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THE INFLUENCE OF CHROMIUM COMPOUNDS ON BORON CARBIDE SINTERING

The paper concerns the activated sintering of boron carbide based materials. The work shows the influence of introduced Cr_3C_2, $CrSi_2$, Cr_3Si modifiers on the sintering of commercial boron carbide. A high-temperature graphite dilatometer was used in order to investigate boron carbide sintering with various additives. The shift of the onset and endset sintering temperature of different sample compositions was determined. The influence of chromium compounds on sintering was explained by XRD phase analysis. The phase changes in the sinters vs. increasing volume fraction of the additives were made. The same analyses were made on samples heat-treated close to the onset sintering temperature.

Keywords: boron carbide, chromium carbide, chromium silicide, activated sintering, dilatometric measurement, XRD, EDS

WPŁYW ZWIĄZKÓW CHROMU NA SPIEKANIE WĘGLIKA BORU

Artykuł dotyczy aktywowanego spiekania materiałów na osnowie węglika boru. W pracy przedstawiono wpływ dodatku wprowadzonych modyfikatorów w postaci Cr_3C_2, $CrSi_2$ oraz Cr_3Si na spiekanie komercyjnego węglika boru. Do badań użyto wysokotemperaturowego grafitowego dylatometru w celu prześledzenia przebiegu procesu spiekania węglika boru ze zmienną zwartością różnych dodatków. W ramach badań dylatometrycznych określono przesunięcie temperatury początku i końca spiekania dla różnych przygotowanych składów materiałowych. Wpływ dodatków związków na bazie chromu na spiekanie badanych tworzyw wyjaśniono przy użyciu analizy XRD. Przeprowadzono analizę zmian fazowych spieków w funkcji wzrastającego udziału objętościowego dodatków. Te same badania wykonano również dla wybranych składów wygrzewanych w temperaturach bliskich temperaturze początku spiekania. Przeprowadzono obserwacje mikrostrukturalne SEM.

Słowa kluczowe: węglik boru, węglik chromu, spiekanie aktywowane, badania dylatometryczne, XRD, EDS

INTRODUCTION

Boron carbide is characterized by strong covalent bonds and low self-diffusion. That is why it is difficult to obtain dense material by pressureless sintering at temperatures lower than 2150^oC. Boron carbide powder has to be very pure and very fine in order to be pressurelessly sintered. Such a commercial powder is very expensive and difficult to obtain. There are two ways to solve this problem - to add some sintering additives or to find a way to sinter coarse and cheaper boron carbide. In the literature, most of the research concerns the sintering of this phase by the use of carbon, silica and boron additives [1-4]. In some papers, boron carbide is sintered by the use of hot pressing and the hot isostatic pressing method [5-9].

In this paper the investigation focuses on the pressureless sintering of a commercial boron carbide with a commercial chromium carbide or laboratory made Cr_3Si, $CrSi_2$ chromium silicates as sintering additives. To keep the purity of the systems, the additives should be coarse and the milling period should be short.

EXPERIMENT

In the case of the boron carbide-additive system as the mixture components, boron carbide powder (AB 134566 B4C HS Boron Carbide Grade HS-A H.C. Starck) was used for the matrix. Commercial chromium carbide Cr_3C_2 powder (01000344 H.C. Starck), laboratory synthetized Cr_3Si and $CrSi_2$ powders were used as the sintering additives. The chromium silicate was obtained by the reaction of commercial metallic chromium powder and laboratory recycled silicon powder. The boron carbide, an additive and phenol-formaldehyde resin as a carbon precursor for the granulation process and oxide reduction purposes were homogenized together in a rotary mill in order to obtain B_4C - $0 \div 2$ vol.% Cr_3C_2, B_4C - $0 \div 2$ vol.% $CrSi_2$ and B_4C - $0 \div 2$ vol.% Cr_3Si mixtures. The homogenization process was done in isopropanol alcohol with the use of WC-Co milling media for 12 hours. Then the powder mixtures were granulated using a 0.5 mm sieve, preliminary uniaxially pressed (100 MPa) and then finally isostatically pressed under 250 MPa pressure. A high-

