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COMPOSITES THEORY AND PRACTICE

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INFLUENCE OF SINTERING TEMPERATURE AND CrB_2 ADDITION ON PROPERTIES OF TITANIUM DIBORIDE PRODUCED BY SPARK PLASMA SINTERING

The effect of a 5 vol.% chromium diboride addition on the microstructure and properties of sintered titanium diboride was investigated. The preliminary results of studies of TiB_2-5CrB_2 composites sintered by SPS were discussed. The density, Young's modulus and Vickers hardness of the obtained sinters were examined. Microstructural examinations were carried out by SEM. It was found that sintering TiB_2 ceramics by SPS at temperatures of 2000 and 2200°C for 10 minutes is not sufficient. The results of testing the physical and mechanical properties of TiB_2-5CrB_2 composites have shown that the use of CrB_2 may be a good way to obtain a composite material for high performance applications. The best properties were obtained by the composite materials sintered at 2200°C. The results will serve as a basis for further optimization of the SPS process for composite fabrication.

Keywords: spark plasma sintering (SPS), composites, titanium diboride (TiB_2), chromium diboride (CrB_2)

WPŁYW TEMPERATURY SPIEKANIA ORAZ DODATKU CrB_2 NA WŁAŚCIWOŚCI DWUBORKU TYTANU OTRZYMANEGO METODĄ PLAZMOWEGO SPIEKANIA ISKROWEGO

W pracy zbadano wpływ dodatku dwuborku chromu w ilości 5% obj. na mikrostrukturę oraz właściwości spiekanego dwuborku tytanu. Praca przedstawia wstępne wyniki badań dotyczące spiekania kompozytów TiB_2-5CrB_2 metodą iskrowego spiekania plazmowego (SPS). Dla porównania wytworzono ceramikę TiB_2 bez stosowania dodatków do spiekania. Proces spiekania przeprowadzono w temperaturach 2000 oraz 2200°C w czasie 10 minut. Dla otrzymanych spieków przeprowadzono badania gęstości, modułu Younga oraz twardości metodą Vickersa. Przeprowadzono również obserwacje mikrostrukturalne, stosując skaningową mikroskopię elektronową (SEM). Stwierdzono, że spiekanie ceramiki TiB_2 metodą SPS w temperturach 2000 oraz 2200°C w czasie 10 min jest niewystarczające. Wyniki badań właściwości fizycznych i mechanicznych kompozytów TiB_2-5CrB_2 wykazały, że zastosowanie CrB_2 może być dobrą drogą do otrzymania materiału kompozytowego o wysokich właściwościach. Dla kompozytów TiB_2-5CrB_2 spiekanych w 2200°C uzyskano najlepsze właściwości. Otrzymane wyniki będą stanowić podstawę do optymalizacji warunków procesu SPS dla kompozytów TiB_2-5CrB_2.

Słowa kluczowe: iskrowe spiekanie plazmowe (SPS), kompozyty, dwuborek tytanu (TiB_2), dwuborek chromu (CrB_2)

INTRODUCTION

In recent years, the use of ceramic materials has significantly increased in various applications due to the unique characteristics of these materials. Titanium diboride (TiB_2) is a ceramic material with excellent hardness, low density, high Young's modulus, corrosion resistance and electrical conductivity. It is difficult to sinter TiB_2 by common methods because of its low self-diffusion rate. Moreover, the difficulties of the sintering process arise from the very high melting point of TiB_2 ceramics and the presence of TiO_2 and B_2O_3 oxide layers that have a negative influence on the densification and reactions with the metal matrix [1-3]. Several studies reported on the use of various techniques for fabricating TiB_2 ceramics such as hot isostatic pressing (HIP) [2], the high temperature-high pressure (HT-HP) method [3], self-propagating high-temperature synthesis (SHS) [4, 5], Pulse Plasma Sintering (PPS) [6, 7] and Spark Plasma Sintering (SPS) [8-10].

