

HIGH DENSITY BORON CARBIDE CERAMICS

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Porous preforms of $B_4C + C$ and $B_4C + C + Si$ materials were impregnated by liquid (molten) silicon to obtain high-density product with a relative density of 99.0 % and porosity of 0.9%. Silicon impregnation was carried out by saturating the samples through the pores of the $SiC + C$ sacrificial preforms. This method allows to reduce both the dissolution of boron carbide grains in the silicon solution and the formation of the $B_{12}(C, Si, B)_3$ phase. This reduces the fragility of the product and thereby improves the mechanical characteristics of the B_4C ceramics.

Keywords: reaction-bonded boron carbide (RBBC), silicization, sacrificial preforms, silicon carbide, molten silicon.

INTRODUCTION

Boron carbide is a unique material combining low density ($\rho = 2.51 \text{ g/cm}^3$) and a low thermal coefficient of linear expansion (TCLE) ($4.35 \times 10^{-6} \text{ K}^{-1}$) with high hardness ($H_{\mu} = 49 \text{ GPa}$), which makes it usable as structural material in engineering, space, nuclear and other industries, as well as in the production of armored materials [1]. Dense boron carbide materials are obtained by hot pressing boron carbide powder (with a dispersion of $0.5 - 2.0 \mu\text{m}$) with solid nanoscale activators (B–C, Al–C, B_4C , etc.) in an amount of $1 - 3 \text{ vol.}\%$ [2 – 4]. However, despite the low density ($\rho = 2.55 \text{ g/cm}^3$) and high mechanical properties ($\sigma_{fl} = 380 - 400 \text{ MPa}$, $K_{Ic} = 3.5 - 3.8 \text{ MPa}\cdot\text{m}^{1/2}$, $HV 33 - 35 \text{ GPa}$ [5]), hot pressing has a number of disadvantages associated with the use of equipment consuming lots of power, the inability to obtain products of complex geometric shape without additional machining, the need for micro- and nanoscale raw powders and high temperatures of the hot-pressing process ($T = 2100 - 2150^\circ\text{C}$) [6].

In recent years, manufacturing of reaction-bonded materials by impregnating porous boron carbide preforms with molten silicon [7 – 11], which is analogous to the method of

reactive sintering (silicification) of materials based on silicon carbide [12 – 14], has been widely developed. Reactive-sintered silicon carbide materials (SiSiC) are obtained by impregnating porous preforms consisting of multifraction powders of silicon carbide and carbon black (fraction 1 consists of a powder with a size range of $20 - 50 \mu\text{m}$, fraction 2 — of $3 - 10 \mu\text{m}$ and, if necessary, fraction 3 — of $0.8 - 5.0 \mu\text{m}$) with molten silicon. Silicon dissolves carbon in its composition, saturating the melt to the solubility limit of silicon carbide in silicon, then crystallizes as a secondary β -SiC phase on the surface of the primary grains of silicon carbide [15]. The SiSiC materials obtained are nonporous and exhibit increased brittleness (because of the significant content of free silicon in the sintered material – $10 - 15 \text{ vol.}\%$), which significantly reduces the basic mechanical characteristics: $\sigma_{fl} = 320 - 360 \text{ MPa}$, $K_{Ic} = 3.0 - 3.5 \text{ MPa}\cdot\text{m}^{1/2}$, $HV 20 - 21 \text{ GPa}$ [12 – 14].

A similar technology for producing reaction-bonded boron carbide (RBBC) has a number of features. In particular, boron carbide is highly reactive in molten silicon, which leads to the formation of a more brittle $B_{12}(C, Si, B)_3$ phase on the surface of B_4C grains [15], which significantly reduces mechanical properties (in particular, $HV 22 - 24 \text{ GPa}$), in contrast to the high values of hot-pressed materials ($IV 33 - 35 \text{ GPa}$) [5]. The traditional method of obtaining RBBC materials is to impregnate the preforms with excess silicon, which increases the volume of dissolved grains of boron carbide and increases the content of free silicon in the sintered material, and, consequently, leads to an increase in brittleness of the ceramic.

