APPLICATION OF SPARK PLASMA SINTERING AS A METHOD FOR PRODUCING NEW CERAMIC MATERIALS FROM SILICON PRODUCTION WASTE

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ABSTRACT

The article presents some existing methods of producing silicon carbide, forms and types of silicon carbide, various compositions and formulations, production technology. The authors proposed a new method of processing silicon production waste - microsilica by spark plasma sintering with a carbon-containing reducing agent (soot) which produces a silicon carbide compound. Studies have shown that sintered silicon carbide has improved strength properties. Thus, the possibility of application of production wastes to create new composite materials characterized by a certain complex of properties is confirmed.

Keywords: silicon carbide, silicon production waste, microsilica, spark plasma sintering, ceramics.

INTRODUCTION

Silicon carbide is one of the most important high-temperature materials with high hardness, chemical stability, resistance to high temperatures and ionizing radiation. Silicon carbide is used to produce ferrosilicon, solar silicon, abrasive and metal-cutting materials and tools, heat-resistant ceramics. Silicon carbide in the form of nanoscale particles and monocrystalline fibers has very valuable and interesting properties. Such silicon carbide is used to produce ceramics and composite materials, as well as to create products with a developed surface [1, 2].

In industry, silicon carbide is produced mainly by the carbothermal reduction of silicon dioxide. The synthesis is carried out at temperatures of 1200- 220°C depending on the nature of chemicals used and process modes. In some cases, carbothermic reduction can produce silicon carbide nanofibers in yields of up to 20 - 30 % silicon. The industrial method of producing silicon carbide is based on the ohmic heating of a conductive charge of silicon dioxide and coke or the heating of silica with a carbon-containing material in resistance furnaces [3, 4]. There is also a known method of obtaining silicon carbide nanofibers by chemical vapor deposition methods, but there is a common disadvantage in their low productivity and high cost of the resulting product [1].

The authors of paper propose a method of obtaining nanofibrous silicon carbide based on silicon powder and carbon-containing material (carbonaceous rocks of natural origin, quartz, ungraphite carbon) by its high-temperature heating in an inert medium at 1400-2100°C for 5 - 30 minutes [5]. The disadvantages of this method are high process temperature, low silicon carbide yield (16 - 30 %), high content of various metal

impurities in the product.

In paper the authors present a method of obtaining extended silicon carbide fibers with a diameter of 50-200 nm by pyrolysis of organosilicon compounds at temperatures of 1500 - 1600°C [6]. At the same time, the high temperature of synthesis, low product yield and high cost of the initial components are disadvantages of this method.

There is also a known method of producing β-carbide-silicon nanofibers by physical vapor deposition. These fibers get deposited on a base near a source of gaseous products. The synthesis is carried out at 1800 - 2300°C using a mixture of silicon and carbon, hydrogen as a carrier gas, and metal powders as a catalyst. The disadvantages of this method are high power consumption, complexity of hardware design, increased explosion hazards associated with the use of hydrogen [1].

A known method of obtaining silicon carbide by interaction of silicon dioxide with carbon at 2200 - 2400°C is the most common method [7]. The disadvantage of this method is the inability to produce high-purity semiconductor-quality silicon carbide.

Methods of obtaining silicon carbide are given in papers [8, 9] by synthesis at 1800 - 2300°C from a charge containing silicon dioxide powder and carbon in the form of ground graphite or soot. When silicon dioxide interacts with carbon, a solid-state reaction takes place, the rate and completeness of which depend on the degree of contact between the solid particles of the initial components. This is achieved by deep grinding of the initial charge substances and high temperature. A disadvantage is the inability to organize uniform heating of the charge and staged advance of the combustion front. Therefore, the process is carried out only in reactors of small volume, as well as the low yield of good product (not more than 75 %) and its insufficient purity.

In the paper, the target product was obtained by heating silicon dioxide and a carbon-containing substance in a plasma flow from a jet plasmatron [10].

