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Research article

Научная статья



Obtaining ceramics from boron carbide with chromium-based additives (Cr_3C_2 , CrB_2)

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Abstract. This study presents the results of spark plasma sintering of powders within the boron–carbon–chromium system, focusing on boron carbide (B_4C), chromium carbide (Cr_3C_2), and chromium diboride (CrB_2). The powders were synthesized using the original vacuum-free direct current arc reactor, where the starting powder mixture was exposed to an arc discharge for 60 s under a direct current of 200 A. Bulk samples based on B_4C and CrB_2 were sintered under identical conditions, with a temperature of 1800°C and a pressure of 60 MPa, while the sintering of Cr_3C_2 -based ceramics was conducted at 1300°C and 30 MPa. In some cases, sintering additives – 25 wt. % Cr_3C_2 and 20 wt. % CrB_2 – were introduced during the sintering of B_4C -based bulk samples. The phase composition of the sintered samples was analyzed using X-ray diffraction (XRD), while the microstructure and elemental composition were examined via scanning electron microscopy (SEM). The hardness of the sintered ceramics was measured using a Vickers indenter under a load of 1 kg, revealing hardness values of 22.7 ± 1.8 GPa for B_4C , 12.6 ± 0.3 GPa for CrB_2 , and 11.4 ± 0.1 GPa for Cr_3C_2 . The introduction of 25 wt. % Cr_3C_2 as a sintering additive in B_4C -based ceramics reduced the hardness to 17.7 ± 5.6 GPa; however, it significantly improved the fracture toughness, increasing it from 2.5 ± 0.2 to 3.3 ± 0.3 $\text{MPa} \cdot \text{m}^{1/2}$. Conversely, the addition of 20 wt. % CrB_2 during B_4C sintering led to an increase in the bulk sample's hardness from 22.7 ± 1.8 GPa to 26.8 ± 1.3 GPa.

Keywords: composite ceramics, B_4C , CrB_2 , Cr_3C_2 , vacuum-free arc discharge method, spark plasma synthesis, hardness

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Получение керамики из карбида бора с добавками на основе хрома (Cr_3C_2 , CrB_2)

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Аннотация. Представлены результаты исследования процесса искрового плазменного спекания порошков системы «бор–углерод–хром», а именно карбидов бора и хрома, а также диборида хрома. Синтез порошков (B_4C , CrB_2 и Cr_3C_2) для спекания осуществлялся с использованием оригинального безвакуумного электродугового реактора постоянного тока при длительности обработки исходной смеси порошков воздействием дугового разряда 60 с и силе тока, установленной на источнике постоянного тока, 200 А. Спекание объемных образцов на основе карбида бора (B_4C) и диборида хрома (CrB_2) проводилось при одинаковых параметрах – температуре $t = 1800^\circ\text{C}$ и давлении $P = 60$ МПа, а спекание керамического

образца на основе карбида хрома (Cr_3C_2) – при $t = 1300^\circ\text{C}$ и $P = 30$ МПа. Также в процессе спекания объемных образцов на основе карбида бора в ряде случаев применялись спекающие добавки – 25 мас. % Cr_3C_2 и 20 мас. % CrB_2 . Посредством рентгеновской дифрактометрии был изучен фазовый состав спеченных образцов. Микроструктуру и элементный состав полученных образцов определяли с помощью растровой электронной микроскопии. Твердость спеченной керамики оценивали с использованием твердомера с наконечником Виккерса при малой нагрузке в 1 кг – установлено, что твердость образца B_4C составляет $22,7 \pm 1,8$ ГПа, CrB_2 – $12,6 \pm 0,3$ ГПа, Cr_3C_2 – $11,4 \pm 0,1$ ГПа. Введение спекающей добавки в виде 25 мас. % Cr_3C_2 при получении керамики на основе B_4C привело к снижению твердости до $17,7 \pm 5,6$ ГПа, однако наблюдалось повышение трещиностойкости полученного образца с $2,5 \pm 0,2$ до $3,3 \pm 0,3$ МПа·м^{1/2}. Добавка 20 мас. % CrB_2 при спекании B_4C позволила увеличить твердость объемного образца с $22,7 \pm 1,8$ до $26,8 \pm 1,3$ ГПа.

Ключевые слова: композиционная керамика, B_4C , CrB_2 , Cr_3C_2 , безвакуумный электродуговой метод, искровое плазменное спекание, твердость

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Introduction

Boron carbide (B_4C) is one of the most promising superhard materials in its class, widely recognized for its unique properties, including a high melting point ($\sim 2450^\circ\text{C}$ according to the boron carbide phase diagram) and excellent thermal stability [1]. B_4C -based ceramics exhibit outstanding hardness (~ 29 GPa) combined with a relatively low density (2.52 g/cm^3) [2]. These properties make boron carbide highly suitable for a range of applications, such as the production of refractory materials, abrasive products, neutron radiation absorbers [1], coatings for cutting tools [3], and ballistic protection systems [4].