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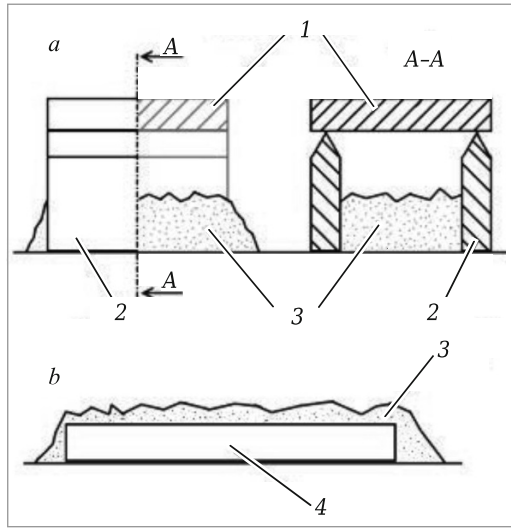


Fig. 1. Schematic of the experimental (a) and traditional (b) method of obtaining RBBC materials for silicization: 1 — (B₄C + C) or (B₄C + Si + C) sample; 2 — sacrificial preform; 3 — silicon; 4 — (B₄C + C) sample.

The purpose of this work is to study new aspects of obtaining RBBC materials, consisting in impregnating porous materials through channels of sacrificial porous preforms, studying the structure, phase composition and physical characteristics of the obtained sintered materials.

MATERIALS AND METHODS

As the initial components, boron carbide powders with $d_{0.5} = 42.0 \mu\text{m}$ (B₄C_{lg}) and $d_{0.5} = 2.5 \mu\text{m}$ (B₄C_{sm}), K-354 grade carbon black and Lg00 grade silicon crushed to $d_{0.5} = 1.0 \mu\text{m}$ were used. The composition of the materials is given in Table 1. The starting powders in the desired ratio (Table 1) were mixed in a drum mixer for 20 hrs, the powders were plasticized and granulated. From the mixtures, specimens of dimensions 50 × 50 × 8 mm were pressed by semi-dry molding at a pressure of 100 MPa, dried and subjected to silicification. The samples were placed on the tip of

TABLE 1. Initial Composition of Preforms of the Investigated RBBC-Materials.

Composition number	Content of the material, wt.%, in the composition of the workpiece			
	B ₄ C _{lg}	B ₄ C _{sm}	carbon black	Si
1	60	25	15	—
2	56	24	15	5
3*	60	25	15	—

* RBBC-materials obtained by the traditional reaction bonding method.

the sacrificial preforms (in the form of triangular or 5-facet prisms), between which grits of silicon were poured. Silicon, infiltrating the sacrificial preforms of (SiC + C), saturated them and diffused through the pores into the porous boron carbide samples. An illustration of the setup of samples for silicization is shown in Fig. 1a. This method of producing boron carbide materials reduces the amount of free silicon in the sintered ceramic, reduces its brittleness and increases its mechanical properties, and also reduces the cost of sand-blasting. For comparison of the properties, samples were prepared according to the traditional technology of reaction bonding (composition 3, see Table 1) – direct impregnation of a porous preform with excess silicon (Fig. 1b).

It has been shown [15] that for the Si (L) + C (s) > SiC (s) reaction to take place in SiSiC when 15 wt.% of carbon black is introduced, the apparent density ρ should be 2.37 g/cm³ for $\Pi = 25.9\%$, as calculated according to the equation

$$\rho = \frac{3.21}{1 + 2.33 \cdot x_C}, \tag{1}$$

where x_C is carbon content in the preform, expressed in weight fractions; 3.21 and 2.33 are the density of silicon carbide and silicon, respectively. However, in real conditions, the manufactured preforms have $\rho = 2.20 - 2.22 \text{ g/cm}^3$, which corresponds to $\Pi = 31.0 - 31.5\%$. The discrepancy between the calculated and practical values of porosity (under the condition of a finite non-porous material) is compensated by a high content of free silicon (up to 10 – 15 vol.%).