Obtaining nanostructured silicon carbide powders using a two-jet plasmatron is given in paper [11]. The paper theoretically and experimentally established conditions for the formation of silicon carbide when heating silicon-containing raw materials and hydrocarbons in a stream of nitrogen and nitrogen-hydrogen plasma [12]. Three jet plasmatrons with a total capacity of 150 kW were used as plasma sources.

The authors of papers suggest ways to produce silicon carbide for microwave technology, optoelectronics, and power engineering [13, 14]. Silicon carbide is prepared from a charge containing nanopowders of silicon-containing (SiO, SiO_2, H_2SiO_3) and carbon-containing (carbohydrate of the general formula $C_n(H_2O)_m$, where $n \geq 12$; $m = n - 1$, polyatomic alcohol of the general formula $C_nH_{2n+2}O_n$, where $n \geq 2$ aldehydic or ketone derivatives of polyatomic alcohols of the general formula $(CH_2O)_n$, where $n \geq 3$) components prepared in deionized water followed by stepwise heating in three stages: to a temperature of 145 - 195°C holding 1.5 - 3.0 h, to 800 - 1000°C holding 0.4 - 1.0 h and to 1450 - 1650°C holding 1.0 - 1.5 h. Powder of silicon carbide of white color of high purity - 1×10^{-5} at. % with the yield of a good product of about 80 - 85% is obtained.

A promising use of man-made waste products from coke, silicon, and high-silicon ferroalloys production is their use in electrothermal processes. When using highly dispersed waste products from coke production and ferroalloy (silicon) production as raw materials, it is possible to produce silicon carbide micropowders [15].

The study of reductive processing of technogenic microsilica using lignite semicoke is of certain technological interest in terms of obtaining the so-called “milling-free” silicon carbide from highly dispersed charge materials by furnace synthesis in the form of micropowders of 1 - 5 μm in size, followed by their chemical enrichment. During the research we used man-made microsilica formed in the production of silicon (MK-Kr) and high-silicon ferrosilicon (MK-FS) containing 93.92 and 93.00 % silicon dioxide, respectively, with a specific surface area of 25000 $m^2 kg^{-1}$, and lignite semicoke from Berezovskiy deposit of Kansk-Achinsk basin containing, % wt. carbon - 81.9; volatiles - 9.5; ash - 8.6, with specific surface 264000 $m^2 kg^{-1}$. Studied technological options provide production of silicon carbide with reproducible phase, chemical and granulometric compositions and can be considered as a technological basis for the design of industrial production of grinding-free silicon carbide from briquetted highly dispersed charge of microsilica-lignite semicoke [16, 17].

Paper proposes a method that involves mixing

silica-containing material with carbonaceous material. In this case, quartzite up to 0.5 mm in an amount of 75 - 80 wt. % is fed for mixing as silica-containing material [18]. Pet coke previously passed the stage of delayed coking at 1150 - 1300°C for 0.3 - 0.5 h together with heavy pyrolysis resin in an amount of 1 - 6 wt. %, crushed to a particle size of not more than 5 mm in an amount 15 - 22 wt. % is fed for mixing as a carbonaceous material. Invention technical result is to increase the electrical resistance of charge, reduce energy costs and increase the yield of commercial product.

Despite the rather extensive methodology of silicon carbide production, the problem of obtaining its required parameters in terms of purity, degree of dispersion, productivity and other characteristics remains relevant. In this case, the process of producing silicon carbide is characterized by multi-parameter technology. It is necessary to consider the fractional composition of initial silicon dioxide, to select plasma-forming and transporting gases, enthalpy (temperature) of gas-discharge plasma, to consider the heat exchange of powder particles with the plasma flow, as well as no contaminants in plasma [19, 20]. Thus, the authors of this article propose a method of obtaining silicon carbide using silicon production waste, namely microsilica, based on a literature-patent search. It is known that the production of technical silicon produces silicon dust (microsilica), which is deposited in huge quantities, negatively affecting the health of population in the surrounding region, as well as having a detrimental effect on the environment and ecology [21, 22].