temperature dilatometer, with a graphite heating element and graphite measuring parts was used for sintering investigations. Shrinkage recording was made with the accuracy of 1 μm. The sintering process was performed in flowing argon. The sintering temperature was 2150°C without holding at this temperature. The rate of temperature was 15°C/min. The phase changes versus temperature during sintering were measured by use of XRD. The quantitative phase composition was calculated using the Rietveld method.

RESULTS AND DISCUSSION

The changes in relative shrinkage vs. the temperature of the prepared boron carbide mixtures with Cr_3C_2, $CrSi_2$ and Cr_3Si are illustrated in Figures 1-3. In the case of the Cr_3C_2 and $CrSi_2$ additive, the materials were sintered up to 2150°C, for the B_4C-Cr_3Si composites the process was stopped earlier because of material deformation. For each figure of relative shrinkage a chart of derivate of linear dimension change is enclosed.
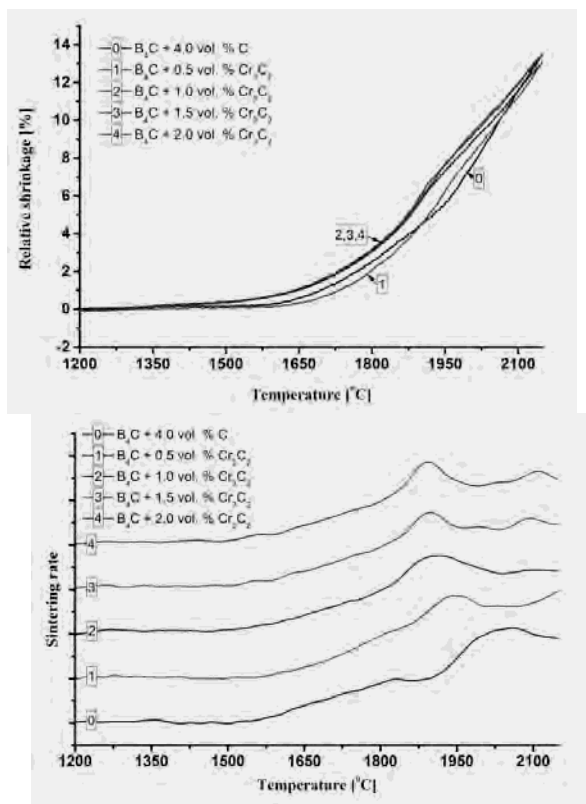

Fig. 1. Relative shrinkage of boron carbide with addition of Cr_3C_2 phase
Rys. 1. Skurcz względny węglika boru z dodatkiem fazy Cr_3C_2

In the case of the investigated systems, the observations made by measurements of linear changes vs. temperature showed that only the used Cr_3Si and $CrSi_2$ additives can intensify the sintering processes during the heating of boron carbide materials. The visible and significant shift of the endset sintering temperature is in the case of the Cr_3Si additive and it is circa 100°C. The onset sintering temperature does not visibly change for