Zhang et al. [9] obtained monolithic TiB_2 ceramics by spark plasma sintering (SPS) applying a sintering temperature ranging from 1200 to 1800°C. The results indicate that TiB_2 ceramics sintered at 1800°C provide the optimal combination of dense microstructure and excellent properties, including a relative density of 97.6%, microhardness of 29.6 ±2.5 GPa, flexural strength of 538 ±45 MPa, and fracture toughness of

5.2 ±0.4 $MPam^{1/2}$. Sulima et al. [3] sintered the TiB_2 ceramic using the HP-HT method. TiB_2 was obtained without using sintering agents. The sintered ceramics were characterized by a very high density and isotropy of the properties. It was indicated that applying the temperature of 1500°C and pressure of 7.2 GPa permits obtaining TiB_2 ceramics without cracks. However, Khanra et al. [5] showed that the titanium diboride powder produced by the SHS technique can be sintered at 1700°C and demonstrates excellent sinterability. Spark Plasma Sintering is one of the most promising sintering methods. In this method a pulsed direct current is used to heat the specimens. The SPS method comprises three main mechanisms of action: (a) the application of uniaxial pressure; (b) the application of pulsed voltage; and (c) the resistance heating of graphite dies and the sample. The SPS process is performed using electric discharges of high intensity but low voltage [11]. The heating is accomplished by spark discharges in voids between the particles. A pulsed current during SPS sintering is usually applied during the consolidation of materials that conduct electric current. Figure 1 illustrates the flow of DC pulse current through the particles [12-15].

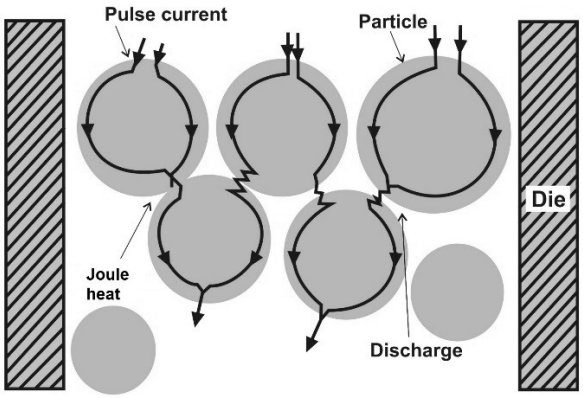

Fig. 1. Schematic diagram of pulsed current that flows through powder particles [13, 16]

Rys. 1. Schemat przepływu prądu przez spiekany proszek [13, 16]

Several studies [16-22] reported on the application of sintering agents such as Fe, Cu, Co, Ti, B_4C, CrB_2, $MoSi_2$, $TiSi_2$, $CrSi_2$, SiC or Si_3N_4 which enhance the densification of titanium diboride. Moreover, metallic sinter additives such as Ti, Fe, Ni, Cr, Co and Mo are often used to promote liquid phase sintering [23-27]. Mukhopadhyay et al. [28] performed the sintering process of TiB_2 ceramic containing various proportions of $MoSi_2$ by hot pressing. The incorporation of 2.5 wt.% $MoSi_2$, as a sinter-additive in TiB_2 leads to near theoretical densification, and improvements in the mechanical properties compared with monolithic TiB_2. However, degradation in the mechanical properties with an increase in $MoSi_2$ content, beyond 5 wt.% was critically recorded. In contrast, Raju et al. [29] reports the effect of a $TiSi_2$ addition (up to 10 wt.%) and temperature on the hardness and strength of TiB_2. The experimental results clearly confirm the advantage of using $TiSi_2$ as a sintering-aid to improve densification as well as to retain high temperature strength and hardness properties. It was indicated that the TiB_2-2.5 wt.% $TiSi_2$ composite exhibited the best hardness and strength values at high temperatures. Zhang et al. [23] investigated the influence of titanium on the properties of the TiB_2 ceramic produced by SPS. It was shown that the densification temperature of the TiB_2 ceramic was significantly decreased and the grain growth was effectively prohibited due to the formation of TiB at the TiB_2 grain boundaries. The TiB_2 ceramic sintered at 1650°C is characterized by an attractive combination of dense microstructure and excellent mechanical properties. The high density and fine-grained microstructure influenced an improvement in the mechanical properties of the TiB_2 ceramic with a 2.5 wt.% Ti addition.

In this paper, the microstructure and selected physical and mechanical properties of TiB_2-5CrB_2 composites obtained by SPS were investigated.

EXPERIMENTAL PROCEDURE

The materials used in the experimental study are titanium diboride (H.C. Starck, 1.5÷2.5 μm average grain size, purity 99.9 wt.%) and chromium diboride (GoodFellow, 3÷10 μm average grain size, purity 99.8.%). The morphology of the powder particles was obtained by a scanning electron microscope (Fig. 2). Powder mixtures of 95 vol.% TiB_2 with 5 vol.% CrB_2 were prepared in a Turbula mixer for 8 hours. The TiB_2 ceramics were sintered without the use of sintering agents.

