INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of Polydisperse Boron Carbide
and Synthesis of a Ceramic on Its Basis

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Abstract—Results obtained in a study of the process of synthesis of a polydisperse boron carbide powder (average particle size 2.10 μm) characterized by a broad particle size distribution are presented. The process in which a ceramic is produced from the thus synthesized boron carbide by hot compaction was also analyzed. In some cases, a sintering additive, highly dispersed chromium carbide powder (average particle size 7.13 μm), was used. The hot compaction was performed in argon at moderate parameters: pressure 35 MPa and temperature 1950°C. The porosity and water-absorption capacity of the samples obtained are very low and do not exceed 0.02%. The average values of the bending and compression strengths were 406 and 1553 MPa, respectively. A microhardness of about 42 GPa was reached in sintering of boron carbide. The microhardness in sintering of boron carbide with addition of chromium carbide was 45–46 GPa.

Keywords: boron carbide, chromium carbide, nanofibrous carbon, hot compaction, sintering additive, microhardness

Boron carbide $B_{12}C_3$ (B_4C) has a high melting point, considerable hardness, low density, and chemical inertness, being widely used for these reasons in modern technology [1, 2]. For example, it is used as an abrasive in free grinding and polishing. Boron carbide also serves for fabrication of wear-resistant articles, light-weight ceramic armor, and retarding rods in nuclear power engineering.[1]

Boron carbide can be obtained in the following ways: carbothermic reduction of boron oxide [3–7], magnesium-thermic reduction of boron oxide in the presence of carbon [8–10], vapor-phase deposition [11], and synthesis from elements [12–15].

In the carbothermic synthesis, the high temperature of the process leads to a noticeable evaporation of boron oxide [16]. As a result, difficulties are encountered in calculating the stock, and the product obtained contains an admixture of free carbon. The sol-gel method is a variety of this technique. However, sol-gel processes take a long time and occur in multiple stages, with the reagents used frequently being toxic. In the magnesium-thermic synthesis, the process is forcedly performed in argon at its high pressure to suppress the high volatility of magnesium (boiling point 1108°C)[2]. In addition, it becomes necessary to purify the target product by an acid treatment to remove magnesium compounds. In the plasma-chemical synthesis

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[1] Properties, Production, and Use of High-Melting Compounds: Reference Book, Kosolapova, T.Ya., Ed., Moscow: Metallurgiya, 1986, p. 887.

[2] Properties of Elements: Reference Book, Drits, M.E., Ed., Moscow: Metallurgy, 1985, p. 98.

of boron carbide (which is a variety of the vapor-phase deposition), boron chloride serves as a source of boron. That is why the effluent gases contain toxic compounds of chlorine. In these processes, there is a substantial expenditure of the plasma-forming gas, hydrogen (which is combustible and, as a consequence, explosive). In syntheses of high-melting compounds (including boron carbide) from elements, there hardly are any reagents in the reaction products under the optimal conditions. Because there are no contaminations in the process, the impurity-related purity of the product is approximately equal to that of the reagents, and, therefore, it may be very high. Boron carbide of this kind is a promising material for obtaining a high-quality ceramic.

Using boron carbide in the form of articles is hindered by the difficulty in obtaining a high-density ceramic, which is due to the strict directedness of interatomic bonds in this compound, high resistance of boron carbide to plastic deformation, and low self-diffusion [1]. Ceramics based on boron carbide are produced by the conventional hot-compaction and reactive-sintering methods [17] and by the comparatively new method of electric-pulse plasma sintering (EPPS) [18]. It should be noted that its instrumentation is more complex than that of the conventional techniques.