all the types of additives. The derivative of linear dimension change shows that during sintering the process can be divided into two steps (Figs. 1-3).
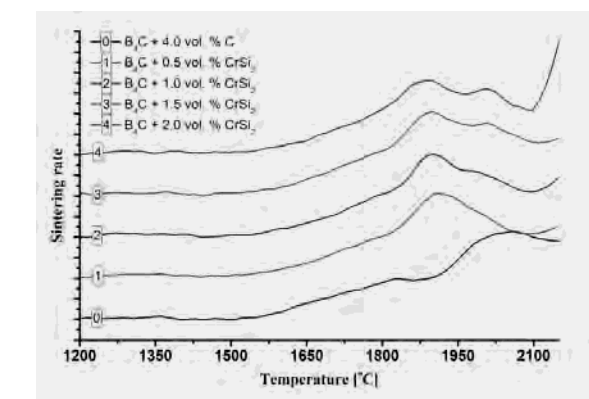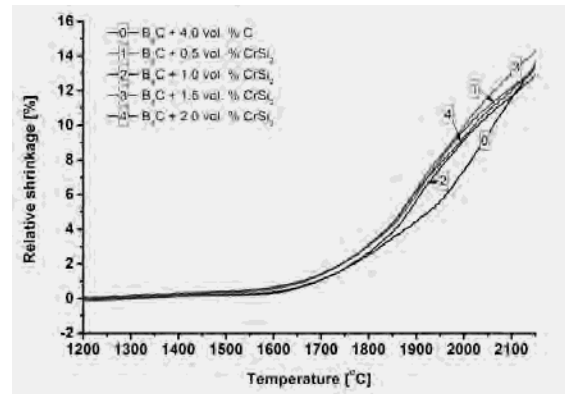

Fig. 2. Relative shrinkage of boron carbide with addition of $CrSi_2$ phase
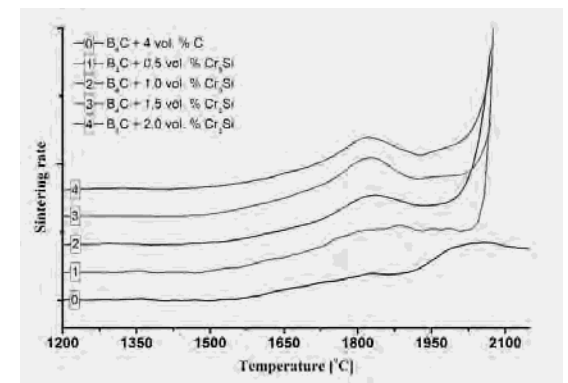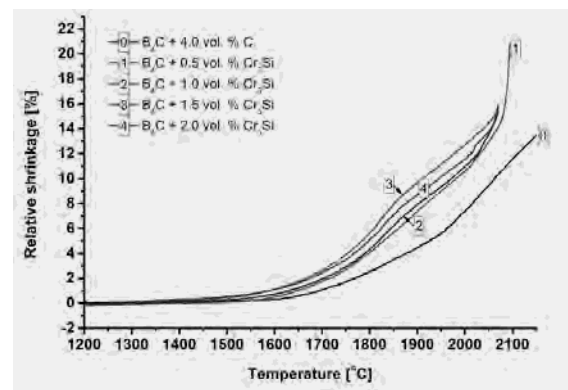Rys. 2. Skurcz względny węglika boru z dodatkiem fazy $CrSi_2$

Fig. 3. Relative shrinkage of boron carbide with addition of Cr_3Si phase
Rys. 3. Skurcz względny węglika boru z dodatkiem fazy Cr_3Si

In the first step, the additives intensify the diffusion processes of the sintered boron carbide. In the second step the liquid phase appears. In the case of the chromium carbide additive, the liquid phase is connected with the formation of chromium diboride (Table 1), the melting point is above 2150°C and its influence on the sintering process is probably limited by free carbon formation (Table 1). In the case of chromium silicates, the temperature of the liquid phase appearance depends on the CrB_2 to SiC ratio in the sinters (Tables 2 and 3). It is presented in the phase diagram (Fig. 4).

