

INORGANIC SYNTHESIS AND INDUSTRIAL  
INORGANIC CHEMISTRY

## Consolidation by Spark Plasma Sintering of a Ceramic Material Based on Silicon Carbide with Good Physicomechanical Properties, Mechanochemically Activated with Boron

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Received February 2, 2018

**Abstract**—Industrial silicon carbide powder was consolidated with boron by the spark-plasma-sintering (SPS) method. It was shown that a preliminary mechanical activation is a promising method for introduction of high concentrations of boron into silicon carbide. The influence exerted by the boron concentration on the sintering and properties of the material based on silicon carbide was examined. A ceramic based on silicon carbide with 10 wt % amorphous boron was obtained with density of 3.12 g cm<sup>-3</sup>, hardness of 31.9 GPa, and crack-resistance coefficient of 5.7 MPa m<sup>1/2</sup>. The ceramic is promising as a construction ceramic for nuclear reactors and gas-turbine engines.

**DOI:** 10.1134/S1070427218020015

Silicon carbide is actively used at present for fabrication of ceramic articles in various industries: engine manufacturing, machine building, oil extraction, oil processing, nuclear power engineering, etc. This is due to the combination of the unique physicomechanical characteristics of SiC, which provides its stable operation in extreme operation conditions: under integrated action of high temperatures and mechanical loads, chemically aggressive media, and exposure to ionizing radiation [1–11]. However, the sintering of silicon carbide to a high density is difficult due to the strong covalence of Si–C bonds and high vapor pressure at temperatures exceeding 2000°C. The sintering activity of silicon carbide can be raised by its alloying with boron, carbon, or combination of these [12]. Upon introduction of boron into silicon carbide, the densification of the material can be intensified due to the formation of solid solutions of boron in silicon carbide and to the increase in the number of crystal-lattice defects in the form of vacancies playing the main part in the course of the diffusion sintering of a material. It has been shown [13, 14] that the sintering of silicon carbide

is noticeably intensified even upon introduction of the intensifier in an amount of 0.5–1 wt %, above which the crystallization of boron carbide phases may occur. However, this phase-formation process has not been fully studied. As the amount of boron forming a solid solution is raised, the system becomes more nonequilibrium, which creates prerequisites for sintering of silicon carbide at temperatures below 1800°C.

A promising way to introduce boron into silicon carbide is by the mechanochemical-activation (MA) method, which is of particular interest owing to the possibility of “deformation mixing” of the mixture components, i.e., mixing of the starting components on the atomic level. The mixing occurs when diffusion processes are hindered, and this makes it possible to stabilize various metastable phases that appear under mechanical treatment and raise the sintering activity of the powder [15].

Of interest for consolidating powder mixtures of silicon carbide and boron is the spark-plasma-sintering (SPS) method. This is the high-rate sintering method

**Table 1.** Initial composition of the industrial silicon carbide powder of F-1000 brand from Volzhskii plant of abrasives

Chemical composition		XRD analysis: quantitative composition	
substance	content, wt %	compound	content, wt %
SiC	≥ 99.649	6H-SiC	≥ 89.92
Fe <sub>2</sub> O <sub>3</sub>	≤ 0.176	15R-SiC	≤ 7.57
TiO <sub>2</sub>	≤ 0.070	C <sub>free</sub>	≤ 0.77
Al <sub>2</sub> O <sub>3</sub> etc.	≤ 0.105	Si <sub>free</sub>	≤ 0.73

in which the energy is released not only throughout the whole macroscopic volume of the powdered stock, but is also scattered just in certain microscopic regions, specifically at points of contact between powder particles [16–21].

The goal of the present study was to examine the influence exerted by the mechanochemical activation of silicon carbide on its sintering activity, consolidate an industrial silicon carbide powder by the SPS method, and analyze the effect of the introduced amount of boron on the sintering and properties of the material.