The performance of B_4C -based ceramics can be enhanced through the introduction of sintering additives. Numerous studies have explored how various additives influence the mechanical properties of boron carbide ceramics. Research findings [5–8] indicate that the addition of carbides and borides of silicon and chromium can significantly improve these properties. For example, study [6] demonstrated that adding Cr_3C_2 as a sintering additive to B_4C significantly increases the densification while achieving a high relative density (up to 95 %) and flexural strength (up to 440 MPa). Previously published studies [5; 9] have shown that the introduction of chromium diboride as a sintering additive can enhance the mechanical properties of boron carbide ceramics. In [5], the addition of 20 mol. % CrB_2 as a sintering additive increased the fracture toughness of the sintered ceramic to $3.5\text{ MPa}\cdot\text{m}^{1/2}$, with a flexural strength of 630 MPa. Similarly, study [9] reported that a B_4C –10mol.% CrB_2 composite exhibited a fracture toughness of $5.25\text{ MPa}\cdot\text{m}^{1/2}$ (compared to $4.33\text{ MPa}\cdot\text{m}^{1/2}$ without additives) and a microhardness of 37.1 GPa (compared to 35.5 GPa without additives).

The primary methods for producing boron carbide include carbothermal reduction of boron oxide [2; 10], self-propagating high-temperature synthesis [11; 12], mechanical activation followed by heat treatment [13], among others. Among advanced synthesis methods, the arc discharge technique stands out due to its ability to achieve extremely high temperatures over a wide range, with rapid heating rates [14]. In the authors' previous studies, the feasibility of synthesizing boron carbide using a vacuum-free arc discharge method with a horizontal discharge circuit was demonstrated. This approach eliminates the need for creating an inert atmosphere in the reaction zone or ensuring airtight conditions in the reaction chamber, as the vacuum-free arc reactor can operate in ambient air. This significantly simplifies the reactor design and reduces the overall processing cycle time [15].

The objective of this study is to investigate the synthesis of boron carbide, chromium diboride, and chromium carbide powders using the vacuum-free arc discharge method, followed by the sintering of the obtained powders. A key focus of this work is the evaluation of the mechanical properties of the resulting ceramic samples and the assessment of how sintering additives, specifically CrB_2 and Cr_3C_2 compounds, influence the mechanical performance of B_4C -based ceramic composites.

Research materials and methods

The synthesis of powders (B_4C , Cr_3C_2 , CrB_2) for sintering was performed using a vacuum-free arc discharge method in a custom-designed reactor with a modified discharge circuit configuration. The schematic diagram of the reactor, along with a detailed description of the synthesis process and material characteristics, can be found in studies [16–18]. The reac-

tor is equipped with a direct current (DC) power source capable of regulating the current within a range of 20 to 220 A. The negative terminal of the power source was connected to an aluminum plate with openings designed to hold graphite crucibles, while the positive terminal was connected to a vertically positioned steel sleeve mounted above the aluminum plate. Starting powders were placed inside the cavity of the graphite crucible and sealed with a graphite lid. The arc discharge was initiated by establishing contact between the electrode and the crucible lid, after which the discharge was maintained for a predetermined duration before being terminated. The operating parameters of the arc reactor used during the synthesis of the powder materials are summarized in Table 1.

The ceramic samples were sintered using the spark plasma sintering (SPS) method with a GT Advanced Technologies SPS 10-4 system. During the fabrication process, the powder materials were simultaneously pressed and sintered under vacuum conditions. Five bulk cylindrical samples, each with a diameter of 12.7 mm and a height of 3 mm, were sintered under conditions selected based on literature data, as detailed in Table 2. The sintered samples included tablets made from boron carbide powders, as well as boron carbide with the addition of chromium carbide and chromium diboride. Before sintering each bulk sample, the starting powders or powder mixtures for each composition were milled in a tungsten carbide ball mill for 5 min.

The phase composition of the synthesized and sintered products was analyzed using X-ray diffraction (XRD) on a Shimadzu XRD 7000 diffractometer with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.54060 \text{ \AA}$). The microstructure and morphology of the synthesized and sintered materials were examined using a Tescan Vega 3 SBU scanning electron microscope (SEM) equipped with an Oxford X-Max 50 energy-dispersive X-ray spectroscopy (EDS) system featuring a Si/Li crystal detector. Transmission electron microscopy (TEM) was performed using a JEOL JEM 2100F microscope equipped with an EX-24063JGT EDS detector to analyze finer structural details.