TABLE 1. **Phase changes of B_4C-Cr_3C_2 system**
TABELA 1. **Zmiany fazowe w układzie B_4C-Cr_3C_2**

Initial phase composition	Sinter phase composition [wt. %]		
	B_4C	CrB_2	C
B_4C	98.6	0	1.4
B_4C + 0.5 vol.% of Cr_3C_2	95.6	1.7	2.7
B_4C + 1.0 vol.% of Cr_3C_2	94.9	2.5	2.6
B_4C + 1.5 vol.% of Cr_3C_2	93.8	3.3	2.8
B_4C + 2.0 vol.% of Cr_3C_2	93.3	3.6	3.1

TABLE 2. **Phase changes of B_4C-$CrSi_2$ system**
TABELA 2. **Zmiany fazowe w układzie B_4C-$CrSi_2$**

Initial phase composition	Sinter phase composition [wt. %]				Phase mol % of SiC - CrB_2 system	
	B_4C	CrB_2	SiC	C	CrB_2	SiC
B_4C + 0.5 vol.% of $CrSi_2$	97.4	1.3	0.1	1.2	88	12
B_4C + 1.0 vol.% of $CrSi_2$	96.8	1.6	0.5	1.1	64	36
B_4C + 1.5 vol.% of $CrSi_2$	96.0	1.9	0.8	1.2	56	44
B_4C + 2.0 vol.% of $CrSi_2$	96.0	1.9	1.0	1.1	51	49

TABLE 3. **Phase changes of B_4C-Cr_3Si system**
TABELA 3. **Zmiany fazowe w układzie B_4C-Cr_3Si**

Initial phase composition	Sinter phase composition [wt. %]				Phase mol % of SiC - CrB_2 system	
	B_4C	CrB_2	SiC	C	CrB_2	SiC
B_4C + 0.5 vol.% of Cr_3Si	96.4	1.9	0.1	1.6	91	9
B_4C + 1.0 vol.% of Cr_3Si	96.1	2.7	0.2	1.1	88	12
B_4C + 1.5 vol.% of Cr_3Si	95.2	3.4	0.3	1.1	86	14
B_4C + 2.0 vol.% of Cr_3Si	93.8	4.4	0.4	1.4	86	14

The samples of the sintered materials were investigated using the XRD method. The results of the phase analysis of the sinters formed at the temperature of 2150°C are collected in Tables 1-3.
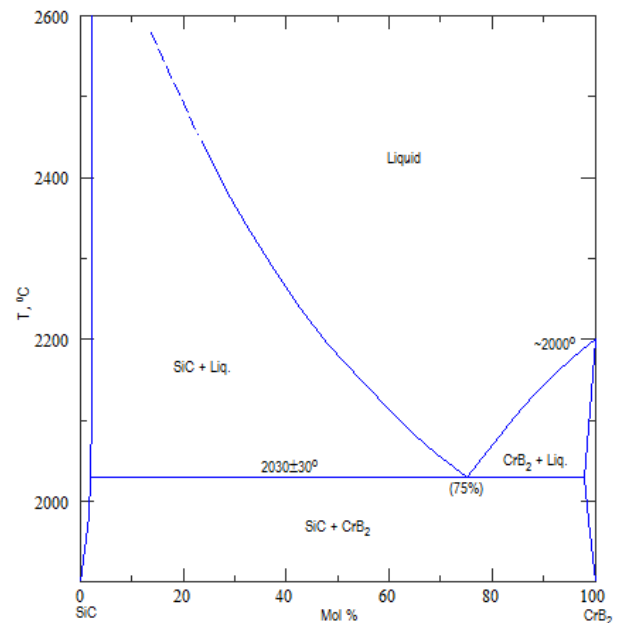

Fig. 4. Phase diagram of SiC – CrB_2 system [10]
Rys. 4. Diagram fazowy układu SiC-CrB_2 [10]

The X-ray analysis shows that during the sintering of B_4C - Cr_3C_2 materials, the diffusion of boron from the boron carbide phase to the chromium carbide phase results in the formation of chromium diboride. In accordance with chemical equation (1) and the XRD results, free carbon appears in the sinters. The higher the addition of chromium carbide, the higher content of free carbon and CrB_2 formed in the sinter. The carbon comes mostly from the chromium carbide and partly from the boron carbide

$$3 \cdot B_4C + 2 \cdot Cr_3C_2 \rightarrow 6 \cdot CrB_2 + 7 \cdot C \qquad (1)$$