## EXPERIMENTAL

As starting components served industrial  $\alpha$ -SiC powder of F-1000 brand (composition listed in Table 1) from Volzhskii plant of abrasives, ground to a submicrometer size ( $D_{50} = 0.215 \mu\text{m}$ ), and amorphous boron [MRTU (Interrepublican Technical Specification) 6-02-292–64]. The grinding was performed in a Retsch PM-400 planetary mill (Germany) in 250-mL drums with tungsten carbide (WC) milling bodies ( $d = 10 \text{ mm}$ ) at a grinding duration of 3 h. The dispersity of the materials was analyzed on a Fritsch Analysette 22 Micro Tec/XT laser particle analyzer. A boron additive was introduced into silicon carbide by the method of mechanochemical activation. The concentration of boron being introduced was 3, 6, 8, and 10 wt %.

Silicon carbide and amorphous boron were mechanically activated in a PM-400 planetary mill in 250-mL drums with WC milling bodies ( $d = 10 \text{ mm}$ ) during 120 min, with a 1 : 10 ratio between the material and milling bodies. On being mechanically activated, the resulting mixtures were twice sieved through a sieve with no. 002 mesh.

The chemical composition of the starting silicon carbide powder of F-1000 brand from Volzhskii plant of abrasives was analyzed on a Shimadzu EDX-8000 energy-dispersive X-ray fluorescence spectrometer (Japan) by the HCAM 439-PC technique. The phase composition of the starting silicon carbide powder was determined with a Bruker D2 Phaser X-ray diffractometer (Germany). After the mechanical activation, the powders were examined by IR spectroscopy on an IR Fourier spectrometer (Thermo Fisher Scientific Inc, U.S.).