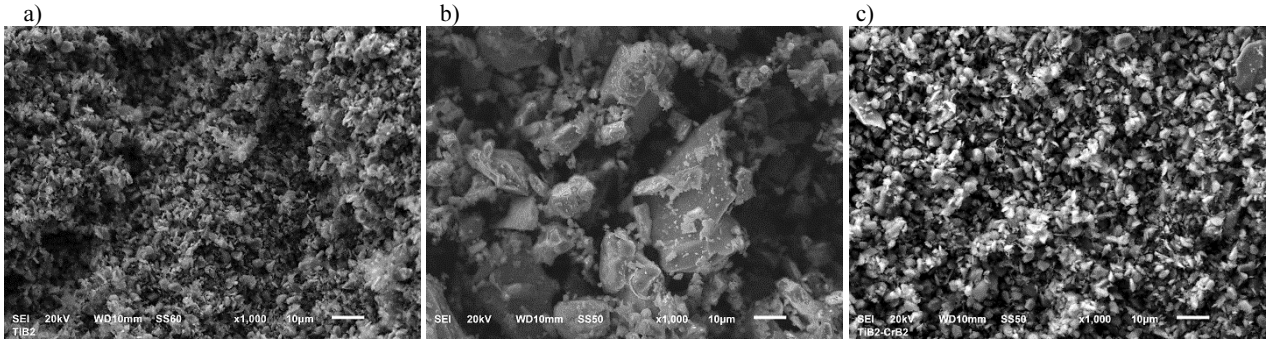

Fig. 2 Morphology of powders: a) TiB_2, b) CrB_2, c) starting powder mixture TiB_2-5 vol.% CrB_2

Rys. 2. Morfologia proszków: a) TiB_2, b) CrB2, c) wyjściowej mieszanki proszków TiB_2-5% obj. CrB_2

The SPS process was carried out using a HPD 5 FCT System GmbH furnace. The powders were sintered in a vacuum chamber, using a cylindrical graphite die. The mixtures were put into a cylindrical graphite die with an inner diameter of 20 mm. Graphite felt was used as thermal insulation. During the SPS process, the sintering temperature was monitored by a pyrometer which was focused on the surface of the die. The powders were sintered at temperatures of 2000°C and 2200°C with a pressure of 35 MPa in vacuum. Maximum pressure was obtained after a duration of 10 min. After that, argon was introduced to the SPS furnace chamber, which acted as a protective gas and the sintering process was carried out. The applied duration and heating rate were 5 minutes and 200°C/min, respectively. Figure 3 shows the change in sintering parameters during the SPS process.

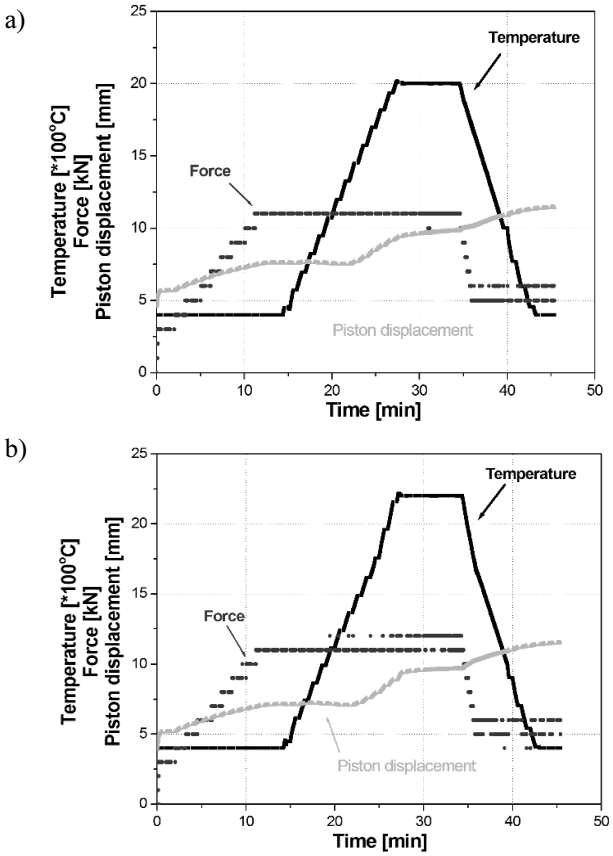

Fig. 3. Change in sintering parameters as function of time registered during SPS at temperatures of: a) 2000°C and b) 2200°C

Rys. 3. Zmiana parametrów spiekania w funkcji czasu rejestrowana podczas procesu SPS dla temperatury: a) 2000°C oraz b) 2200°C

Density was measured with an accuracy of ±1% by the liquid immersion technique using the Archimedes principle. Open porosity (P_o) and apparent density (ρ) were calculated in accordance with relevant standards [30].