EXPERIMENTAL

Initial materials were microsilica powder of fraction less than 45 μm in the amount of 6.25 g and 3.75 g of the carbon component (soot P804T). The specified powders and 150 g of balls were loaded into the Wise Mix Ball Mill Laboratory drum to ensure homogeneous mixing. The mill speed was 200 rpm, mixing time was 24 hours.

Then the obtained mixed powder was sintered on a spark plasma sintering machine “LABOX-650” (Moscow Institute of Steel and Alloys, Moscow) (Fig. 1). The sintering temperature was 1800°C; the duration of holding at this temperature was 10 min.

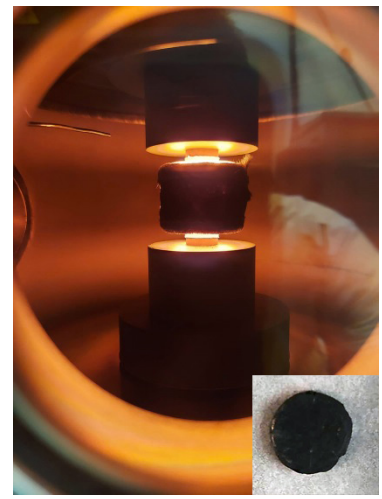


Fig. 1. Spark plasma sintering process and photo of the resulting sample.

RESULTS AND DISCUSSION

Fig. 2 shows the microstructure of sintered silicon carbide and energy dispersion analysis.

Fig. 2 shows that the fracture surface has a dense, even, porceless homogeneous structure. At higher magnifications, you can see that the silicon carbide particles are firmly connected to each other, representing a dense sintered conglomerate. The particles have a rounded globular shape. The type of fracture is granular. The average particle size is 108.418 nm (108 μm).

Fig. 3 shows the energy dispersion analysis (EDA) of sintered silicon carbide. EDA results show that the composition of obtained silicon carbide includes carbon (67.73 %) and silicon (32.27 %) and excludes various impurities.

It is known that spark plasma sintering of powders of microsilica and soot results in the following chemical reaction:

$$SiO_2 + 2C = SiC + 2CO. \quad (1)$$

At high SPS temperatures, impurities burn out and vacuum outgassing of sintered sample surfaces occurs resulting in silicon carbide.

The driving force behind sintering is a decrease in the thermodynamic potential of the system caused by