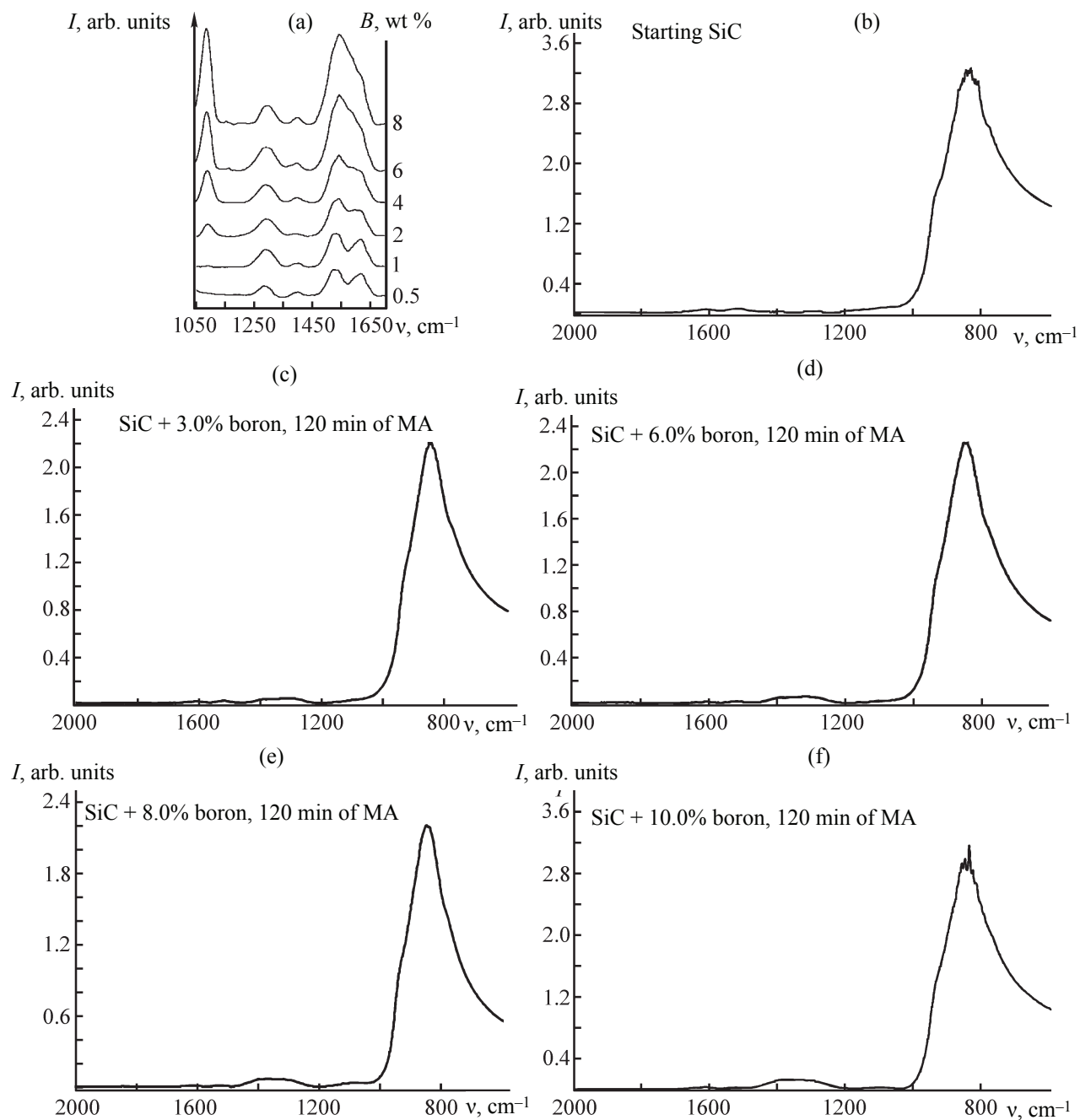
Powder mixtures based on silicon carbide were consolidated in an installation for hybrid spark-plasma sintering (H-HPD 25-SD, FAST/SPS + induction heating), fabricated by FCT company under order from All-Russian Scientific Research Institute of Aviation Materials (project 8598-VIAM). The powders obtained upon mechanical activation were placed in a graphite die mold with inner diameter of 31.5 mm. To exclude any contact between the powder and the die mold and safely extract the finished sample, the inner surface of the mold was covered with a graphite foil. The consolidation rate was 50 to 100 deg  $\text{min}^{-1}$ , the maximum sintering temperature was 1750°C, and the maximum compaction pressure, 47 kN. The time of keeping at the maximum temperature was varied from 5 to 25 min.

The apparent density of the consolidated samples was determined by hydrostatic weighing. The Vickers hardness was measured with an HV-1000 microhardness meter (TIME Group, China) under a load of 1 kg. The crack-resistance coefficient was determined by the Nihara method [22]. Under indentation with a Vickers pyramid, the crack resistance of a material is found as

$$K_{\text{IC}} = 0.048 \left( \frac{l}{a} \right)^{-0.5} \left( \frac{H_V}{E\Phi} \right)^{-0.4} \frac{H_V a^{0.5}}{\Phi}, \quad (1)$$

where  $\Phi$  is a constant ( $\Phi \approx 3$ );  $H_V$ , microhardness (Vickers hardness) (GPa);  $E$ , elasticity modulus (GPa);  $l$ , average length of radial cracks appearing near the indentation of the indenter (Vickers pyramid), measured from the indentation corner ( $\mu\text{m}$ ); and  $a$ , length of the half-diagonal of the indentation made by the Vickers pyramid.

The grain size and other structural parameters were determined with a Jeol JSM-6490LV scanning electron microscope (Japan).