Density was calculated from the following formula:

$$\rho = \frac{m_1}{m_3 - m_2}\rho_L \tag{1}$$

Porosity was calculated from the equation given below:

$$P_o = \frac{m_3 - m_1}{m_3 - m_2}100\% \tag{2}$$

where: m_1 - the weight of a dry sample [g], m_2 - the apparent weight of an immersed sample [g], m_3 - the weight of a sample saturated with liquid [g], ρ_L - the density of water [g/cm^3].

Young's modulus measurements of the sintered composites were also taken, using the ultrasonic method of measuring the transition speed of transverse and longitudinal waves, using a Panametrics Epoch III flaw detector. The accuracy of the calculated Young's modulus is estimated at 2%. Calculations were made using the following formula:

$$E = \rho C_T^2 \frac{3C_L^2 - 4C_T^2}{C_L^2 - C_T^2}100\% \tag{2}$$

where: E - Young's modulus, C_L - velocity of the longitudinal wave, C_T - velocity of the transversal wave, ρ - density of the material.

Hardness measurements by the Vickers method were carried out using a NEXUS 4000 hardness tester under a load of 49.03 N applied for 10 s. Standard deviations of the HV5 values were no more than 4% of the average values. The microstructure of the powder mixtures and sintered products was examined by a JEOL JSM 6610LV scanning electron microscope (SEM). Phase identification of the sintered materials was made by X-ray diffraction (XRD) using Cu Kα radiation with a scintilation detector (Brucker Discover D8).

RESULTS

Tables 1 and 2 list the physical and mechanical properties of the sintered materials. Irrespective of the sintering temperature, the sintered TiB_2 ceramics have a low density, i.e. less than 88% of the theoretical density. These samples were sintered without the use of sintering additives. The values of Young's modulus and hardness of the sintered TiB_2 are also very low (Table 2). For the samples sintered at 2000°C, hardness was not determined due to the high porosity of the examined surface, which resulted in a large distortion of the indentation. The results suggest that sintering TiB_2 ceramics by SPS for 10 minutes at temperatures of 2000°C and 2200°C is not sufficient. Only very moderate changes were observed in the properties of the sintered ceramics with an increasing temperature of sintering. Literature [1, 2, 31] report that sintering pure TiB_2 is very difficult. One of the reasons is that TiB_2 ceramic is a compound characterized by two ionic and covalent bonds which require a very high sintering temperature for consolidation. TiB_2 has a low crystalline boundary

diffusion coefficient, which causes a slow densification speed and long sintering time. Another factor limiting the consolidation process is the formation of a thin layer of oxygen (TiO_2 and B_2O_3) on the surface of the TiB_2 powder [32]. Zhang et al. [9] obtained monolithic TiB_2 ceramics at lower temperatures by spark plasma sintering (SPS). It was shown that TiB_2 sintered at 1800°C is characterized by an optimum combination of physical properties (density), mechanical properties (microhardness, bending strength) and microstructure. These results were obtained using different sintering parameters, i.e. a lower heating rate and higher pressure of 50 MPa. The purity of the applied powders was also different, inferior to the powders supplied by the Starck Company used in the presented studies. All these factors affect the quality and properties of the sintered ceramic materials.