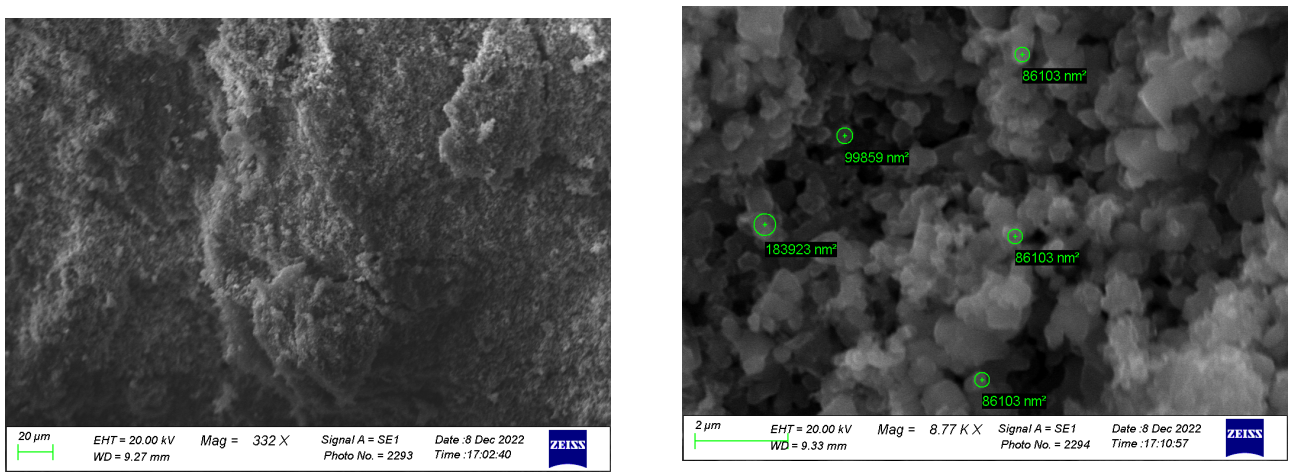
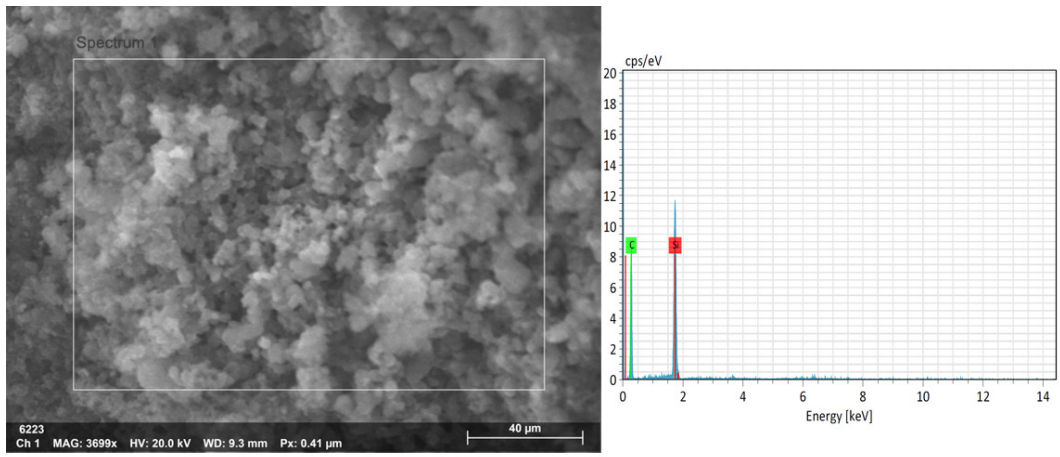


Fig. 2. Silicon carbide fracture microstructure.



Spectrum 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	1280	67.73	67.73	83.07	3.64	5.38
Silicon	14	12076	32.27	32.27	16.93	0.90	2.78
		Sum	**100.00**	**100.00**	**100.00**		

Fig. 3. Microstructure and energy dispersive analysis of obtained silicon carbide.

the synthesis of the new phase. This fact is confirmed by the results of X-ray phase analysis shown in Fig. 4. X-ray phase analysis of obtained silicon carbide sample showed that the initial powder of microsilica and soot as a result of heating under spark plasma sintering is converted into a chemical compound silicon carbide and only one phase β-SiC was detected. In addition, the spark plasma process results in liquid-phase sintering and the formation of gaseous products (CO, SiO, etc.) at appropriate temperatures. Presumably, some of the initial microsilica has not reacted and is found as SiO_2 residual.

Then the sintered sample density was determined by hydrostatic weighing. The sample was weighed in air and water. The density values of the sample were determined by calculation. Electrical conductivity was determined using an eddy-current structureoscope VE-