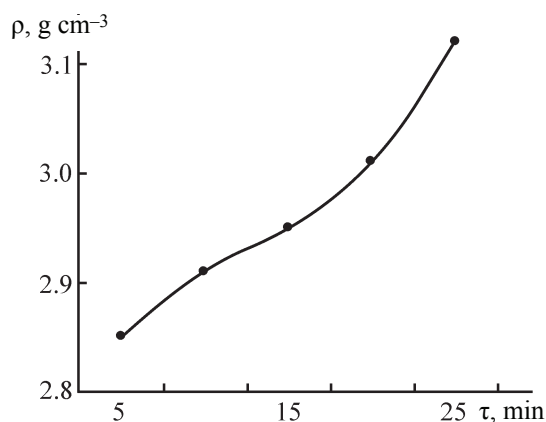


**Fig. 1.** IR spectra of (a) mixtures without preliminary MA [4] and (b) starting ground SiC powder prior to MA. MA of mixtures with 3, 6, 8, and 10 wt % boron (c, d, e, f, respectively). (*I*) Intensity and (*v*) wave number.

### RESULTS AND DISCUSSION

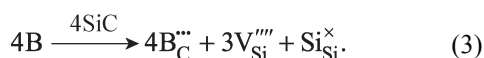
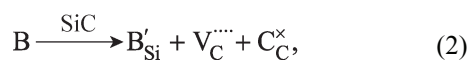
The content of the main substance in the industrial silicon carbide powder of F-1000 brand is more than 99.6 wt % (Table 1). SiC is represented by two polytypes, hexagonal (6H-SiC) and rhombohedral (15R-SiC).

After 10 wt % boron was introduced, the spectrogram (Fig. 1f) contained no peaks associated with the phase of crystalline boron carbide, in contrast to the results presented in Fig. 1a, where boron carbide is formed even upon introduction of the additive in an amount of 2 wt %. This is confirmed by the sharp change in the intensity of



**Fig. 2.** Variation of the density  $\rho$  of samples containing 8 wt % boron with increasing keeping time at the maximum temperature. ( $\tau$ ) Time.

the peak at  $1080\text{ cm}^{-1}$ . Upon MA of mixtures with 3, 6, 8, and 10 wt % boron, a halo appears at  $1200\text{--}1450\text{ cm}^{-1}$ , which is not characteristic of the silicon and boron carbide phases. This compound is a separate phase different from both SiC and  $\text{B}_4\text{C}$  phases, which can be defined as a solid solution of boron in silicon carbide, formed by the reactions



Analysis of the spectrograms of reference mixtures and those obtained in the present study shows that the mechanical activation method is promising for introduction of high boron concentrations into silicon carbide.

To examine how the keeping time at a temperature of  $1750^\circ\text{C}$  affects the degree of sintering of ceramic materials, the silicon carbide powder with 8 wt % boron was consolidated at keeping durations of 5, 10, 15, 20,

and 25 min. The results of calcination at different keeping durations are presented in Fig. 2.

As the keeping duration is raised, the density of silicon carbide samples with 8 wt % boron steadily grows (Fig. 2) and reaches a value of  $3.12\text{ g cm}^{-3}$ , which is close to the theoretical density of SiC ( $\rho_{\text{theor}} = 3.21\text{ g cm}^{-3}$ ), after keeping at  $1750^\circ\text{C}$  for 25 min.

A study of the microstructure of silicon carbide samples with 8 wt % boron, consolidated at various keeping times (Fig. 3), demonstrated that an increase in the keeping duration leads to an insignificant growth of fine grains, with no rise in size observed for coarse grains present in the system. The particle morphology is preserved, and fine particles are not dissolved. This may indicate that there is no liquid phase via which a substance transfer is possible from convex parts and small crystals (i.e., their dissolution) to more planar (or concave) parts and large crystals. A closed intercrystallite porosity about  $1\text{ }\mu\text{m}$  in size remains upon annealing at a temperature of  $1750^\circ\text{C}$ .