Assuming the reaction $3\text{B}_4\text{C} (\text{s}) + \text{Si} (\text{L}) > \text{SiC} (\text{s}) + \text{B}_{12}(\text{C}, \text{Si}, \text{B})_3$ is possible, it is possible using equation (1) to calculate from the density of SiSiC the density of the RBBC preforms optimal for the silicization process

$$\rho = \frac{2.73}{1 + 2.33 \cdot x_C}, \tag{2}$$

$$\rho = \frac{2.76}{1 + 2.33 \cdot x_C}, \tag{3}$$

where 2.73 and 2.76 are the calculated densities of the materials under study in accordance with compositions 1 and 2 in Table 1.

Based on the calculation of the density values according to equation (2) for compositions 1 and 3, the calculated density of preforms should be 2.02 g/cm³, which corresponds to $\Pi = 26.0\%$. Composition 1 preforms obtained in this work had $\rho = 1.90 \text{ g/cm}^3$ ($\Pi = 30.4\%$), which, with the traditional reaction-bonding method (impregnation with excess silicon), leads to a significant dissolution of B₄C grains in the liquid molten silicon and the formation of a negative phase B₁₂(C, Si, B)₃. The dosed amount of silicon entering the preform in accordance with the impregnation method shown in

Fig. 1a limits the formation of the brittle $B_{12}(C, Si, B)_3$ phase and, consequently, improves the mechanical properties if the materials compared to RBBC materials manufactured by the traditional method [7–11].

The situation is similar when calculating the density and porosity of composition 2 preforms according to equation (3): $\rho = 2.04 \text{ g/cm}^3$, $\Pi = 25.9\%$. In practice, it is possible to achieve the following characteristics: $\rho = 1.89 \text{ g/cm}^3$, $\Pi = 31.5\%$. To increase the density of preforms, it is necessary to use submicron fractions of B_4C powder and to increase the molding pressure, which can lead to the formation of transverse cracks that destroy the material.

The samples were sintered in a vacuum oven at 1600°C for 10 min. Excess silicon on the surface of composition 3 samples was removed by sandblasting. The density and porosity of the sintered samples were determined by hydrostatic weighing. The relative density was calculated from the theoretical density. X-ray phase analysis (XRD) was carried out using a Rigaku Smartlab 3 unit. The elastic modulus was determined by the dynamic method on a ZVUK-230 device, measuring the resonance frequency of longitudinal vibrations. The microstructure of the samples was examined on an optical microscope Techno Meiji IM 7200 and on an electronic scanning microscope (SEM) Quanta 200. The research equipment was provided by the SPbGTI (TU) Engineering Center.

RESULTS AND DISCUSSION

In the sintering of SiSiC materials, silicon, which absorbs into the porous preform, dissolves carbon, saturating the melt to the limit of solubility of silicon carbide in silicon, then the secondary silicon carbide (SiC^{II}) phase of the cubic modification (β -SiC) crystallizes on the surface of the primary grains (SiC^I) [16–18]. RBBC material sintered according to conventional reaction sintering technology is characterized by the presence of B_4C grains, the SiC^{II} phase partially dissolved in silicon, and the phase of silicon solid solution in boron carbide $B_{12}(C, Si, B)_3$, crystallized on the grains of boron carbide in dense annular layers. Such material structure is referred to as “core-shell” [19–22]. The grains of the original boron carbide play the role of the “core”, and the “shell” is the phase of silicon solid solution in boron carbide, interconnected to form a 3-dimensional matrix. The dense phase of $B_{12}(C, Si, B)_3$ prevents the movement of silicon deep into the porous preform, so increased porosity is characteristic for RBBC materials manufactured by the traditional method. To increase the contact of silicon with carbon particles, 5 wt.% silicon powder ($d_{0.5} = 1.0 \mu\text{m}$) was added to the composition 2 material (see Table 1).

