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MECHANICAL PROPERTIES OF HOT-PRESSED BORON CARBIDE MATERIALS

In the paper, a research study is presented that was carried out for the purpose of obtaining composite materials based on a commercial micron boron carbide. A hot pressing process was performed to produce all the necessary materials. Chromium carbides, chromium silicides, and chromium boride were used as sintering activators, and as the phases generating thermal stresses (to improve fracture toughness). Some additives were introduced, their amounts not exceeding 5% of the total volume of the sample. In the case where large amounts of the introduced phases were applied, the sintering temperature was reduced by 120°C as regards the boron carbide sintered with carbon. The phase composition and the structure of the sinters produced were analyzed. The microstructure of polished and chemically etched (in molten salts) samples was investigated using scanning electron microscopy. The elastic properties, hardness, bending strength, and fracture toughness of the products were also determined.

Keywords: boron carbide, chromium silicide, chromium carbide, chromium monoboride, hot-pressing, mechanical properties

WŁAŚCIWOŚCI MECHANICZNE PRASOWANYCH NA GORĄCO TWORZYW WĘGLIKA BORU

Przeprowadzone w niniejszej pracy badania dotyczą otrzymywania tworzyw kompozytowych na bazie mikronowego komercyjnego węgliku boru. Tworzywa otrzymane zostały w procesie prasowania na gorąco. Jako aktywatory spiekania, a zarazem faz generujących naprężenia cieplne w celu podniesienia odporności na kruche pękanie wykorzystano węglík chromu, krzemki chromu oraz borek chromu. Dodatki wprowadzano w ilościach do 5% obj. W przypadku użycia dużych ilości wprowadzonych faz obniżono temperaturę spiekania o 120°C w stosunku do węgliku boru spiekanego z dodatkiem węgla. Wytworzone spieki poddano analizie fazowej oraz strukturalnej. Na wypolerowanych i wytrawionych chemicznie (w stopionych solach) próbkach tworzyw dokonano obserwacji mikrostrukturalnych metodą skaningowej mikroskopii elektronowej. Materiał poddano również badaniom w celu wyznaczenia właściwości sprężystych, twardości, wytrzymałości na zginanie oraz odporności na kruche pękanie.

Słowa kluczowe: węglík boru, krzemki chromu, węglík chromu, borek chromu, prasowanie na gorąco, właściwości mechaniczne

INTRODUCTION

Boron carbide B_4C is characterized by low density (2.52 g/cm^3), very high hardness (36 GPa), high bending strength (570 MPa for material obtained by hot isostatic pressing), and extremely high resistance to wear, and, owing to those properties, it has been widely applied; its main applications are nozzles for sand blasting, abrasive elements, elements of nuclear reactors, and ballistic shields [1-4]. A significant drawback is the relatively low fracture toughness, which is $2.5\div 3.7 \text{ MPam}^{1/2}$ [5, 6]. From the economic point of view, the cost of producing submicron powders and the issue of obtaining dense sinters are regarded as problems. For this reason, extensive research is conducted both on the use of additives to allow the sintering of boron carbide at temperatures considerably below 2240°C (eutectic B_4C-C), and on the use of a hot-pressing method.

In the scientific reference literature available, there are no indications referring to the use of boron carbide or of a composite formed on its basis with phases such as chromium carbides, chromium silicides, or chromium borides to be applied during sintering. Commonly used additives include carbon, boron, silicon, Cr_2O_3 , Al, Mg, Ni, Fe, Cu, AlF_2 , Be_2C , TiB_2 , and W_2B_5 [7-13]. The most common additives are carbon and silicon. In the first case, the eutectic between carbon and boron carbide is used, which reduces the sintering temperature to 2150°C, but it does not lead to full densification [12]. However, using silicon as an additive for sintering, densification improvement was observed as a result of the formation of SiB_x phases showing a melting point between 1270°C and 2100°C, which, in turn, leads to liquid phase sintering and improves the

mechanical properties of composites produced in this way by creating a residual thermal stress [7]. Some other authors add boron and silicon carbide, instead of silicon, to activate the sintering process; they obtain a very high density of 99% and very good mechanical properties [1]. In the case of hot isostatic pressing, those additives make it possible to obtain a dense material even at 1850°C. In another paper, the authors reported that they added boron, carbon, and silicon carbide and they produced a material based on boron carbide by free sintering with a maximum density of 96% at temperatures exceeding 2150°C [14]. In the reference literature, there is also information on the additives of chromium [10] and chromium compounds, mainly chromium diboride [6], as well as of mixtures of several activators containing chromium carbide. [15]. In the case of added chromium diboride, it was possible to produce sinters at a temperature of 1950°C and a pressure of 50 MPa to make composite materials showing a density of 99%, bending strength of 630 MPa and K_{Ic} equal to 3.5 MPam^{1/2} [6].