The fabrication of a dense ceramic based on boron carbide is facilitated by using sintering additives. As sintering additives can serve high-melting oxides of rare-earth metals: Dy_2O_3, Eu_2O_3, and Sm_2O_3 [19], and high-melting oxygen-free compounds chromium diboride CrB_2 [20], titanium diboride TiB_2 [17], and chromium carbide Cr_3C_2 [21]. In [21], the ceramic was fabricated by the reactive sintering. At a temperature of 2070°C and chromium carbide content in the stock of 20 wt %, the sample density reached 95% of the theoretical value. Also, it is possible to use metallic alloys as sintering additives: silicocalcium [22] and alloys of silicon with aluminum [23]. These additives make the ceramic denser due to the formation of intermediate compounds that are in the liquid phase at the sintering temperature. However, use of these alloys causes a substantial grain growth, which impairs the crack resistance of articles. It should be noted that silicon alloys with aluminum and calcium are easily fusible. For silicocalcium with 20 wt % calcium, the liquid phase is formed at 760°C, for alloys of the Si–Al system, it appears nearly at any composition at 577°C.[3] Therefore, articles

fabricated with these sintering additives cannot be used at high temperatures.

It should be noted in view of the aforesaid that published data on how the type of a carbon material affects the synthesis parameters from elements and, especially, its characteristics are scarce. In particular, nearly no information is available about application of nanofibrous carbon (NFC) produced in catalytic pyrolysis of light hydrocarbons as a reagent of this kind [24]. At the same time, it has been found that the NFC is an effective reagent for synthesis of, e.g., a highly dispersed zirconium carbide powder with broad particle size distribution [25]. In addition, there is absolutely no information about application of such a boron carbide powder for fabrication of ceramics.

The goal of our study was to examine the process in which boron carbide is synthesized from elements with the NFC as a carbon material, with the subsequent sintering by hot compaction of the thus synthesized boron carbide, and to examine some characteristics of the resulting ceramic.

EXPERIMENTAL

Nanofibrous carbon is constituted by 4–8-mm granules formed by closely woven fibers with diameter of 30–100 nm. The NFC is sufficiently pure: the impurities it contains are residual amounts of the starting catalyst (90 wt % Ni/10 wt % Al_2O_3); their content does not exceed 1 wt %. To be used in a synthesis, the NFC was ground into a powder in an agate mortar and sieved through sieve with 100-μm mesh. The specific surface area of the NFC is approximately 150 m^2 g^{-1}, which substantially exceeds that of the lamp black (~75 m^2 g^{-1}) [24, 26]. As the other reagent served amorphous boron of B-99V brand [TU (Technical Specification) 1-92-154–90], which contained more than 99 wt % boron. Therefore, it would be expected that high-purity boron carbide should be obtained with these reagents. Prior to being used, both the reagents were kept in a furnace at 100°C to remove moisture.

Amorphous boron and NFC were mixed in 79 : 21 mass ratio (41 : 10 molar ratio) to obtain boron carbide of composition $B_{4.1}C$, and the mixture was sieved through a sieve with 100-μm mesh. The components were mixed in an AGO-2S planetary ball mill at an acceleration of 20 g, mixing duration of 5 min, and charge to ball mass ratio of 8 : 150.

[3] Constitution Diagrams of Binary Metallic Systems: Reference Book in 3 vols., Lyakishev, N.P. Ed., Moscow, Mashinostroenie, 1996, vol. 1, pp. 124 and 820.

In the present study, it was necessary to obtain boron carbide in the powdered state. Therefore, the process temperature should be certainly lower than the melting point of boron carbide (2450°C) [1]. The melting points of the starting reagents (boron and carbon) are 2075 and 4000°C, respectively.[4] Therefore, the carbide-formation reaction will be of the solid-phase type at the process temperature below 2075°C. It is known [1] that this reaction begins at ~1600°C, but there is no evidence that it can be complete at this temperature. Preliminary experiments demonstrated that, with the stock heated to temperatures of 1600 and 1700°C, the reaction products were X-ray-amorphous at any time of keeping the stock in the reaction space. Therefore, experiments on obtaining boron carbide were performed at a higher temperature, 1800°C. It is necessary to take into account that this reaction is exothermic, and, therefore, the temperature in the reaction zone increases. This temperature, which is adiabatic, was calculated by equating the formation heat of boron carbide to its enthalpy by the procedure reported in [27]. This temperature was, in the case of stock heating to 1800°C, 2494 K = 2221°C. The real process temperature is lower than the adiabatic value and exceeds that instrumentally set in the furnace. With consideration for the loss of heat (predominantly via radiation), it can be estimated at ~1900°C. The experiments on synthesis of boron carbide were performed in an indirectly heated induction furnace. A stock with mass of approximately 10 g was charged into a cylindrical glassy-carbon crucible placed in a quartz reactor. The reactor was mounted in the vertical position in a multiple-coil inductor of the furnace. The process was performed in an inert atmosphere, in a flow of argon. This precluded the undesirable nitrogenation of boron and boron carbide. The temperature calibration was performed against the melting points of manganese sulfide (1615°C) and platinum (1770°C). The presence of boron carbide in the reaction products was determined by X-ray diffraction analysis on a DRON-3 diffractometer with CuKα radiation (λ = 0.15406 Å). The size of crystallites in the boron carbide phase was determined by the Scherrer formula with consideration for the instrumental broadening [28]. The content of impurities in the resulting boron carbide was found by the X-ray fluorescence method on an ARL-Advant'x analyzer with Rh anode of the X-ray tube. The total boron in boron carbide samples was determined via their fusion with soda ash, and the content of boron