In the case of the $CrSi_2$ and Cr_3Si additive, the chromium diboride is also formed as a product of boron, coming from the boron carbide, and chromium from the chromium silicate in accordance with the proposed equation (2) and (3). The amount of CrB_2 phase increases with an increase in $CrSi_2$ content. Simultaneously the silicon carbide phase appears as a reaction result of silicon from the chromium silicate and boron coming from the boron carbide. The more additive, the higher concentration of silicon carbide in the sinter. A constant content of free carbon from boron carbide was also recorded

$$B_4C + 3C + 2 \cdot CrSi_2 \rightarrow 2 \cdot CrB_2 + 4 \cdot SiC \qquad (2)$$
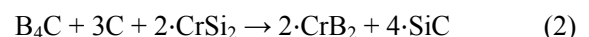
In comparison to the B_4C - $CrSi_2$ system, in the case of the Cr_3Si additive, a greater chromium diboride phase and a lesser silicon carbide phase are formed during the sintering process. Moreover free carbon was detected. It follows from equation (3)

$$3 \cdot B_4C + 2 \cdot Cr_3Si \rightarrow 6 \cdot CrB_2 + 2 \cdot SiC + C \qquad (3)$$
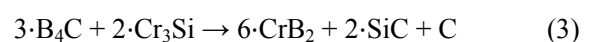
In the B_4C - Cr_3Si system, the calculated mol.% of CrB_2 (Table 3) is higher than in the case of the $CrSi_2$

additive (Table 2). The mol.% of chromium diboride decreases with an increase in $CrSi_2$ content and it shifts to the eutectic point of the CrB_2 - SiC system (Fig. 4). It correlates with liquid phase sintering at 2050°C recorded during the dilatometric measurements (Fig. 3). In comparison, in the B_4C - $CrSi_2$ system the addition of a higher than 1 vol.% chromium silicates causes the liquid phase to intensify the sintering process at temperatures above 2100°C.

To explain what exactly happened with the phase composition during sintering, phase (XRD) analyses were conducted in characteristic points of the sintering curve. The samples containing the maximum addition of sintering modifier were heated up to the desired temperature, held for 15 min and rapidly cooled down. The examinations were made for B_4C - 2 vol.% Cr_3C_2 and B_4C - 2 vol.% $CrSi_2$ are presented in Tables 4 and 5, respectively. To carry out this examination, samples containing 2 vol.% chromium carbide were held at 1550, 1850 and 1970°C and for the addition of chromium silicate at temperatures of 1550, 1850 and 2000°C.

In the B_4C - Cr_3C_2 system, the chromium carbide disappears below the onset temperature of sintering. Chromium diboride and free carbon are formed.

TABLE 4. **Phase changes of B_4C - 2 vol.% Cr_3C_2 vs. temperature**
TABELA 4. **Zmiany fazowe B_4C - 2% obj. Cr_3C_2 w funkcji temperatury**

Temperature [°C]	Phase composition [wt. %]		
	B_4C	CrB_2	C
1550	90.8	5.7	3.5
1850	95.2	2.8	1.9
1970	94.8	3.6	1.6

TABLE 5. **Phase changes of B_4C - 2 vol.% $CrSi_2$ vs. temperature**
TABELA 5. **Zmiany fazowe B_4C - 2% obj. $CrSi_2$ w funkcji temperatury**

Temperature [°C]	Phase composition [wt. %]			
	B_4C	CrB_2	SiC	C
1550	94.7	1.4	1.0	1.6
1850	94.8	2.4	1.8	1.0
2000	95.2	2.5	1.6	0.7

In the case of the chromium silicate additive, the chromium diboride and silicon carbide formation starts at a lower temperature than 1550°C. The content of the formed phase grows with an increase in temperature during sintering.