Based on a reference literature search, using other phases as additives in boron carbide sintering seems possible. Those phases should be characterized by a relatively low melting point and they should create an opportunity to enter into reaction with the boron carbide to form compounds with good mechanical properties. Therefore, the major objective of this research study was to obtain hot-pressed dense materials based on boron carbide with additives: chromium boride CrB, chromium carbide Cr₃C₂, and chromium silicide Cr₃Si and CrSi₂. The other objective of this study was to search into their mechanical properties.

EXPERIMENT

As a substrate for the preparation of the matrix of the composite, a B₄C - additive phase, a commercial micron (D50 = 1 micrometer) boron carbide powder (Starck, AB 134 566 HS B4C) was used. Chromium carbide powders Cr₃C₂, (CR-301 Atlantic Equipement Engineers) and chromium monoboride CrB, (International Enzymes Limited) powders were used as the sintering additives. Other additives, such as chromium silicides CrSi₂ and Cr₃Si, were directly synthesized from the elements: chromium (Cr-103 Atlantic Equipement Engineers) and silicon; which resulted from recycling. The powders produced were crushed so as to obtain a particle size ranging from 25 to 50 microns, which corresponds to the grain size distribution of commercial powders. It was assumed that a decrease in grain size should have taken place during the processes of milling and homogenization in a rotary vibration mill.

A phenol-formaldehyde resin was used as a carbon substrate necessary to remove oxides from the surface of the boron carbide particles and to facilitate the granulation. The selection of the powders was performed,

selected in such a way as to obtain the following volume fractions of additives: 4% C, 0.5 and 5% of the CrB; 2 and 5% of Cr₃C₂; 1.5 and 5% Cr₃Si; and 1 and 5% CrSi₂. The sets so prepared underwent 2 h homogenization in a high-energy rotary vibration mill, in an environment of isopropyl alcohol with carbide grinding media (WC-Co). Then, after evaporation of the alcohol, the powders were granulated by wiping them through a sieve with a mesh aperture of 0.5 mm. The powders so prepared were put into graphite molds and subjected to the process of hot pressing at a pressure of 25 MPa in an argon flow. As regards the samples containing smaller amounts of additives (2%), as well as the reference sample (B₄C + 4% C), the sintering temperature was 2120°C and it was reduced to 2000°C in the case of the samples with larger amounts of additives (5%). During the ongoing process, the temperature increased by 10°C per minute and the samples were kept 30 minutes at the maximum temperature.

The materials produced under the above described process were analyzed using X-ray diffraction XRD. Next, the ground and polished surfaces of the sintered materials were chemically etched in molten salts (KOH + KNO₃) at a temperature of 450°C. On the surfaces so prepared, their microstructure was examined using a scanning electron microscope (FEI Nova Nano SEM). During the examination, an EDS-based analysis of the elements distribution was carried out on the non-etched sinter surfaces. The elastic properties were measured with the use of 4 MHz ultrasonic heads. The value of Young's modulus (E) and shear modulus (G), the Poisson number (ν), and the anisotropy of module E were determined. All the parameters were measured within the "c" axis parallel to the pressing direction, and, also, in the "a + b" direction perpendicular to the axis of compression. The hardness of the materials produced was measured by the Knoop method, with a load of 1 kg. The flexural strength was determined by the three-point bending of the beam at 40 mm spacing of the supports, and a feed of 1 mm/min. A critical stress intensity factor was calculated based on the Evans' formula using the results of the three-point bending of the beam with a notch at the spacing between the supports being 20 mm, and with a feed of 0.1 mm/min. Abrasion measurements were also performed on the materials by the "dry sand test" method at 2000 rpm (30 min) and with coarse silicon carbide as the abrasive agent. The "ball-on-disk" method was used to measure the friction coefficient of the selected sinters, with silicon nitride balls (3.175 mm) at a pressure of 4 N for 33 min.

RESULTS

The results of the X-ray diffraction phase composition analysis of the materials produced are shown in Table 1.