The density of the sintered ceramic samples was measured using the hydrostatic weighing method

with a specialized attachment for HR-250AZ analytical balances (A&D Company) in distilled water. The hardness of the sintered ceramics was evaluated using a Pruftechnik KB-30S microhardness tester with a Vickers indenter under a load of 1 kg. The fracture toughness of the bulk samples was determined using the indentation method, by measuring the lengths of cracks emanating from the corners of the Vickers indentation marks, as observed in SEM images. These cracks were generated under the same 1 kg load applied with the Pruftechnik KB-30S microhardness tester.

Research results and discussion

The X-ray diffraction analysis (Fig. 1) of the synthesized powder confirms the formation of boron carbide (B_4C) (JCPDS No. 35-798, space group $R\bar{3}m$, rhombohedral crystal system) as a result of exposure to the thermal field generated by an arc discharge initiated in air under normal atmospheric pressure, with a current of 200 A and an exposure time of 60 s applied to the boron–carbon mixture. Notably, traces of unreacted elemental boron were detected in the XRD pattern, indicated by a broad halo within the angular range of $2\theta = 10^\circ\text{--}20^\circ$. In addition, a diffraction peak at $2\theta \approx 26.1^\circ$, corresponding to the graphite phase, was identified in the sample.

Fig. 1 also shows the XRD patterns of the synthesized chromium carbide and chromium diboride powders. According to the diffraction data, the chromium carbide powder consists of a crystalline Cr_3C_2 phase (JCPDS No. 35-0804, orthorhombic structure), while the chromium diboride powder corresponds to the CrB_2 phase (JCPDS No. 34-369, hexagonal structure).

The morphology of the synthesized boron carbide powder was examined using scanning electron microscopy (SEM). A representative SEM image is shown in Fig. 2.

The newly formed boron carbide particles appear as agglomerates with a broad size distribution ranging from ~ 100 to $\sim 500 \text{ }\mu\text{m}$, with the most frequent particle size falling within the $100\text{--}150 \text{ }\mu\text{m}$ range (Fig. 2, *a*, inset). According to elemental analysis, typical particles contain boron (78.93 at. %) and carbon (21.07 at. %),

Table 1. Parameters of synthesis of powder materials

Таблица 1. Параметры синтеза порошковых материалов

Material	Atomic ratio	Current, A	Arc discharge duration, s	Energy input, kWh
B_4C [16]	4.00:1.00	200	60	0.061
Cr_3C_2 [17]	3.00:2.45			0.067
CrB_2 [18]	1.00:2.55			0.064

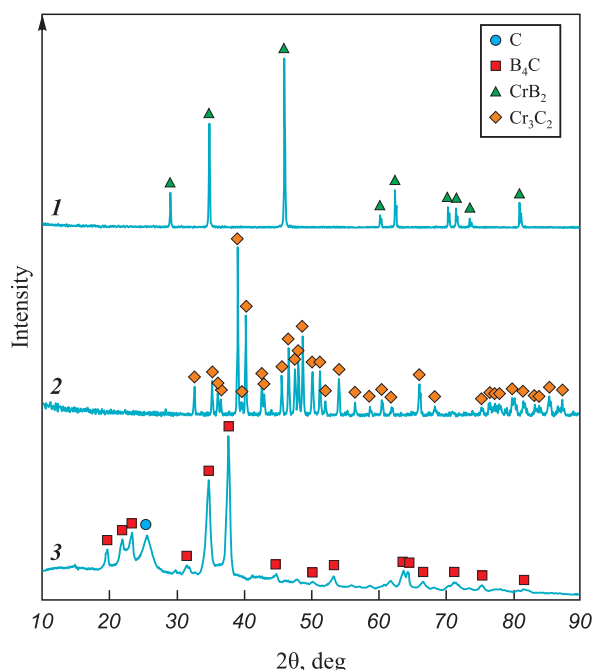


Fig. 1. Typical X-ray diffraction patterns of the synthesized CrB_2 , Cr_3C_2 and B_4C powders

1 – chromium diboride, 2 – chromium carbide, 3 – boron carbide

Рис. 1. Типичные картины рентгеновской дифракции синтезированных порошков CrB_2 , Cr_3C_2 и B_4C

1 – диборид хрома, 2 – карбид хрома, 3 – карбид бора

with an atomic ratio consistent with the stoichiometry of boron carbide (B_4C), as previously confirmed by XRD analysis. A small amount of impurities (not exceeding 2.0 at. %) was also detected in the samples.