as a sum of free boron and boron oxide, via dissolution in a mixture of hydrogen peroxide and nitric acid in conformity with GOST (State Standard) 5744–85. The surface morphology and the particle size of the samples was examined by scanning electron microscopy (SEM) on a Hitachi S-3400N microscope equipped with an Oxford Instruments attachment for energy-dispersive analysis. The specific surface area of the samples was measured on a Quantachrome NOVA 2200e instrument by the method of low-temperature adsorption of nitrogen. The calculation was made by the multiple-point BET method with a Quantachrome™ Nova Win software package. The data obtained were used to estimate from the specific surface area S (m^2 g^{-1}), on the assumption of a spherical shape of particles, their average diameter d (μm):

$$d = \frac{6000}{S\gamma}, \qquad (1)$$

where γ is density (g cm^{-3}).

It is known [1] that the lattice constants of boron carbide depend on its composition. Therefore, we determined the composition of boron carbide by its X-ray diffraction (XRD) analysis by the procedure reported in [29]. X-ray diffraction patterns of a sample (the first at $2\theta = 28–93°$, and the second at $2\theta = 40–130°$) were obtained the Bragg–Brentano configuration on an ARLX'TRA diffractometer. The particle size distribution was determined on a MicroSizer 201 laser analyzer (VA Instruments). A very important parameter of high-melting compounds is their resistance to corrosive media. The thermo-oxidative resistance of the samples was determined by a synchronous thermal analysis on a Netzsch STA 449 C Jupiter instrument.

Experiments aimed to obtain a ceramic from the resulting boron carbide were performed on hot-compaction installation. In some cases, a highly dispersed (average particle size 7.13 μm) powder of higher chromium carbide served as a sintering additive [30]. To determine the bending and compression strengths, a molding powder was originally prepared from the boron carbide powder by the procedure described in [31]. The size of the resulting granules was 200–300 μm. Ceramic samples were fabricated from granulated powders via preliminary molding of raw blanks, performed by cold axial compaction on an EPM-120 mechanical press for double-side compaction. The resulting compacts were poured over with powdered alumina and kept at a temperature of 250°C for 6 h to remove the binder. The subsequent hot compaction was

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[4] Properties of Elements: Reference Book, Drits, M.E., Ed., Moscow: Metallurgiya, 1985, pp. 151 and 197.

performed on a FCT System HPW 400 installation at temperature of 2100°C and pressure of 35 MPa, with the time of keeping equal to 45 min. We determined the porosity and water-absorption capacity of the samples obtained. The samples were used to prepare blanks for determining the mechanical characteristics (bending and compression strengths). All these parameters were determined in conformity with GOST 24409–80. The bending and compression tests with the samples were performed on versatile testing complexes Instron 3366 and Instron 300DX, respectively.