TABLE 1. Phase compositions of sintered boron carbide phase with different additions. Measurement accuracy of 0.5 wt. %

TABELA 1. Składy fazowe spieków węglika boru z różnymi dodatkami. Dokładność pomiaru na poziomie 0,5% mas.

Composition	Sintering temperature [°C]	Composition [wt.%]			
		B ₄ C	CrB ₂	SiC-3C	Grafit
B ₄ C + 2% Cr ₃ C ₂	2120	93.1	5.7	-	1.1
B ₄ C + 5% Cr ₃ C ₂	2000	84.9	13.5	-	1.5
B ₄ C + 1.5% Cr ₃ Si	2120	94.5	4.8	0.4	0.4
B ₄ C + 5% Cr ₃ Si	2000	89.1	9.4	1.5	0
B ₄ C + 1% CrSi ₂	2120	95.4	3.2	1	0.4
B ₄ C + 5% CrSi ₂	2000	89.5	5.5	4.6	0
B ₄ C + 0.5% CrB	2120	96.7	2.2	-	1.1
B ₄ C + 5% CrB	2000	92.1	7.2	-	0.7

Based on the diffraction analysis results, it was found that regardless of the type of sintering activator implemented, a chromium diboride phase appeared in the system and its amount was correlated with the amount of chromium introduced into the system. The silicon-free systems consisted of CrB₂ and a small amount of graphite was found therein, it was a byproduct of the reaction between the chromium carbide and B₄C:

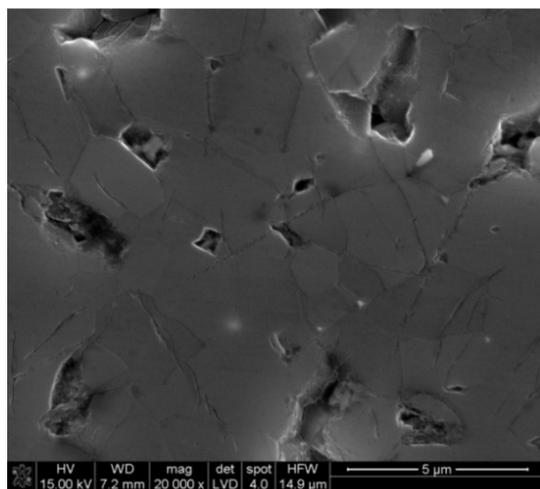


Fig. 2. B₄C + 2 vol. % Cr₃C₂ microstructure
Rys. 2. Mikrostruktura B₄C + 2% obj. Cr₃C₂

When the chromium silicide was added, an apparent decrease was reported in the amount of graphite; it was correlated with the amount of those phases, i.e. the more silicides, the less graphite. This effect is probably due to the reaction between the boron carbide and the respective silicides; the said reaction ran according to the following equations:



The SEM images obtained on the polished and etched surfaces of the materials produced are shown in Figures 1-7. In the majority of cases, the material obtained had a relative density exceeding 99% of the theoretical density; however, after the addition of 5 volume % Cr₃C₂ and 5 volume % CrSi₂, the relative density was slightly above 96%.