Fig. 3 shows the results of transmission electron microscopy of the nanoscale fraction of the synthesized boron carbide (B_4C) powder. As can be seen, the newly formed particles exhibit faceted features and a size distribution ranging from 200 to 700 nm, with most particles falling within the 400–500 nm range.

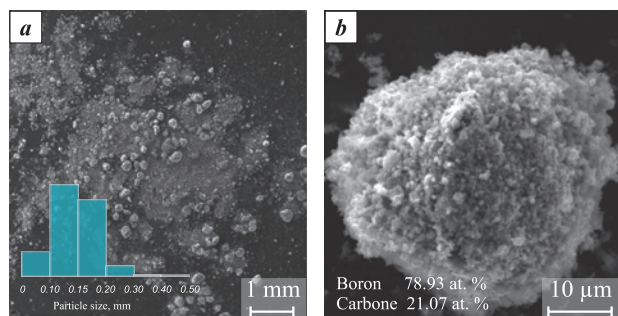


Fig. 2. Typical scanning electron microscopy images of the boron carbide sample in secondary electron mode (a) and backscattered electron mode (b)

Рис. 2. Типичный снимок растровой электронной микроскопии образца карбида бора в режимах вторичных (a) и обратно-рассеянных (b) электронов

The electron diffraction pattern (Fig. 3, c) reveals interplanar spacings of 3.80, 1.89, 1.71, 1.62, 1.40, 1.32, 1.31, 1.26, and 1.21 Å, which, within the permissible measurement error, correspond to the reference interplanar spacings of the B_4C phase (JCPDS No. 35-798, PDF-4+). Additionally, interplanar spacings of 2.34 and 2.09 Å were identified, corresponding within the measurement error to the reference values for the B_{13}C_2 phase (JCPDS No. 71-108, PDF-4+). The identified B_{13}C_2 phase represents a structural variant of boron carbide (B_4C) and is a hyperstoichiometric phase relative to B_4C . Its formation is likely due to the development of localized regions with non-uniform distribution of the starting powders in the reaction zone [19].

Ceramic samples based on boron carbide (B_4C), chromium carbide (Cr_3C_2), and chromium diboride (CrB_2) were subsequently fabricated using the spark plasma sintering (SPS) method. Based on previous studies [5–8], it has been established that the introduction of sintering additives in the form of chromium carbide and chromium diboride enhances the mechanical properties of the final ceramic products. According to the results of study [5], adding 20 wt. % CrB_2 during the sintering of B_4C -based ceramic samples leads to composites with the highest fracture toughness and hardness. In contrast, the addition of 25 wt. % Cr_3C_2 results in samples with the highest density [6], which

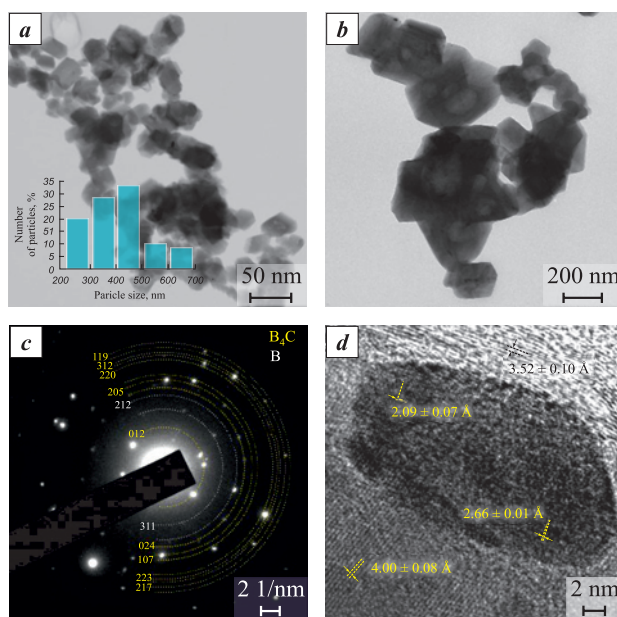


Fig. 3. Typical transmission electron microscopy results

a – dark-field image, b – bright-field image, c – electron diffraction pattern, d – HRTEM image

Рис. 3. Типичные результаты просвечивающей электронной микроскопии

a – темнопольный снимок, b – светопольный снимок, c – электронная дифракция, d – снимок в режиме прямого разрешения

also contributes to improved mechanical properties of the bulk material. Therefore, to enhance the mechanical properties of the ceramics, samples were prepared from powders with the following additives: $B_4C + 20 \text{ wt. \% } CrB_2$ and $B_4C + 25 \text{ wt. \% } Cr_3C_2$. To evaluate the effect of sintering additives on the properties of bulk ceramics, the characteristics of samples made from pure powders were compared with those of sintered samples containing additives. Chromium carbide and chromium diboride powders synthesized via the vacuum-free arc discharge method were used as sintering additives.