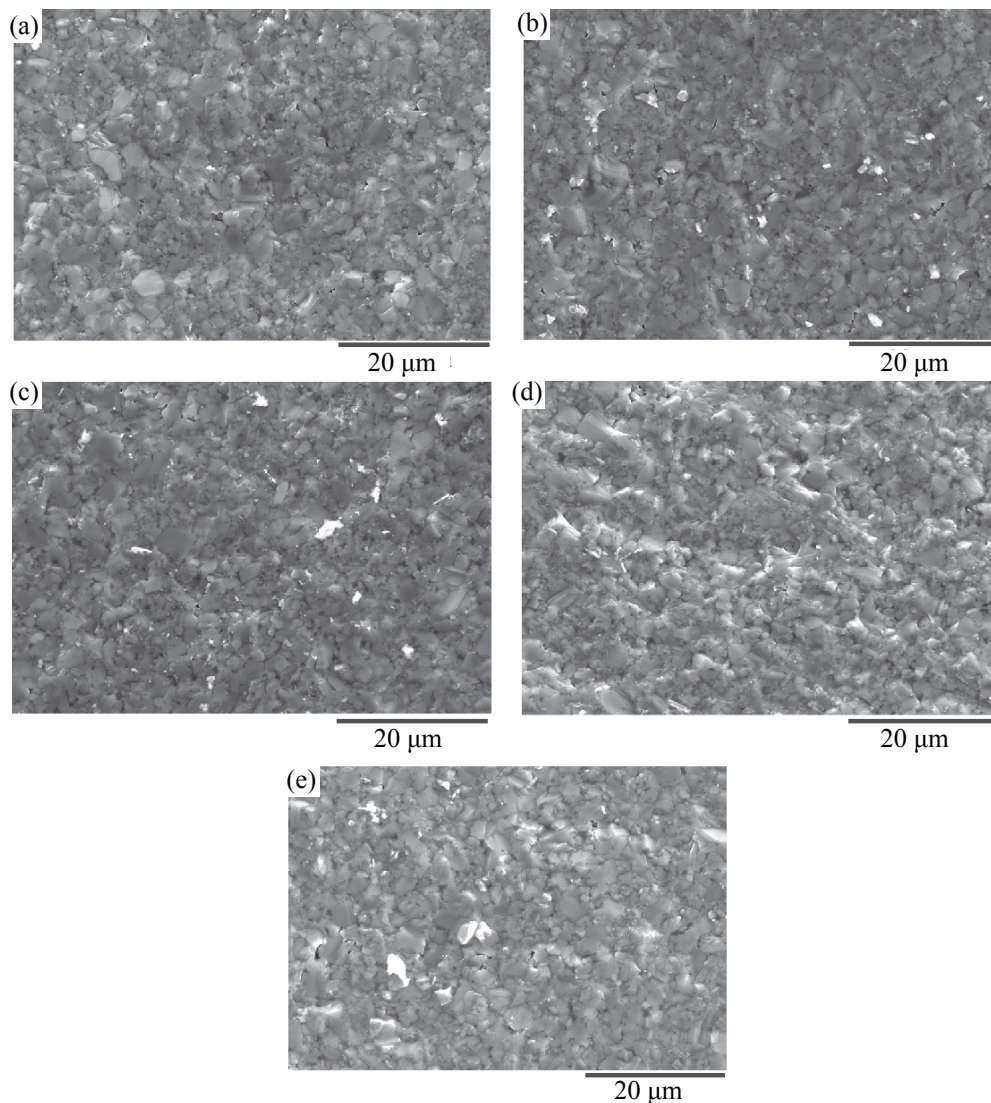
An elemental analysis of the microstructure (Fig. 4) demonstrated the presence of silicon, carbon, and boron in the system. A decrease in the content of silicon within a grain is observed, which may be due to its substitution with boron and formation of a substitutional solid solutions by reaction (2).

To determine how the amount of the boron additive affects the physicomechanical of the ceramic composite material of silicon carbide with 3, 6, 8, and 10 wt % modifier, the mixtures were subjected to modification at a temperature of  $1750^\circ\text{C}$  under a pressure of 47 kN for 25 min. The obtained density, hardness, and crack resistance are demonstrated in Table 2 and Fig. 5.