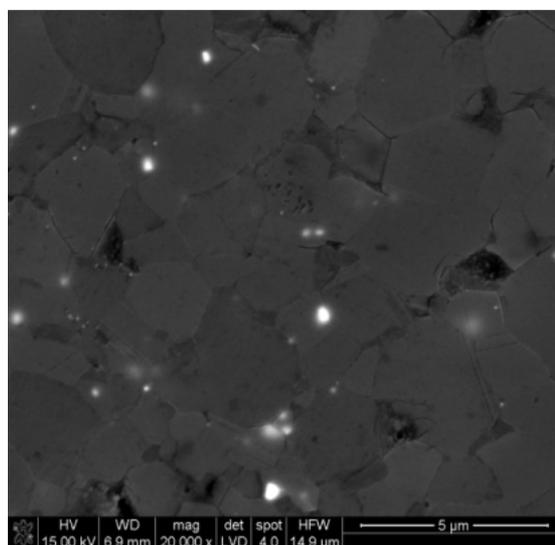


Fig. 1. B₄C + 4 vol. % C microstructure
Rys. 1. Mikrostruktura B₄C + 4% obj. C

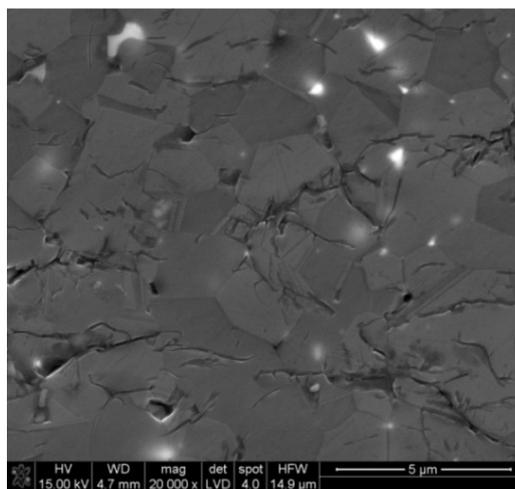


Fig. 3. B₄C + 1 vol. % CrSi₂ microstructure
Rys. 3. Mikrostruktura B₄C + 1% obj. CrSi₂

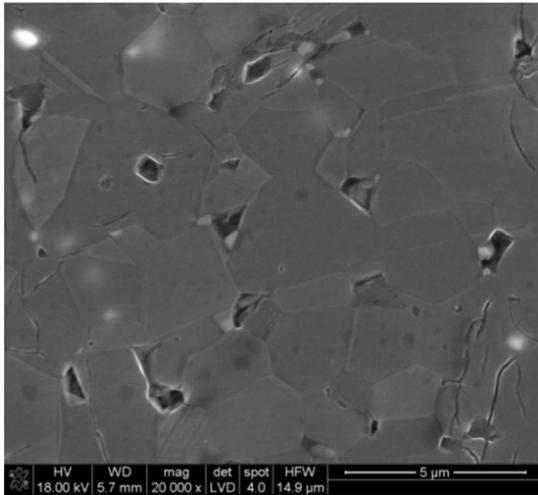


Fig. 4. B₄C + 1.5 vol.% Cr₃Si microstructure
Rys. 4. Mikrostruktura B₄C + 1,5% obj. Cr₃Si

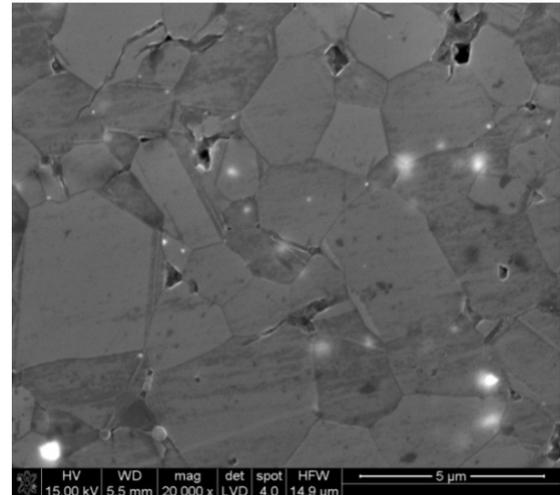


Fig. 5. B₄C + 0.5 vol.% CrB microstructure
Rys. 5. Mikrostruktura B₄C + 0,5% obj. CrB

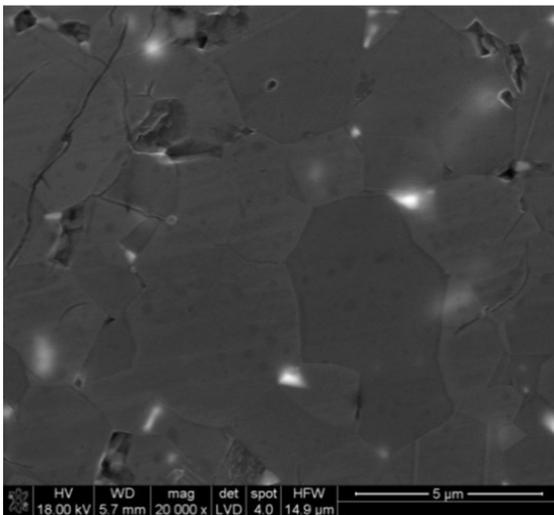


Fig. 6. B₄C + 5 vol.% Cr₃Si microstructure
Rys. 6. Mikrostruktura B₄C + 5% obj. Cr₃Si