Fig. 4 presents scanning electron microscopy images of the sintered ceramic samples based on B_4C , CrB_2 , and Cr_3C_2 . According to the XRD patterns, no phase transitions were detected after sintering, and the phase composition remained nearly identical to that of the powders synthesized by the vacuum-free arc discharge method.

The surface of the bulk boron carbide (B_4C) sample (Fig. 4, *a-c*) exhibits distinct structural features, particularly regions with multiple clustered carbon particle (agglomerates) reaching up to up to $\sim 17 \mu m$ in size. Additionally, changes in the phase composition

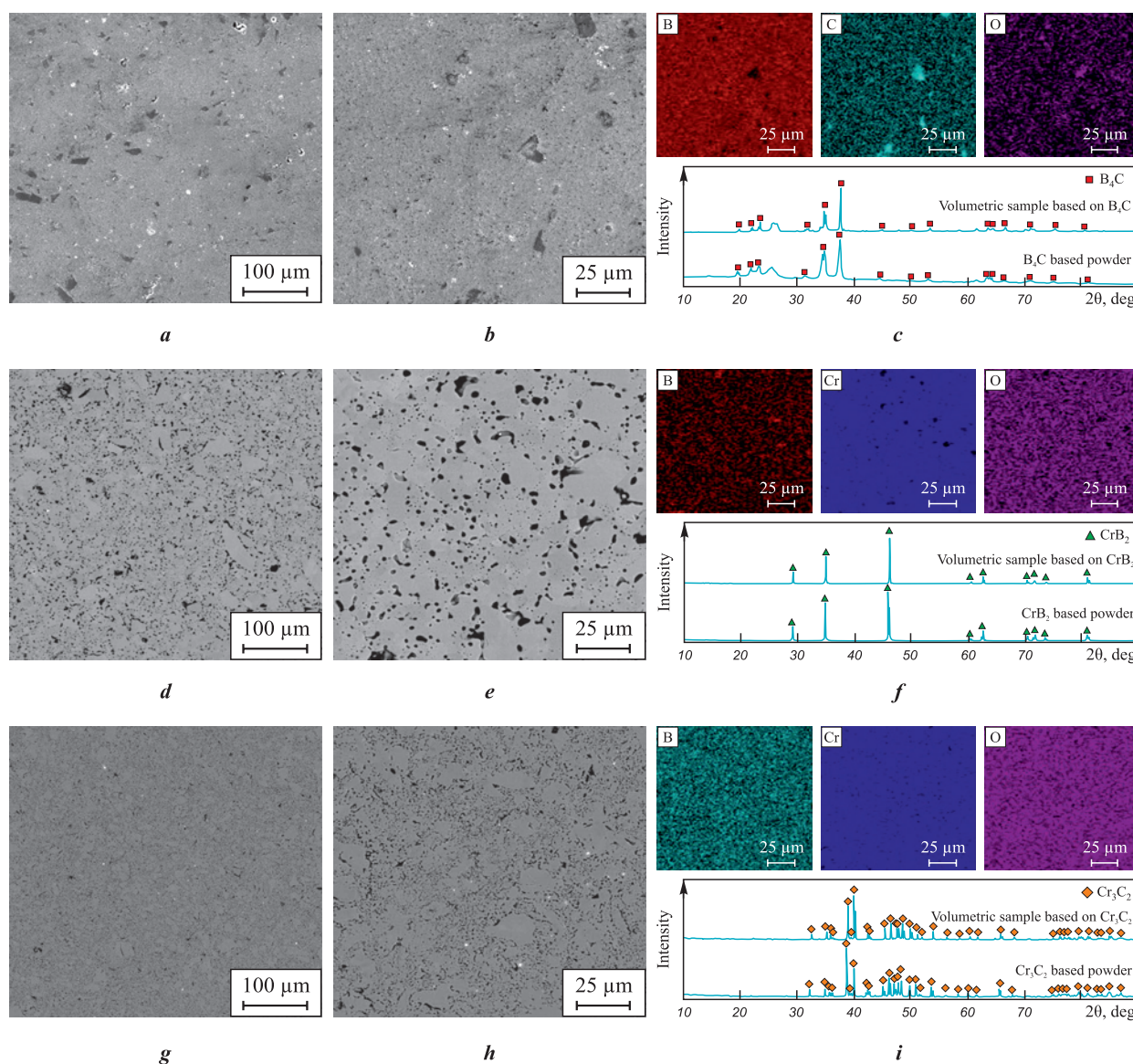


Fig. 4. Typical SEM images in backscattered electron mode with elemental distribution maps and XRD patterns of the ceramic samples

