silicon carbide can also be formed due to the interaction of gaseous silicon monoxide with solid carbon “2”. This interaction is also leading in the reduction process, and the degree of its development determines the completeness of the silicon extraction into carbide.



**Figure 6.** Scheme of interactions in the process of carbon-thermal synthesis of silicon carbide.

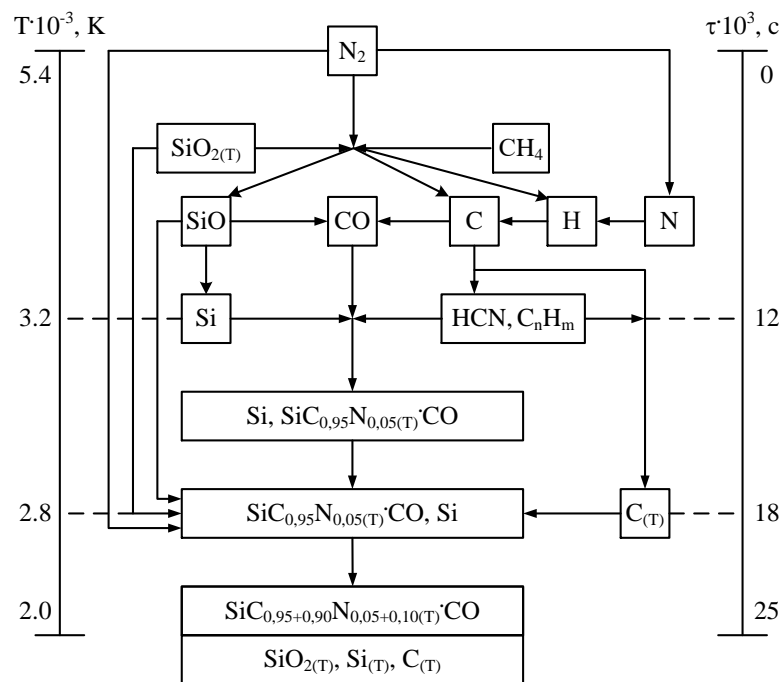


**Figure 7.** Temperature dependence of the composition of gaseous and phase composition of condensed products of microsilica reaction with methane in the nitrogen plasma flow ( $\bar{a}$ ,  $\pm \Delta a$  – average arithmetic values and confidence intervals of concentrations).

Thus, the reduction of silicon carbide to carbide is largely accomplished through the formation of a melt “4”, which at high rates of chemical reactions and sufficiently long exposures can be processed

without significant accumulation. The resulting silicon carbide at a later stage interacts with the silicon-oxygen melt “3” until it disappears completely.

Based on the analysis of morphological features of a nanoscale silicon carbide powder deposited in the form of faceted particles, that indicates their formation by the “vapour – crystal” mechanism and the temperature dependences of the gaseous and phase compositions of the condensed synthesis products in the temperature range 2000-4000 K (figure 7), a generalized hypothetical scheme is presented in figure 8. It seems expedient to distinguish in the plasma flow a number of spatially separated zones different in temperature conditions and, therefore, in the type of processes with a dominant development in them.



**Figure 8.** Scheme of interactions in the plasma-metallurgical production of silicon carbide

In the first, high-temperature zone, limited above by the initial temperature of the plasma flow, the processes occur that ensure the formation of reaction mixtures of the necessary compositions: evaporation, dissociation and reduction of silicon dioxide, disproportionation of silicon carbide, pyrolysis of methane, carbon “gasification”. A characteristic feature of the gasification of silicon dioxide is the formation of the volatile monoxide SiO as an intermediate product. In the second zone, which is limited by the temperature interval 3200-2800 K, within which a significant decrease in the concentration of the main carbidizer, hydrogen cyanide, occurs, it is possible to assume with a high probability that the carbide formation proceeds during the interaction in the gas phase. In addition, sorption processes actively occur on the surface of the formed super-small carbide particles, that lead to their saturation with process gases and gaseous synthesis products. In the third zone, limited by the interval 2800-2000 K, nitriding of silicon carbide particles occurs, the nitrogen content of which is a function of the quenching temperature and, consequently, the duration of nitriding of the particles formed in the stream.

Thus, for the conditions of nitrogen plasma flow of an industrial reactor the features of carbide formation have been studied, and a single-channel version of the mechanism for the formation of silicon nanocarbide with the participation of silicon and cyanide vapours by the “vapour – crystal” scheme has been revealed.



## 5. Conclusion

Plasma-metallurgical technology allows silicon carbide to be obtained in the form of a nanopowder with a minimum of surface defects, and the control of the synthesis process (regulation of the gas phase composition, introduction of certain additives) provides the required composition. The silicon carbide powder obtained in this way meets the requirements for components of electrodeposited composite coatings and can be used in electroplating. When using the technology of furnace synthesis silicon carbide is obtained in the form of micropowder, the synthesis temperature can be reduced by 800-900° (compared to traditional furnace synthesis), and the duration – up to 20-40 minutes, which makes it possible to perform a continuous process, to organize environmentally friendly production, to reduce the power consumption by almost 2 times, to reduce significantly the cost of production and, accordingly, expand the possibilities of its use.

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