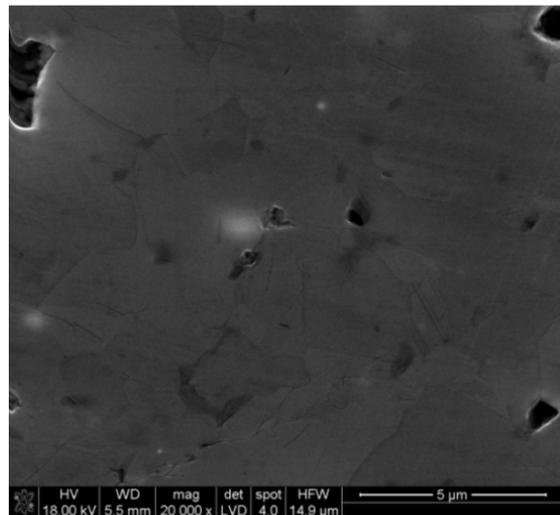


Fig. 7. B₄C + 5 vol.% CrB microstructure
Rys. 7. Mikrostruktura B₄C + 5% obj. CrB

The results obtained confirm that the small addition of Cr₃C₂ phase and CrSi₂ phase that support the sintering process have no significant impact on the microstructure of the sinters produced (Figs. 2 and 3). No increase reported in the grain size may be attributed to the occurrence of carbon residues in the case of chromium carbide and silicon carbide (white areas in of microstructure image), as well as in the case of chromium silicide, Cr₃Si, and chromium boride CrB are introduced into the system, an increase in the grain size is manifested. The component phases of the materials in the form of carbon and chromium diboride, which were absent on the micro-structural images, were removed by etching the boron carbide in molten salts. The presence of those phases was confirmed by an XRD phase analysis (Table 1). The results of the element distribution analysis using EDS, made on the non-etched surfaces of the samples, are shown in Figures 8 and 9.

In the case of the addition of chromium carbide, the EDS analysis confirmed the presence of a chromium diboride phase (white areas), whereas in the case of the addition of the chromium silicide (Cr₃Si), the EDS analysis showed phases of chromium diboride (white areas) and silicon carbide (light gray areas); those phases were a product of the reaction between the chromium silicide and boron carbide.

The values of the elastic properties measured by the ultrasonic method are summarized in Table 2. The values of the mechanical properties, such as toughness, critical stress intensity factor, and flexural strength, as well as wear resistance of the materials and the coefficient of friction values are summarized in Table 3.

The results obtained under the research project confirm that the boron carbide-based materials produced using the hot pressing process exhibit elastic properties, the anisotropy of which is above 10%. However, the anisotropy of the majority of the used additions is

below the value measured for the reference boron carbide. The additives introduced into the matrix of B_4C do not cause any noticeable changes in the measured, in the same direction, values of the elastic properties; they do not affect the hardness of the tested materials either. In Table 3, a significant increase in the flexural strength values in the case of the Cr_3C_2 addition, smaller amounts of $CrSi_2$ and CrB is shown; this may be owing

to the residual stress present therein. For the majority of the produced materials, a slight increase is observed in the fracture toughness compared to the reference sample of boron carbide. The additions introduced reduce the effect of abrasive wear of the examined materials compared to the reference sample. The value of the friction coefficient remains at a similar level for all the tested materials.