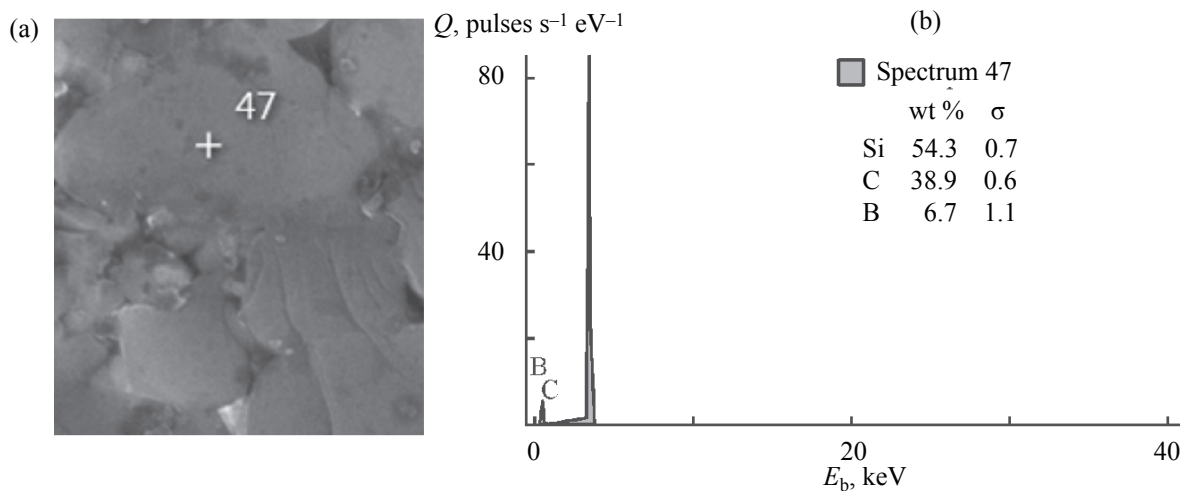
Analysis of how the density varies with increasing boron concentration (Fig. 5a) enables a conclusion that introduction of a large amount of boron results in that the density of silicon carbide grows. This may be due to

**Table 2.** Density, hardness, and crack resistance of consolidated samples with varied content of boron

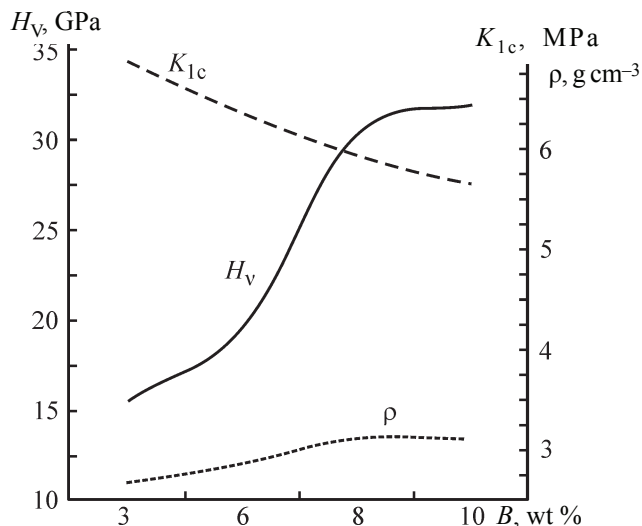
Run no.	System	$\rho$ , $\text{g cm}^{-3}$	Hardness $H_V$ , GPa	$K_{Ic}$ , $\text{MPa m}^{1/2}$
1	SiC + 3 wt % B	2.67	$15.5 \pm 1.1$	$6.88 \pm 0.46$
2	SiC + 6 wt % B	2.87	$19.6 \pm 0.6$	$6.36 \pm 0.40$
3	SiC + 8 wt % B	3.12	$30.3 \pm 0.6$	$5.93 \pm 0.40$
4	SiC + 10 wt % B	3.12	$31.9 \pm 0.5$	$5.65 \pm 0.32$



**Fig. 3.** Cross-sectional micrographs of silicon carbide samples with 8 wt % boron, produced by the SPS method at keeping durations of (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 min.