TABLE 1. **The density and porosity of materials sintered by SPS method**
TABELA 1. **Gęstość oraz porowatość spiekanych materiałów przy użyciu metody SPS**

Sintered materials	Sintering conditions		Apparent density ρ_0		Porosity P_o [%]
	T [°C]	Time [min]	[g/cm^3]	[%]	
TiB_2	2000	10	3.58 ±0.02	80 ±0.3	25.32
	2200		3.94 ±0.01	88 ±0.3	10.92
TiB_2-5CrB_2	2000	10	4.29 ±0.02	87 ±0.3	11.37
	2200		4.73 ±0.02	95 ±0.3	3.74

TABLE 2. **Properties of materials sintered by SPS method.**
TABELA 2. **Właściwości spiekanych materiałów przy użyciu metody SPS**

Sintered materials	Sintering conditions		Young's modulus E		Poisson's rate ν
	T [°C]	Time [min]	[GPa]	[%]	
TiB_2	2000	10	282 ±7	52	0.11
	2200		340 ±9	61	0.10
TiB_2-5CrB_2	2000	10	453 ±13	84	0.20
	2200		477 ±14	87	0.21

Figure 4 shows an example of the microstructure of the sintered TiB_2 ceramics. SEM examinations of the microstructure revealed a high level of porosity in the sintered TiB_2 ceramics. Large pores are observed on the surface of TiB_2 sintered at 2000°C (Fig. 4a). Accordingly, the relative density of the sintered ceramics is only 80% of the theoretical density. The porosity of the sintered ceramic material decreases with an increasing sintering temperature from 25.32 to 10.93% for 2000 and 2200°C, respectively (Table 1). The X-ray examinations confirmed the presence of TiB_2 in the sintered material (Fig. 5). The sintered ceramics obtained at 2000 and 2200°C have the same phase composition. The XRD spectra made for the sintered TiB_2 suggest that it also contains titanium.

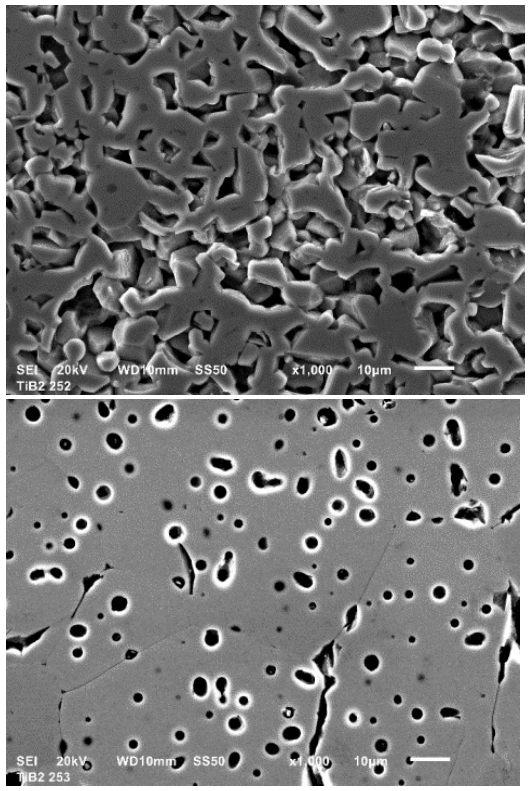

Fig. 4. SEM images of microstructure of TiB_2 sintered at temperatures of: a) 2000°C, b) 2200°C

Rys. 4. Obrazy SEM mikrostruktury TiB_2 spiekanego w temperaturze: a) 2000°C, b) 2200°C

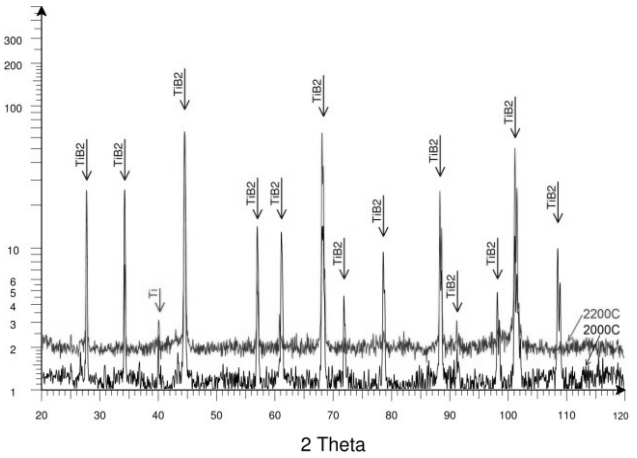

Fig. 5. X-ray diffraction pattern of TiB_2 sintered by SPS method

Rys. 5. Dyfraktogram rentgenowski dla ceramiki TiB_2 spiekanej metodą SPS

To improve the composite properties, an addition of 5% CrB_2 was introduced to the TiB_2 powder. So far, TiB_2-CrB_2 composites have been sintered by pressure-assisted methods [18, 27]. The application of SPS is a new method of ceramic composites treatment. The results of the physical and mechanical studies of the TiB_2-5CrB_2 composite properties (Tables 1 and 2) show that the use of CrB_2 gives promising results in manufacturing composite materials for high performance applications. The composites have a high sintered density and low porosity. An increase of approximately

40÷50% was also obtained in the value of Young's modulus, while the hardness of the sintered ceramic composites doubled. In spite of this, the results are not satisfactory (Tables 1 and 2).