The existence of the phases found by XRD in the B_4C - Cr_3C_2 system was confirmed by EDS point analysis and illustrated in Figure 5, and for the composites in the B_4C - $CrSi_2$ system in Figure 6. The EDS analysis shows two phases for materials with the chromium carbide additive and three phases for the chromium silicate additive: a dark boron carbide phase, a grey silicon carbide phase (in the case of the $CrSi_2$ additive) and a white chromium diboride phase. The other elements on the point EDS analysis are visible because the detector collects the average value from the measured zone with the diameter of 1 μm. Chromium as a heavier element than silica has a stronger signal collected by the detector, which identifies the white phase as chromium diboride. On the other hand the analysis of the boron carbide-chromium carbide material shown in Figure 5 in connection with the phase analysis confirm that chromium diboride is the white phase also in Figure 6.
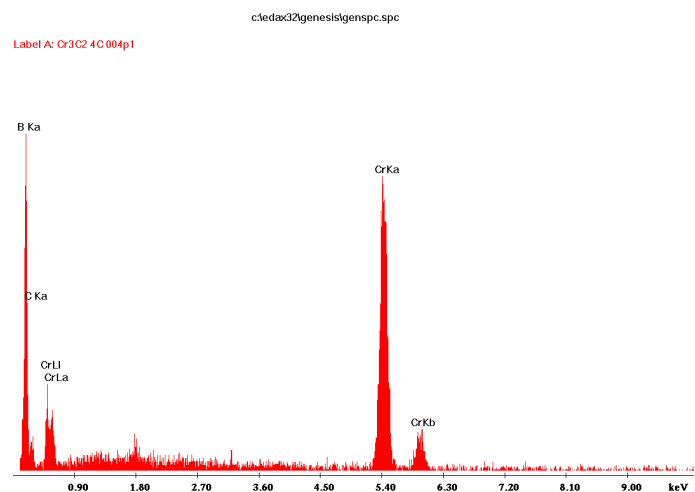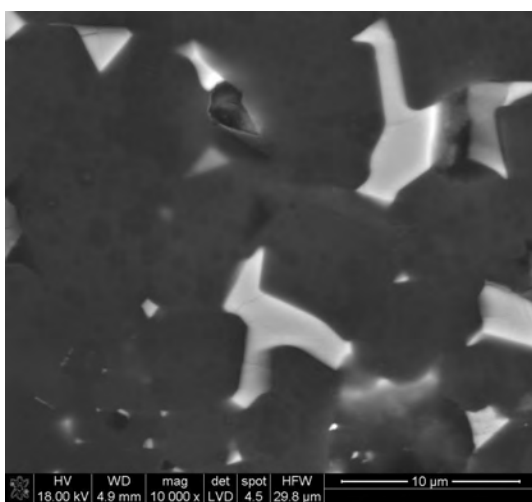