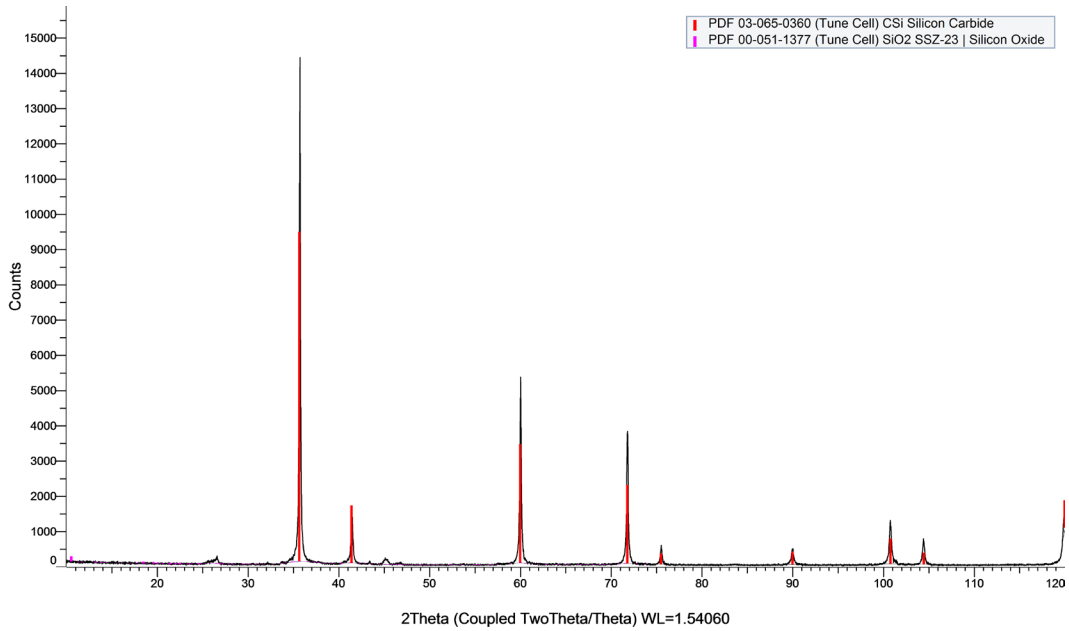


Fig. 4. Sintered silicon carbide X-Ray phase analysis.

Table 1. Results of physical and mechanical tests of sintered silicon carbide sample.

Parameter	Silicon carbide
Hardness, HB	236.1
Electrical conductivity, Ohm $^{-1}$	no
Compressive strength, kN:	
- crack formation	7
- fracture	18

26NP. Results are shown in Table 1.

Table 1 shows that the obtained material is characterized by increased strength and density, since the high rates of heating and cooling of the material during SPS contribute to the predominance of compaction processes over the diffusion mechanisms of grain growth, resulting in a sample of high hardness. This is due to the absence of recrystallization process which unstrengthens the material [23, 24]. Also obtained silicon carbide is characterized by a lack of electrical conductivity, which is associated with the absence of various impurities (e.g., boron, gallium, aluminum, etc.), contributing to the semi conductivity effect.

CONCLUSIONS

Thus, studies show that the method of spark plasma sintering makes it possible to obtain a porous ceramic consisting of pure silicon carbide from SiO_2 micro- and nano-powders in combination with a carbon-containing material (soot). The sintering process is made possible by the following main influencing factors, such as high pressure, which promotes powder compaction kinetics, and combustion, which synthesizes mechanically activated Si and C particles as a result of the SiO_2 reduction reaction. It should be noted that a necessary and important condition for high mechanical properties of the obtained ceramics (silicon carbide) is a process of powder homogenization, namely, mixing the initial powders of microsilica and carbon black for a day. The samples processed at 1800°C for 10 minutes consolidated by the SPS method were cooled slowly at room temperature, which eliminated the appearance of thermal stresses and, as a result, eliminated the effect of heterogeneous structure of the obtained samples.

In addition, the methodology proposed by the authors of the work not only contributes to obtaining advanced ceramic materials, but also solves the problem of recycling industrial waste silicon production in Kazakhstan (on the example of microsilica as a

waste of the "TauKenTemir" enterprise) and reduce energy intensity of production. In this way the problem of decarbonisation of the mining and metallurgical complex of the Republic of Kazakhstan is solved. For example, according to recent data, 86.6 % of emissions in Kazakhstan come from the industrial sector, including 53.45 % from mining, totalling 11.2 million tonnes. The energy intensity of Kazakhstan's products is also 2 times higher than the average for CIS countries.

The results of this work suggest that submicron waste powders are promising products to produce dense ceramics based on silicon carbide. The authors suggest using more dispersed powders (sub- and nano-sized) as starting materials because powder dispersion directly influences the possibility and time of consolidation process, i.e. the higher the powder dispersion, the shorter the consolidation process time. Work in this direction is still in progress. The authors also propose to test lower temperatures in the process of liquid-phase reaction sintering of silicon carbide, as the direct synthesis of elemental silicon and carbon contributes to a decrease in this parameter.

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