The presence of Si, $B_{12}(C, Si, B)_3$, β -SiC phases and a small amount of boron carbide in the material, as shown earlier [7–11], was confirmed by the results of XRD analysis of the composition 3 sample (Fig. 2, 3). High intensity of the silicon peaks indicates its high content in the sintered mate-

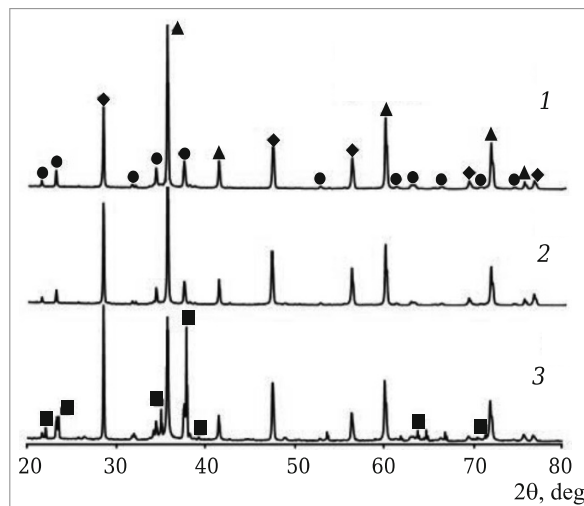


Fig. 2. X-ray diffraction patterns of materials of compositions 1–3 (see Table 1): ● $B_{12}(C, Si, B)_3$; ◆ Si; ▲ β -SiC; ■ B_4C .

rial. A lower content of silicon (the intensity of the Si peaks is smaller) was recorded in the material of composition 1. Due to the dosed (optimal) amount of silicon entering the preform, the content of the $B_{12}(C, Si, B)_3$ phase is lower (Fig. 2, 1). Silicon is easily absorbed into the porous preform, partially dissolving B_4C grains and forming thin layers of the $B_{12}(C, Si, B)_3$ phase on their surface (unlike in the case of the composition 3 material). Most of the incoming silicon dissolves carbon or partially dissolves boron carbide to form the β -SiC phase (the intensity of the β -SiC peaks is higher than for the material of composition 3). Most likely, B_4C grains dissolve less in the material of composition 1 than in a RBBC sintered by the traditional method (composition 3). Due to dosed impregnation, liquid silicon dissolves the surface layers of boron carbide grains by saturating the melt with carbon to form secondary β -SiC. In the material of composition 3, a deeper dissolution of boron carbide grains occurs in the upper layers of the sample preform, which makes it difficult to completely saturate the material (including the bulk volume) with molten silicon and, therefore, to achieve high density (close to theoretical). When 5 wt.% Si is introduced into the starting material (composition 2), Si and β -SiC are also present in the sintered sample (Fig. 2, 2). The intensity of the peaks corresponding to the $B_{12}(C, Si, B)_3$ phase decreases, and of the peaks corresponding to the secondary silicon carbide phase – increases.

The density of the obtained materials (compositions 1 and 2) is higher than the density of RBBC sintered according to the traditional reaction bonding method (Table 2). The sacrificial sample material (5-facet prism of composition SiC + C) is silicated to $\rho = 99.4 – 99.6\%$. Due to poor impregnation of the porous preforms with molten silicon, the composition 3 samples do not reach a high density.

Figure 3 shows the microstructure of RBBC materials. The microstructure of the composition 1 material is charac-

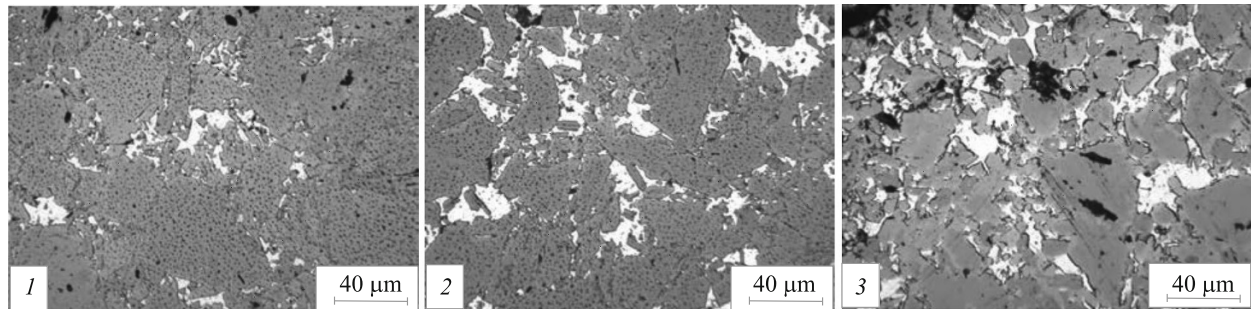


Fig. 3. Microstructure of the materials of compositions 1 – 3: gray) grains of boron carbide with a surface layer of silicon solid solution in B_4C ; white) silicon and secondary silicon carbide.