a-c – B_4C ; *d-f* – CrB_2 ; *g-i* – Cr_3C_2

Рис. 4. Типичные РЭМ-снимки в режиме обратно-рассеянных электронов с картами распределения химических элементов и РФА керамического образца

a-c – B_4C ; *d-f* – CrB_2 ; *g-i* – Cr_3C_2

of the bulk sample were observed compared to the starting powder. According to the X-ray diffraction analysis (Fig. 4, *c*), the diffraction halo within the angular range of $2\theta = 10\div 20^\circ$, corresponding to amorphous boron particles, becomes less pronounced after sintering. This change in phase composition can be attributed to the reaction between amorphous boron and carbon particles during the sintering process, leading to the formation of boron carbide (B_4C) and the agglomeration of free carbon (Fig. 4, *c*, carbon distribution map).

Elemental analysis (Fig. 4, *c*) shows that the boron carbide sample contains boron (64.90 at. %) and carbon (29.03 at. %), with an atomic ratio consistent with the B_4C stoichiometry previously determined by XRD. In addition, trace amounts of oxide impurities (no more than 2.0 at. %) were identified in the sample. Elemental distribution maps also reveal the presence of oxide compounds on the sample surface (Fig. 4, *c*), which likely originate from the starting powders, such as boron oxide (B_2O_3) particles present in the raw boron powder. However, the identification of these compounds via XRD is challenging due to their low concentration relative to the total sample volume.

SEM images of the chromium diboride (CrB_2) ceramic (Fig. 4, *d-f*) reveal light and dark globular

regions on the sample surface at low magnifications, associated with the distribution of the primary components. Boron particle clusters up to $\sim 10\ \mu m$ in size were also identified on the CrB_2 sample surface. Elemental analysis (Fig. 4, *f*) indicates that the sample contains boron (69.80 at. %) and chromium (28.46 at. %) in an atomic ratio corresponding to the stoichiometry of CrB_2 . A small amount of oxide compounds (not exceeding 2.0 at. %) was also detected on the sample surface.

The surface of the pure chromium carbide (Cr_3C_2) ceramic sample (Fig. 4, *g-i*) also shows dark regions in the SEM images, corresponding to carbon particle agglomerates with sizes up to $5\ \mu m$. Elemental analysis confirms a uniform distribution of chromium and carbon, with average contents of 48.54 at. % (C) and 48.52 at. % (Cr). A small amount of oxide compounds (not exceeding 3.0 at. %) was also identified.

Fig. 5 presents SEM images and XRD results of the sintered boron carbide-based ceramic samples with additives (20 wt. % CrB_2 and 25 wt. % Cr_3C_2).

According to the X-ray diffraction analysis (Fig. 5, *a*), the sample sintered from boron carbide powder with the addition of 25 wt. % chromium