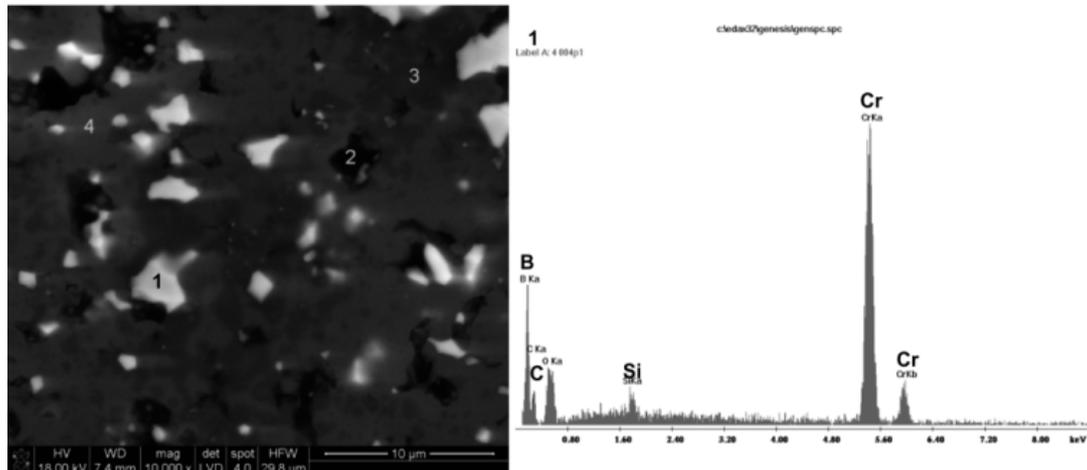


Fig. 8. EDS analysis of material containing 5% addition of chromium carbide

Rys. 8. Analiza EDS tworzywa zawierającego 5% dodatek węgla chromu

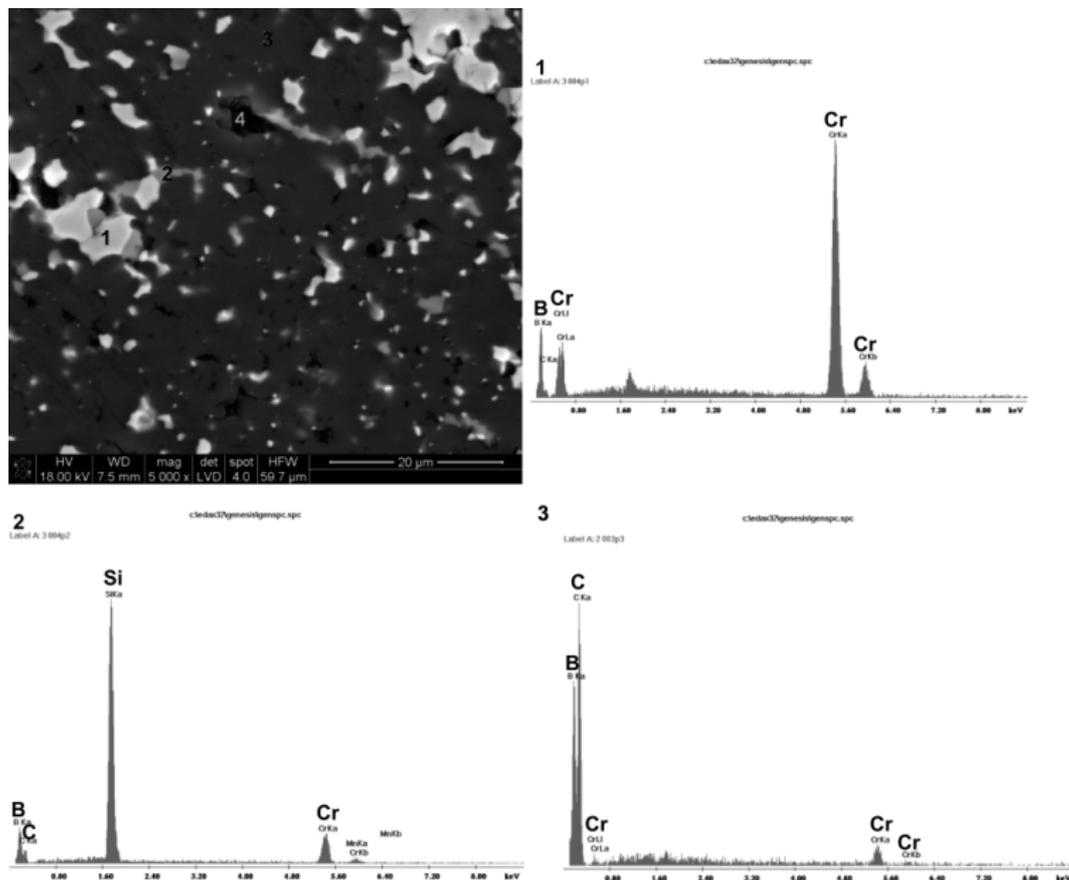


Fig. 9. EDS analysis of material containing 5% addition of chromium silicide Cr_3Si

Fig. 9. Analiza EDS tworzywa zawierającego 5% dodatek krzemku chromu Cr_3Si

TABLE 2. Flexural properties of sinters with boron carbide matrix
TABELA 2. Właściwości sprężyste spieków o osnowie węgliku boru