Fig. 5. SEM microstructure and EDS point analysis of B_4C + 2 vol. % Cr_3C_2

Rys. 5. Mikrostruktura SEM oraz analiza punktowa EDS tworzywa B_4C + 2% obj. Cr_3C_2
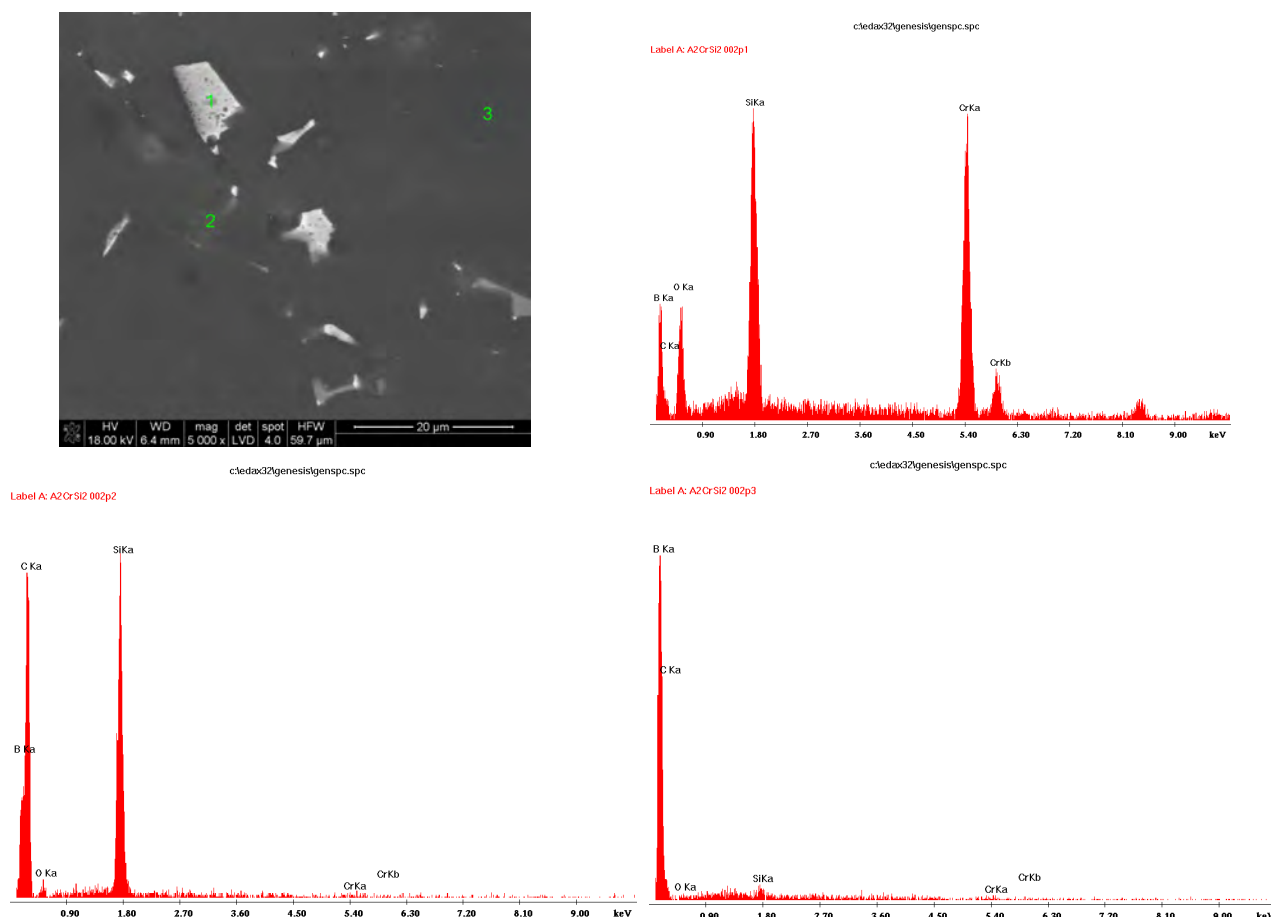
Fig. 6. SEM microstructure and EDS point analysis of B_4C + 2 vol.% $CrSi_2$

Rys. 6. Mikrostruktura SEM oraz analiza punktowa EDS tworzywa B_4C + 2% obj. $CrSi_2$

CONCLUSIONS

Analysing the research results of the boron carbide--chromium compounds systems, it can be claimed that additives have little influence on sintering in the case of the used boron carbide and can only decrease the sintering temperature to 2050°C in the case of chromium silicate additives. In the case of chromium carbide, the obtained sinters are composed of boron carbide, chromium diboride and free carbon coming mostly from chromium carbide and partly from boron carbide. The addition of chromium silicates results in the formation of chromium diboride, silicon carbide and free carbon. The concentration of silicon carbide in the sinters depends on the stoichiometry of the chromium silicate additive. The decrease in sintering temperature depends on the quantity of liquid phase and on the CrB_2/SiC ratio. It is possible to improve sintering by establishing the additive grain size, homogenization method, sintering parameters and initial mixture composition.

Acknowledgement

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