In another set of experiments, we determined the density and microhardness of the hot-compacted ceramic and examined its microstructure. For comparison, not only boron carbide was sintered, but also its mixtures with addition of 6 and 20 wt % chromium carbide. Powders of boron and chromium carbides were dispersed and mixed in acetone and then dried at room temperature for 24 h. Experiments on obtaining a ceramic were performed on a hot-compaction installation designed at the Institute of Automation and Electrometry (IAE), Siberian Branch, Russian Academy of Sciences. The process was carried out in an inert gas (argon) at a compaction pressure of approximately 35 MPa and temperature of about 1950°C. The temperature was chosen with consideration for the fact the sintering of boron carbide at this temperature will be of the solid-phase type, whereas chromium carbide melts[5] at this temperature and thereby provides a liquid-phase sintering. The calculated density of the samples containing chromium carbide was calculated with consideration for the density and content of this compound in the starting stock. The true density of the ceramic was found from the ratio between the mass and volume of a sample. The relative density was determined from the ratio between the true density and that reported in the literature[6] for monolithic articles. Microstructural studies were carried out by SEM on Carl Zeiss EVO 50 microscope for cleaved samples and Hitachi S-3400 N microscope with Oxford Instruments INCA Energy 350 attachment for elemental analysis for ground samples. Because the ceramic is a nonconducting material, magnetron sputtering was used to deposit a layer of a gold–palladium alloy with thickness of 2–3 nm onto
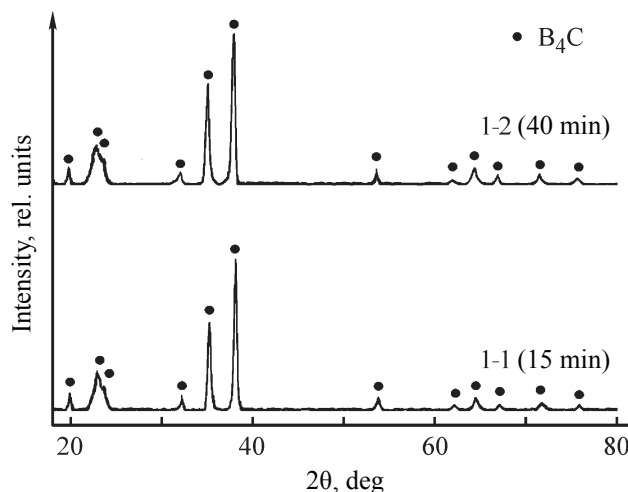

Fig. 1. Diffraction patterns of boron carbide samples.

polished samples. Additionally, the microhardness was determined on ground surfaces. The microhardness was measured in conformity with GOST 2999–75 on a 402 MVD (Wolpert Group) automated microhardness meter under a load of 500 g. To find the average value, no less than five indents were formed on a single sample. Conventionally, this instrument is used to determine the microhardness of not only ceramic materials, but also a number of metal-based alloys [32].

RESULTS AND DISCUSSION

Boron carbide samples were obtained by heating the stock to a temperature of 1800°C for 15 min, with the subsequent keeping for 15 and 40 min (sample nos. 1-1 and 1-2, respectively). After a prescribed heating time ended, the crucible with reaction products was cooled in a flow of argon to room temperature.

X-ray diffraction analysis. The diffraction patterns of sample nos. 1-1 and 1-2, shown in Fig. 1, are nearly identical. The patterns have diffraction peaks of only a single phase, B_4C.

To calculate the average size of crystallites, their values for separate reflections were summed and then divided by the number of peaks for which the calculation was performed. The crystallite sizes in sample nos. 1-1 and 1-2, calculated for the reflections {012}, {104}, and {102} by the Scherrer equation were 17 and 20 nm, respectively.

Determining the elemental composition of the samples. The X-ray fluorescence analysis demonstrated that the content of impurities (Cr, Ni, Fe, Ti, Al, Ca, Si, S, Mn, Cu) in both samples is on the trace level. In sample

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[5] Properties, Production, and Use of High-Melting Compounds: Reference Book, Kosolapova, T.Ya., Ed., Moscow: Metallurgiya, 1986, p. 173.