Composition	Sintering temperature [°C]	axis	E [GPa]	G [GPa]	ν	A [%]
B ₄ C	2120	a+b	407.84 ± 12.35	175.46 ± 1.31	0.162 ± 0.014	25.2
		c	305.02 ± 8.78	124.65 ± 5.06	0.224 ± 0.017	
B ₄ C + 2% Cr ₃ C ₂	2120	a+b	426.93 ± 4.85	181.92 ± 0.96	0.173 ± 0.006	40.6
		c	253.58 ± 39.81	97.9 ± 2.53	0.295 ± 0.028	
B ₄ C + 5% Cr ₃ C ₂	2000	a+b	382.83 ± 2.54	162.82 ± 0.42	0.176 ± 0.003	7.2
		c	355.26 ± 21.96	146.06 ± 4.6	0.216 ± 0.024	
B ₄ C + 1.5% Cr ₃ Si	2120	a+b	436.93 ± 1.91	186.04 ± 0.46	0.174 ± 0.002	12.1
		c	383.86 ± 7.63	155.21 ± 2.65	0.237 ± 0.009	
B ₄ C + 5% Cr ₃ Si	2000	a+b	411.76 ± 4.9	175.57 ± 0.97	0.173 ± 0.006	16.2
		c	345.12 ± 32.26	143.54 ± 3.56	0.202 ± 0.033	
B ₄ C + 1% CrSi ₂	2120	a+b	443.2 ± 1.57	188.56 ± 0.55	0.175 ± 0.002	13.5
		c	383.3 ± 54.44	158.74 ± 7.06	0.207 ± 0.048	
B ₄ C + 5% CrSi ₂	2000	a+b	399.77 ± 8.74	169.18 ± 1.15	0.181 ± 0.009	13.9
		c	344.25 ± 21.96	143.55 ± 4.15	0.199 ± 0.024	
B ₄ C + 0.5% CrB	2120	a+b	438.72 ± 2.65	186.92 ± 0.79	0.174 ± 0.004	36.4
		c	278.9 ± 22.78	113.71 ± 2.9	0.226 ± 0.026	
B ₄ C + 5% CrB	2000	a+b	394.43 ± 2.54	168.27 ± 0.97	0.172 ± 0.003	10.7
		c	352.07 ± 17.44	149.07 ± 2.75	0.181 ± 0.022	

TABLE 3. Mechanical properties of sinters with boron carbide matrix
TABELA 3. Właściwości mechaniczne spieków o osnowie węgliku boru

Composition	Sintering temperature [°C]	HK 1 kg [GPa]	Bending strength [GPa]	K_{Ic} [GPa]	Wear [cm ³]	Friction coefficient
B ₄ C	2120	18.6 ± 0.5	392 ± 27	4.3 ± 0.8	0.006	0.64 ± 0.16
B ₄ C + 2% Cr ₃ C ₂	2120	19.5 ± 0.6	557 ± 70	4.56 ± 0.4	0.001	0.63 ± 0.10
B ₄ C + 5% Cr ₃ C ₂	2000	16.3 ± 0.7	478 ± 54	4.94 ± 0.6	0.005	0.59 ± 0.15
B ₄ C + 1.5% Cr ₃ Si	2120	19.7 ± 0.6	384 ± 45	4.57 ± 0.8	0.001	----
B ₄ C + 5% Cr ₃ Si	2000	18.8 ± 1.1	330 ± 8	4.54 ± 0.5	0.002	----
B ₄ C + 1% CrSi ₂	2120	19.0 ± 0.7	481 ± 25	4.08 ± 0.3	0.001	----
B ₄ C + 5% CrSi ₂	2000	17.5 ± 1.1	345 ± 22	4.86 ± 0.3	0.003	----
B ₄ C + 0.5% CrB	2120	18.4 ± 0.7	508 ± 48	4.75 ± 0.2	0.001	----
B ₄ C + 5% CrB	2000	16.7 ± 1.7	361 ± 20	4.38 ± 0.3	0.002	----

SUMMARY

Dense boron carbide composites were produced containing inclusions, i.e. a sintering process supporting additions and phases resulting from the reaction between those additions and B₄C. The hot-pressing temperature decreased even by 120°C with respect to the boron carbide sintered with the added carbon. The introduction of chromium carbide promotes an increase in flexural strength even by more than 100 MPa. As for the majority of the sintered materials with sintering additives, their fracture toughness increases compared to the reference sample of boron carbide. The materials produced are characterized by a lower anisotropy of their elastic properties, and this is in contrast with the reference sample. The additives introduced do not significantly change the elastic properties of the composites. The introduction of the additives considerably helps reduce the wear of materials. The friction coefficient value does not change.

Acknowledgments

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