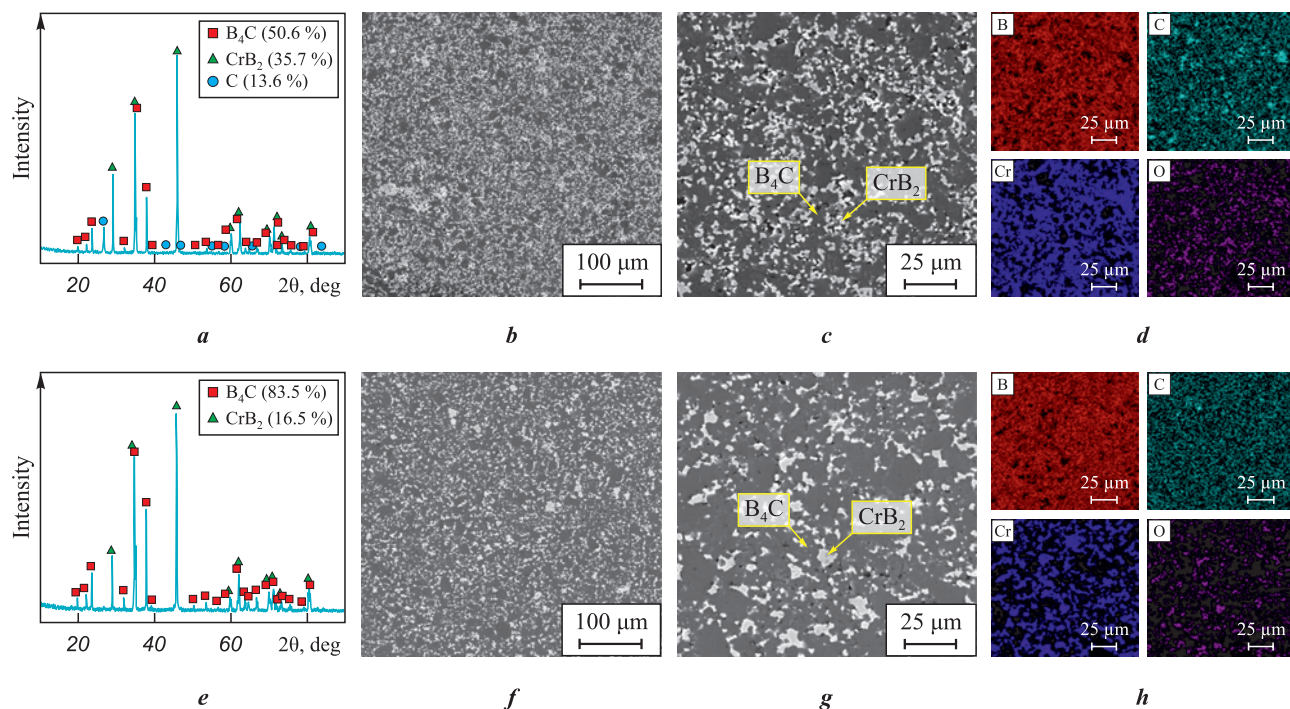


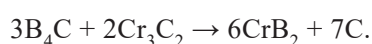
Fig. 5. Typical X-ray diffraction patterns and backscattered electron SEM images with elemental distribution maps of composite materials

a-d – B_4C + 25 wt. % Cr_3C_2 ; *e-h* – B_4C + 20 wt. % CrB_2

Рис. 5. Типичные картины рентгеновской дифракции и РЭМ-снимки в режиме обратно-рассеянных электронов с картами распределения химических элементов композиционных материалов

a-d – B_4C + 25 мас. % Cr_3C_2 ; *e-h* – B_4C + 20 мас. % CrB_2

carbide contains CrB_2 (JCPDS No. 89-3533), B_4C (JCPDS No. 35-798), and C (JCPDS No. 75-3078) phases. The formation of chromium diboride during the sintering of the $\text{B}_4\text{C} + 25 \text{ wt. \% Cr}_3\text{C}_2$ composite is attributed to the diffusion of boron atoms from the boron carbide phase into the chromium carbide phase at high temperatures. This process results in the formation of CrB_2 and the release of free carbon from B_4C and Cr_3C_2 compounds. The free carbon can either react with boron atoms to form additional boron carbide phases or accumulate in localized carbon-rich regions, as indicated by the carbon distribution map (Fig. 5, c). The formation of chromium diboride (CrB_2) in this system follows the chemical reaction [20]:



The sample surface (Fig. 5, b, c) displays both light and dark regions. The light regions correspond to the CrB_2 phase, while the darker areas are associated with boron carbide. Additionally, pores up to $10 \mu\text{m}$ in size were observed.

Elemental analysis (Fig. 5, d) shows that the light regions represent the chromium diboride phase with traces of carbon. These areas contain carbon (20.57 at. %), boron (68.47 at. %), and chromium (10.96 at. %), confirming the presence of CrB_2 . A small amount of oxide compounds (up to 1.10 at. %) was also

detected. According to the elemental analysis results, the dark regions correspond to the boron carbide phase, with elemental analysis revealing boron (72.11 at. %), carbon (24.5 at. %), and chromium (2.96 at. %), which is consistent with the B_4C phase composition. Minor impurities (up to 1.0 at. %) were also present in the sample.

Fig. 5, e–h shows the XRD results and SEM images of the sintered ceramic sample made from boron carbide powder with the addition of 20 wt. % chromium diboride, captured in secondary electron mode. The diffraction peaks observed in the XRD pattern (Fig. 5, e) correspond to the characteristic peaks of the crystalline phases CrB_2 (JCPDS No. 89-3533) and B_4C (JCPDS No. 35-798).

The surface of the $\text{B}_4\text{C} + 20 \text{ wt. \% CrB}_2$ sample (Fig. 5, f, g) features both light and dark regions, along with pores up to $5 \mu\text{m}$ in size. The sample also displays distinct structural features, including carbon particle clusters measuring up to $4 \mu\text{m}$.