[6] Properties, Production, and Use of High-Melting Compounds: Reference Book, Kosolapova, T.Ya., Ed., Moscow: Metallurgiya, 1986, p.55.
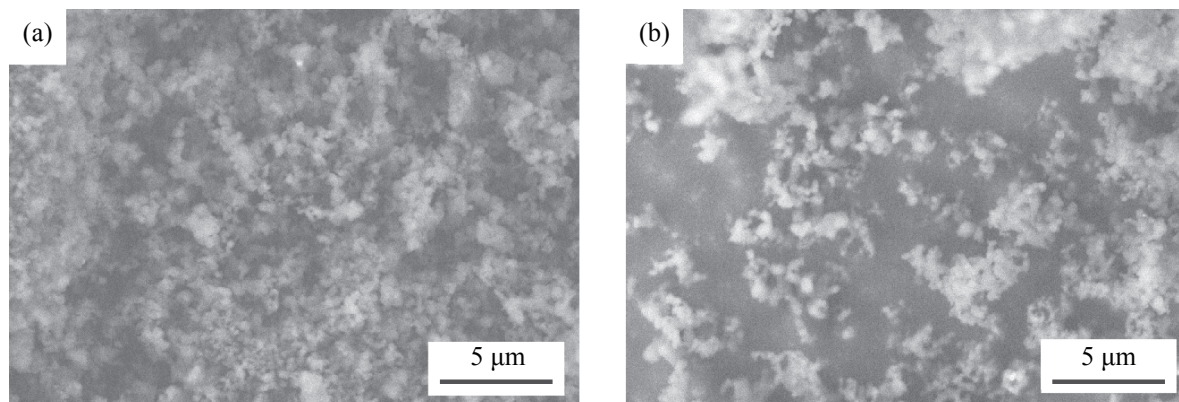
Fig. 2. SEM images of boron carbide sample nos. (a) 1-1 and (b) 1-2.

no. 1-1, the total content of light elements (up to fluorine inclusive) is 98.44 wt %, and that in sample no. 1-2, 99.06 wt %. If we take into account that the synthesis was performed in an inert gas, their substantial content of oxygen and nitrogen in the samples is nearly impossible. Consequently, these values are predominantly related to the total content of boron and carbon. The values of the total content of boron for sample no. 1-1 and 1-2 are nearly the same: 79.38 ± 1.5 and 78.95 ± 1.5 wt %, which is close to the theoretical value (78.26 wt %). The content of boron for the same samples was, as sum of free boron and boron oxide, 0.47 ± 0.1 and 0.45 ± 0.1 wt %.

Electron-microscopic analysis. SEM micrographs of the samples are shown in Fig. 2. According to SEM data, sample nos. 1-1 and 1-2 are highly dispersed homogeneous powders. The particle sizes of the samples do not exceed 1 μm. It can also be concluded that raising the synthesis duration from 15 to 40 min has no significant effect on the size or morphology of the particles obtained.

Results of determining the specific surface area. For sample nos. 1-1 and 1-2, the specific surface areas were 5.4 and 4.2 m^2 g^{-1}. These data were used to estimate, on the assumption of a spherical particle size, the average particle diameter by formula (1) to be 441 and 567 nm, respectively.

Determining the lattice constants of boron carbide. The following rhombohedral-lattice constants were obtained for sample nos. 1-1 and 1-2: a 0.5601 ± 0008 nm and $c = 1.21 ±0.01$ nm. These values correspond to boron carbide of composition $B_{4.00}C$ [1].

Sedimentation analysis. The histogram of the boron carbide sample no. 1-1 is presented in Fig. 3.

The procedure reported in [33] was used to determine by the "geometric" method for sample no. 1-1 the average particle size (2.10 μm), standard deviation (2.47), and the histogram asymmetry parameter (–0.20). It is believed [33] that, at standard deviations in the range 2.00–4.00, the particles are "poorly sorted." Thus, particles of sample no. 1-1 have a broad size distribution (they are polydisperse). In our opinion, this must positively affect the process of obtaining a dense ceramic. The comparatively small value of the degree of asymmetry confirms that the distribution curve is symmetric. The sizes of "primary" particles, estimated from the specific surface area by equation (1), are substantially smaller (441 nm for sample no. 1-1 and 567 nm for sample 1-2).

Thermogravimetric analysis. When heated, boron carbide is oxidized by the most thermodynamically probable reaction [1]:

$$B_4C + 4O_2 = 2B_2O_3 + CO_2. \qquad (2)$$
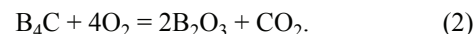
To the full oxidation of boron carbide by this reaction corresponds a gain in sample mass to (140/56) 100 = 250 wt %, i.e., that by 150 wt %.