It was found that another important factor influencing the microstructure and properties of the tested composites are the SPS sintering conditions. The results show that with an increase in sintering temperature, the properties of the sintered composites improve. The maximum relative density of 95% was achieved by the TiB_2-$5CrB_2$ composite sintered at 2200°C for 10 minutes. For this composite, also the highest values of Young's modulus (477 GPa) and hardness (1636 HV0.1) were achieved. Literature quotes studies in which a very high density was obtained in the sintered TiB_2 ceramics with varying contents of CrB_2. Holcombe and Dykes [33] obtained a density of 84 and 90% of the theoretical density for TiB_2 with an addition of 3% CrB_2 applying pressureless sintering at 1900 and 2100°C, respectively. The same authors reported obtaining a still higher density of 95 and 98% of the theoretical density by microwave sintering under similar conditions. On the other hand, Konigshofer et al. [31] obtained a density of 98.9% with the addition of 0.5% CrB_2 to TiB_2 hot pressed at a temperature of 1800°C and pressure of 45 MPa.

Figures 6 and 7 show different microstructures of the sintered TiB_2-$5CrB_2$ composites. The composite produced at 2000°C is characterized by a microstructure with a high level of porosity (Fig. 6a). An increase in sintering temperature reduced this porosity (Fig. 6b). The content of pores in the microstructure is lower and there are areas free from pores and fully consolidated. Figure 8 shows the X-ray diffraction patterns (XRD) obtained for the TiB_2-$5CrB_2$ composites. The formation of a reaction product phase during sintering can lead to improved diffusion, and thus to improved sintering kinetics [34, 36]. The examined results suggest that the next stage of the studies should be devoted to optimization of the SPS process conditions, mainly the sintering time, temperature and pressure. It is expected that due to determining the optimal conditions of the TiB_2-$5CrB_2$ composite sintering process, it will be possible to make sintered materials of high performance, examined in more detail during further activities in the studies.

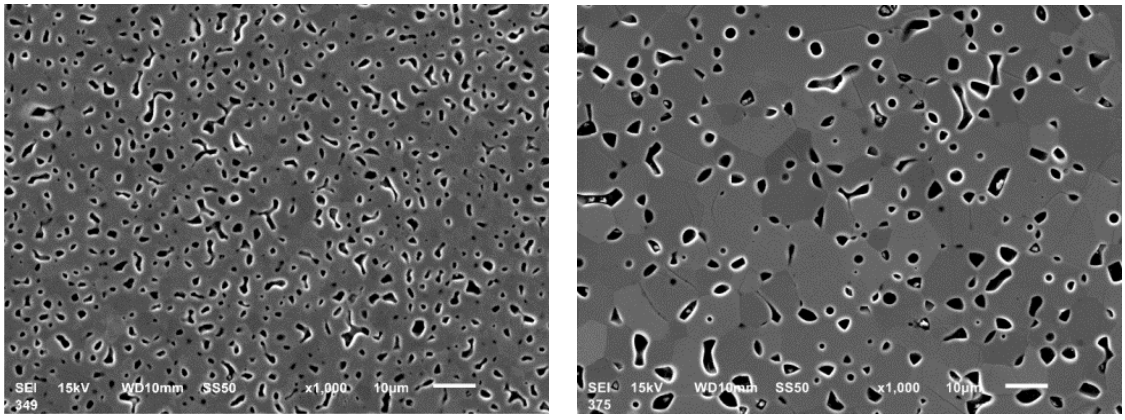

Fig. 6. SEM images of TiB_2-$5CrB_2$ composites sintered at temperatures of: a) 2000°C, b) 2200°C

Rys. 6. Obrazy SEM kompozytu TiB_2-$5CrB_2$ spiekanego w temperaturze: a) 2000°C, b) 2200°C