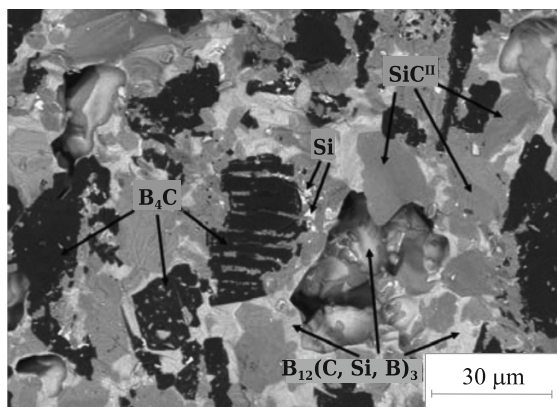


Fig. 4. Microstructure of the material of composition 3.

terized by the presence of large grains of boron carbide, $d_{0.5} = 39.5 \mu\text{m}$ (see Table 2), which even in the presence of a surface layer (phase $B_{12}(C, Si, B)_3$) indicates low dissolution of B_4C grains in molten silicon (see Fig. 3, 1). The introduction of additional Si into the material increases the solubility of B_4C grains ($d_{0.5} = 31.8 \mu\text{m}$) to form the $B_{12}(C, Si, B)_3$ phase (see Fig. 3, 2). The greatest dissolution of grains is characteristic of the material of composition 3 ($d_{0.5} = 22.3 \mu\text{m}$). Porosity is observed in the zones of weak bonding of molten silicon with B_4C grains (see Fig. 3, 3). On the surface of B_4C grains without access to silicon, the $B_{12}(C, Si, B)_3$ phase does not form, and consequently, XRD of materials with high porosity (composition 3) indicates the presence of B_4C (see Fig. 2, 3). The resulting SEM photograph of the RBBC microstructure (Fig. 4) demonstrates the presence of B_4C , $B_{12}(C, Si, B)_3$, SiC^{II} (β -SiC), and Si phases and pores in the material, confirming the conclusions drawn from the optical microscope microstructure analysis (see Fig. 3).

The method used in this work to impregnate porous preforms with molten silicon through the pores of sacrificial samples makes it possible to obtain high-density ($\rho_{\text{rel}} = 99.0\%$) materials based on boron carbide, which, presumably, will have an increased level of mechanical characteristics compared to materials obtained by the traditional technology of impregnating with excess silicon.

TABLE 2. Properties of Reaction-Bonded Boron Carbide Ceramics.

Composition number	Density ($\rho \pm 0.02$), g/cm^3	Relative density ($\rho_{\text{rel}} \pm 0.1$), %	Porosity ($(\Pi \pm 0.1)$, vol.%)	B_4C grain size ($d_{0.5}$), μm
1	2.70	99.0	0.9	39.5
2	2.72	98.7	1.2	31.8
3	2.55	93.5	6.4	22.3

CONCLUSION

1. By impregnating porous preforms of ($B_4C + C$) and ($B_4C + Si + C$) with molten silicon through the pores of sacrificial samples of the composition ($SiC + C$), high-density materials ($\rho_{\text{rel}} = 99.0\%$) with low porosity ($\Pi = 0.9\%$) were obtained.

2. The structure of the obtained materials is represented by large grains of boron carbide, which are close in size to the original ones, which characterizes their lower solubility in molten silicon in comparison with materials obtained by the traditional technology of impregnating with excess silicon.

3. The proposed sintering method makes it possible to obtain boron carbide ceramics with a reduced content of free silicon and the $B_{12}(C, Si, B)_3$ phase, which strengthens the material and, as a result, improves its mechanical properties.

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