The derivatograms of the samples are nearly identical. The results of a thermal analysis of sample no. 1-1 are shown in Fig. 4.

The oxidation onset temperature of the sample is ~550°C. The gain in mass for the sample was 218–100 ≈ 118 wt % (fraction of the oxidized carbide: 118/250 ≈ 0.47). Thus, boron carbide is partly oxidized in the temperature range under study. The most probable reason is the protective effect by the liquid film of boron oxide being formed (melting point ~450°C [1]). The absence at 600–700°C of a DSC peak corresponding to the exothermic process accompanied by the loss of mass indirectly confirms the absence of an unreacted carbon
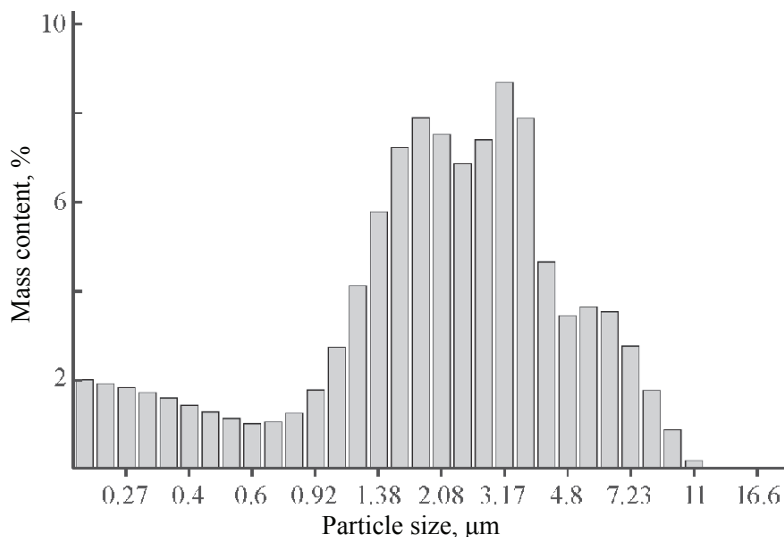
Fig. 3. Histogram for boron carbide sample no. 1-1.

material in the sample. The absence of the exothermic peak at a temperature of ~450°C is indicative of the zero or extremely insignificant content of B_2O_3 in the sample.

Results obtained in determining the porosity, water-absorption capacity, and bending and compression strengths. The values of porosity (0.01–0.02%) and water-absorption capacity (0.01%) of the sintered sample are very small. The bending strengths for five samples subjected to tests were 318, 464, 380, 432, and 437 MPa (arithmetic mean 406 MPa). The compression strengths for eight samples were 2098.9, 1717.1, 2017.6, 1484.2, 1022.5, 1568.9, 1467.0, and 1043.9 MPa (average value 1553 ± 256 MPa). The bending and compression strengths exhibit a wide scatter. A possible reason is that there is no experience in fabrication of a molding powder from a material of this kind. Nevertheless, the obtained average values are rather large. For example, the bending strength of a hot-compacted sample with porosity of 1% was, according to published data, 340 MPa, and the compression strength of samples that were sintered in a vacuum and had various compression strengths were in the range 1100–1660 MPa.[7]

In fabrication of samples on the hot-compaction installation designed at IAE, it was found that the shrinking of a sample (I) composed of only boron carbide begins at a temperature of ~1700°C, and that of samples with a sintering additive of 6 (II) and 20 wt % chromium