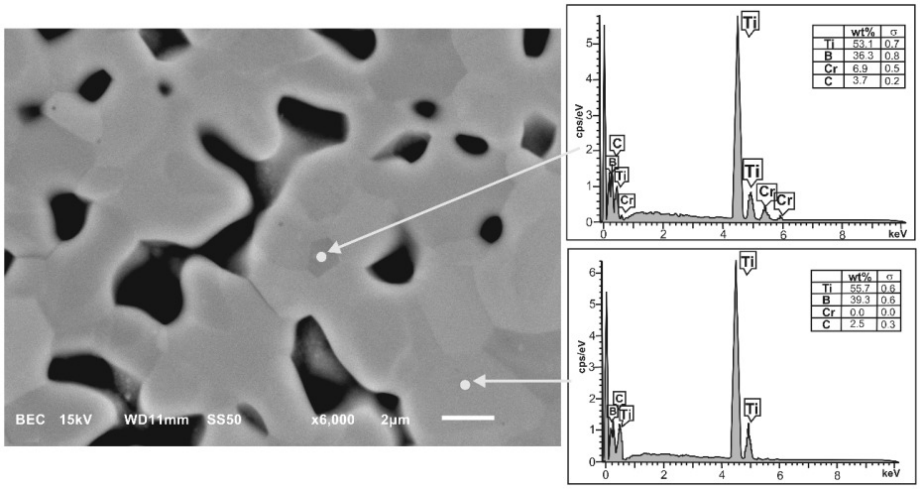

Fig. 7. SEM images of TiB_2-$5CrB_2$ composites sintered at temperature of 2200°C with corresponding point analysis (EDS)

Rys. 7. Obrazy SEM kompozytu TiB_2-$5CrB_2$ spiekanego w temperaturze 2200°C wraz z punktową analizą składu chemicznego (EDS)

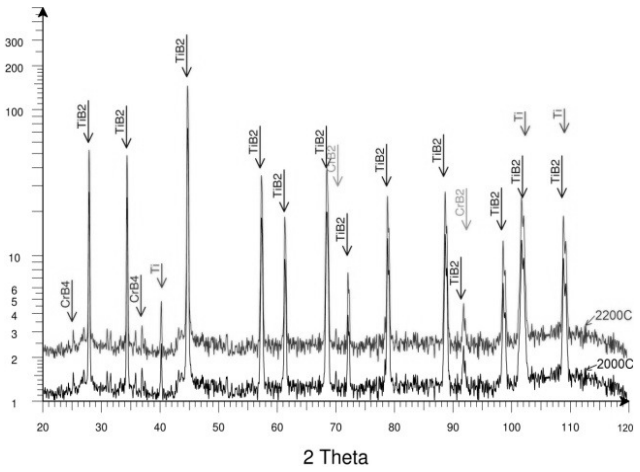

Fig. 8. X-ray diffraction pattern of TiB_2-5CrB_2 composite sintered by SPS method

Rys. 8. Dyfraktogram rentgenowski dla kompozytu TiB_2-5CrB_2 spiekanego metodą SPS

The problem is interesting considering the fact that the TiB_2-CrB_2 composites obtained in other studies [34], were characterized by a high density and hardness combined with excellent resistance to oxidation. The authors proved that the addition of even 2.5 vol.% CrB_2 introduced to TiB_2 gives a density of > 96%, when the method of hot pressing is applied at 1750°C and a pressure of 35 MPa. The addition of CrB_2 was found to facilitate the sintering process and inhibit grain growth during densification. The solid solution formation of TiB_2 and CrB_2 were also confirmed. Therefore, the TiB_2-5CrB_2 composite can be one of the candidate materials for high temperature structural applications.

CONCLUSIONS

The SPS process was applied to densify the TiB_2 ceramic and TiB_2-5CrB_2 composite. The following conclusions can be derived from the present research:

- The applied SPS conditions (the temperatures of 2000 and 2200°C, pressure of 35 MPa and duration of 10 minutes) were found to be insufficient to produce TiB_2 ceramics of high density.
- In the case of TiB_2-5CrB_2 composites, an important factor influencing the microstructure and properties is the sintering temperature. An increase in sintering temperature was observed to improve the properties of the composite.
- A maximum relative density of 95% was obtained in the TiB2-5CrB2 composite sintered by SPS at 2200ºC for 10 minutes. The Young's modulus and Vickers hardness were 477 GPa and 1636 HV0.1, respectively.

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