Elemental analysis (Fig. 5, h) reveals that the light regions contain boron (68.3 at. %), chromium (17.21 at. %), and carbon (12.99 at. %), indicating the presence of chromium diboride grains (Fig. 5, e). Oxygen was also detected in these regions, with a concentration of up to 1.5 at. %. In contrast, the dark regions contain boron (75.66 at. %), carbon (22.30 at. %), and chromium (1.66 at. %), suggesting these areas cor-

Table 2. Sintering parameters and characteristics of ceramic samples

Таблица 2. Параметры спекания и характеристики керамических образцов

Sintering method	Phase composition	Theoretical/ measured density, g/cm ³	Relative density, %	Hardness, GPa	Sintering parameters				Reference
					<i>t</i> , °C	<i>P</i> , MPa	Δ <i>t</i> /Δ <i>τ</i> , °C/min	Δ <i>τ</i>	
Literature data									
SPS	B ₄ C	–	78.6	12.2	1850	60	100	5	[21]
SPS	B ₄ C	–	97.8	35.3 ± 2.6	2100	50	50	10	[22]
SPS	CrB ₂	–	97.0	16.0	1800	50	100	15	[23]
SPS	Cr ₃ C ₂	–	98.9	18.9	1300	30	100	10	[24]
Hot pressing	B ₄ C + 20 wt. % CrB ₂	–	99.0	–	1900	50	40	60	[5]
Hot pressing	B ₄ C + 25 wt. % Cr ₃ C ₂	–	90.0	–	2030	–	10	60	[6; 8]
Experimental data from this study									
SPS	B ₄ C	2.52/2.40	95.2	22.7 ± 1.8	1800	60	100	10	–
SPS	CrB ₂	5.20/4.81	92.5	12.6 ± 0.3	1800	60	100	10	–
SPS	Cr ₃ C ₂	6.68/6.08	91.0	11.4 ± 0.1	1300	30	100	10	–
SPS	B ₄ C + 20 wt. % CrB ₂	2.92/2.81	96.2	26.8 ± 1.3	1800	60	100	10	–
SPS	B ₄ C + 25 wt. % Cr ₃ C ₂	3.43/3.03	88.3	17.7 ± 5.6	1800	60	100	10	–

respond to boron carbide grains (Fig. 5, g). Trace amounts of oxide compounds (up to 1.0 at. %) were also identified in these regions.

The ceramic samples were subjected to Vickers hardness testing under a load of 1 kg. The test results, along with the sample characteristics, are presented in Table 2.

The theoretical density of the composite materials was calculated based on the phase composition of the bulk ceramic samples. Quantitative analysis of the crystalline phases (Fig. 5, a, e) was performed using PowderCell 2.4 software. Following this analysis, the theoretical density of the composite materials was determined using the density values of the identified phases (B_4C , CrB_2 , and C).

The data presented in Table 2 reveals the following hardness trend: $B_4C + 20 \text{ wt. \% } CrB_2 > B_4C > B_4C + 25 \text{ wt. \% } Cr_3C_2 > CrB_2 > Cr_3C_2$, specifically $26.8 > 22.7 > 17.7 > 12.6 > 11.4 \text{ GPa}$. The introduction of chromium diboride as a sintering additive led to an increase in the relative density of the bulk ceramic sample from 95.2 to 96.2 %, which is consistent with experimental data from [25]. This increase in density also contributed to improved mechanical properties, as reflected by the rise in hardness from 22.7 to 26.8 GPa.

The addition of chromium carbide during the sintering process resulted in a decrease in both the density and mechanical properties of the ceramic, reducing the hardness to 17.7 GPa. This decrease in relative density is attributed to the formation of porous regions containing a significant amount of free carbon. For the B_4C sample with Cr_3C_2 addition, fracture toughness was also investigated. The results showed that the fracture toughness of pure boron carbide was $2.5 \pm 0.2 \text{ MPa}\cdot\text{m}^{1/2}$, while the introduction of 25 wt. % Cr_3C_2 increased this value to $3.3 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$, which is comparable to the results reported in [5; 9].

Conclusion

In this study, the fabrication of bulk ceramics based on compounds from the boron–carbon–chromium system was successfully demonstrated. The powders used for sintering the bulk samples included boron carbide (B_4C), chromium carbide (Cr_3C_2), and chromium diboride (CrB_2). Notably, these powders were synthesized using a vacuum-free direct current arc reactor specifically developed by the authors of this research. The hardness of the B_4C -based ceramic was measured at 22.7 GPa, and the incorporation of 20 wt. % CrB_2 as a sintering additive led to an increase in hardness to 26.8 GPa. Furthermore, the addition of 25 wt. % Cr_3C_2 enhanced the fracture toughness

from 2.5 to $3.3 \text{ MPa}\cdot\text{m}^{1/2}$. The hardness of ceramics based on chromium carbide and chromium diboride was found to be 11.4 and 12.6 GPa, respectively.

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