carbide (III), at ~1500°C. It is important to note that, according to published data [21], the densification of only boron carbide commenced at a temperature of 1800–1830°C, and, upon addition of 10 wt % chromium carbide, at 1750°C. Because the process was performed below the melting point of boron carbide, the most probable reason for the comparably low shrinking-onset temperature is, in the given case, the polydispersity (broad particle size distribution) of the boron carbide powder, as well as the high dispersity of the powders of boron and chromium carbides. The relative densities of the hot-compacted samples were (%): I 95.0, II 96.0, and III 96.5. Thus, using a sintering additive has nearly no effect on
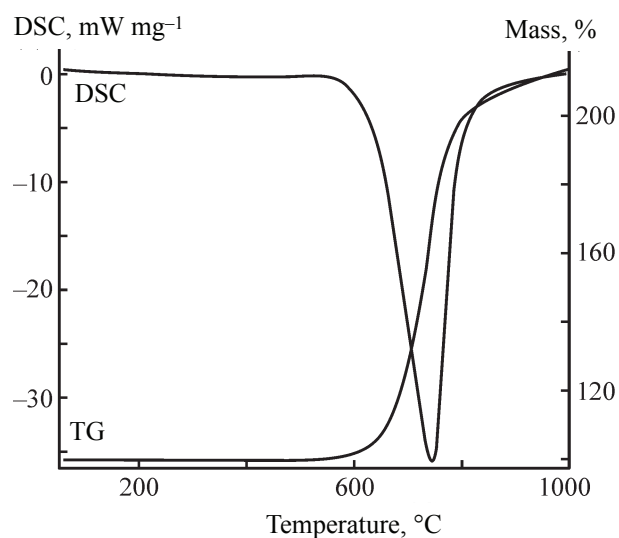

Fig. 4. Curves of thermogravimetry (TG) and differential scanning calorimetry (DSC) of a boron carbide sample no. 1-1.

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[7] Properties, Production, and Use of High-Melting Compounds: Reference Book, Kosolapova, T.Ya., Ed., Moscow: Metallurgiya, 1986, pp. 523 and 531.
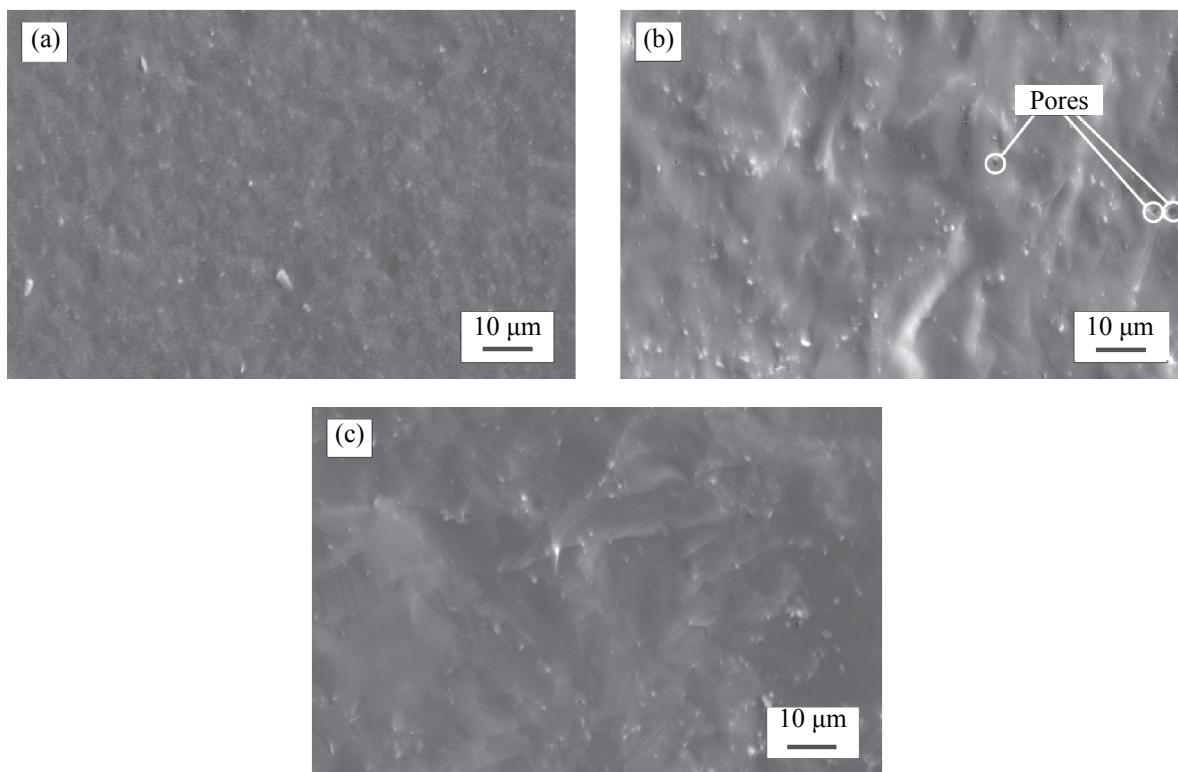
Fig. 5. Micrographs of cleaved surfaces: (a) sample I of pure boron carbide, (b) sample II, (c) sample III.