**Fig. 4.** Elemental analysis of the microstructure of a silicon carbide sample with 8 wt % boron, produced by the SPS method at a temperature of 1750°C and keeping duration of 25 min. (*Q*) Intensity and (*E<sub>b</sub>*) binding energy.



**Fig. 5.** Influence exerted by the amount  $B$  of the boron additive on the density  $\rho$ , hardness  $H_V$ , and crack-resistance coefficient  $K_{1c}$  of samples of SiC-based ceramic materials.

the formation of a solid solution in which boron mostly substitutes silicon and crystal-lattice defects are formed as carbon vacancies. The number of the vacancies being formed is directly proportional to the content of boron in the system. This is so because IR spectroscopy demonstrated that the intensity of the peak associated with the new compound of boron with silicon carbide grows (Fig. 1), and, consequently, so does the amount of this compound in the system.

The substitution of silicon with boron occurs on the surface, as shown in [23], and lowers the surface energy and the activation energy of the atomic diffusion, which leads to a decrease in the activation energy of the sintering process [12].

The maximum density of 3.12 g cm<sup>-3</sup> is reached on introducing 8 wt % boron and remains unchanged on raising the boron content to 10 wt %, which indicates that a dense-sintered skeleton is formed. On passing to the high-density state, i.e., when the density exceeds 95% of the theoretical value, the hardness becomes higher due to the increasing volume fraction of connections between pores. The increase in the hardness of the dense-sintered material from 30.3 to 31.9 GPa upon introduction of 10 wt % boron can be accounted for by the growth of silicon carbide crystals, which is confirmed by the results obtained in determining the crack-resistance coefficient. The values of  $K_{1c}$  decrease with increasing content of boron due to the change of the destruction mechanism of the material from the intercrystallite to the transcrystallite

type. In the case of the intercrystallite mechanism, the crack-propagation resistance can be accounted for by the development of a porous structure in which the energy of a crack is expended for its transfer along grain boundaries, where stresses are concentrated. The development of a denser structure leads to a decrease in the number of stress concentrators in the form of micropores at grain boundaries, which facilitates the recrystallization in the final stage of sintering. This, in turn, results in that the material disintegrates by the transcrystallite mechanism, i.e., with a crack propagating across grains of the sintered skeleton. With this mechanism, the crack propagation path becomes shorter and the material is disintegrated under a lower external impact.

## CONCLUSIONS

(1) The mechanical activation used in the stage of mixing of silicon carbide and boron powders makes it possible to raise the content of the additive being introduced to 10 wt % without precipitation of crystalline compounds of boron with carbon and silicon.

(2) Raising the amount of the boron additive favors densification of silicon carbide to its high-density state at a temperature of 1750°C by the diffusion sintering mechanism in which the main role is played by defects in the form of vacancies. The formation of a solid solution can intensify the sintering due to its segregation on the grain surface, which makes lower the surface energy and the activation energy of the atomic-diffusion process.

(3) Introduction of boron leads to growth of fine grains due to the segregation of the solid solution being formed, which, in turn, favors a decrease in the surface energy of the grains. In this case, no noticeable growth of coarse grains is observed because of the low curvature and, consequently, small driving force of the recrystallization process.

(4) The spark-plasma-sintering treatment at a temperature of 1750°C with keeping for 25 min makes it possible to obtain a high-density material based on silicon carbide with 10 wt % boron and the following properties: Vickers hardness 31.9 GPa and crack-resistance coefficient 5.65 MPa m<sup>1/2</sup>.

## ACKNOWLEDGMENTS

The study was carried out in the framework of implementation of integrated avenue of research 14.1 :

Ceramic composite construction materials (“Strategic areas of development of materials and their processing technologies for the period of time till 2030”).

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