this parameter. An analysis of the disintegration surface of cleaved samples (Fig. 5) demonstrated the formation of a dense structure and the absence of coarse pores and discontinuities. An insignificant amount of closed pores is observed in samples containing chromium carbide. The pores are spherical and their volume fraction is small, which has no adverse effect on the properties of the material. At a higher content of chromium carbide, the porosity strongly decreases and the presence of a cast structure is observed, which is accounted for by the melting of the sintering additive in the course of sintering. The intergrain boundaries are nearly indistinguishable in all cases.

A qualitative elemental analysis of the samples demonstrated a homogeneous distribution of chromium in a ceramic sample, which points to its uniform structure. Also, it was found by studying the surface structure of the samples that the grain size of sample III containing 20 wt % chromium carbide is about 0.5 μm (Fig. 6). For the rest of the samples, the grain sizes are approximately the same.

The microhardness had the following values (GPa): 41 ± 3.2 for sample I, 46 ± 2.8 for sample II, and 45 ± 2.4 for sample III. These results demonstrate that using a sintering additive (highly dispersed chromium carbide in the given case) leads to an increase in the microhardness of the samples. These values are comparatively large. The reference literature[8] reports that they are within the range 29.7–47.9 GPa for hot-compacted samples composed of only boron carbide.

CONCLUSIONS

The process in which a polydisperse powder of boron carbide is synthesized from elements, amorphous boron and nanofibrous carbon, was examined, with the subsequent analysis of the process in which a ceramic based on this powder. The synthesis was performed in an inert gas, argon. The X-ray diffraction and X-ray fluorescence methods of analysis demonstrated that the reaction products contain only a single phase, boron carbide, with insignificant content of impurities (≤1.5 wt %). The optimal process parameters were the following: boron : carbon molar ratio of 4.1 : 1 and keeping at a temperature of 1900°C for 15 min. Boron carbide

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[8] Properties, Production, and Use of High-Melting Compounds: Reference Book, Kosolapova, T.Ya., Ed., Moscow: Metallurgiya, 1986, p. 565.
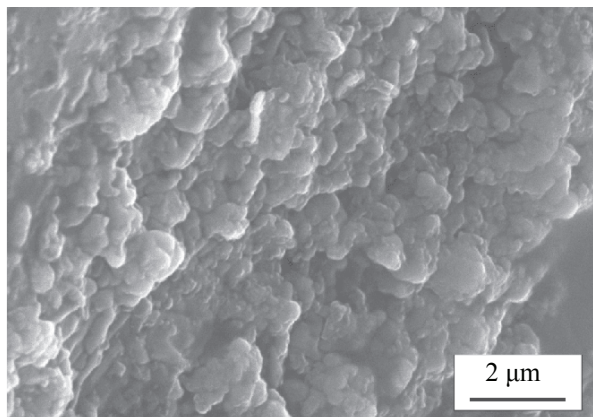
Fig. 6. Structure of sample III.

has a high dispersity (average particle size 2.10 μm) and a broad particle size distribution. Additionally, the process of sintering by hot compaction of a polydisperse boron carbide was studied (including that with sintering additive, highly dispersed chromium carbide) and some characteristics of the resulting ceramic were examined. At comparatively not large parameters (compaction pressure ~35 MPa and temperature ~1900°C), samples with high-quality characteristics were obtained: porosity and water-absorption capacity not exceeding 0.02%, average bending strength 406 MPa, average compression strength 1553 MPa, relative density 95.0–96.5%, microhardness ~42 GPa. With a sintering additive (chromium carbide), the microhardness increased to 45–46 GPa.

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CONFLICT OF INTEREST

The authors state that there is no conflict of interest to be disclosed in the present communication.

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