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Structure and mechanical properties of B_4C–CrB_2 composites prepared by spark plasma sintering

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B_4C–CrB_2 ceramic composites were synthesized by spark plasma sintering from a powder mixture containing 72 wt.% B_4C and 28 wt.% CrB_2 at 1800°C and 1900°C under a pressure of 70 MPa. The ceramics were investigated by X-ray diffraction, performing Rietveld refinements, and by scanning electron microscopy. The composite obtained at 1800°C consisted of the two initial phases, B_4C and CrB_2; it exhibited a relative density of 97.6% and a hardness of 34.1 GPa. Increasing the sintering temperature to 1900°C resulted in a significant reduction of the amount of CrB_2 phase, associated with the formation of a liquid phase, leading to increased porosity; the hardness reached 37.4 GPa.

Boron carbide / Multiphase systems / Crystal structure / Ball milling / Hardness

Introduction

The intensive development of materials science opens broad opportunities for the creation of new materials with tailored properties, for application in various fields, also under extreme operating conditions such as high temperatures, mechanical loads, and aggressive environments. A compound attracting particular attention is boron carbide (B_4C), which is characterized by a high melting point (2450°C [1]), low density (2.5 $g \cdot cm^{-3}$), high hardness (25.5 GPa) [2], and excellent chemical resistance.

An efficient method to synthesize ceramic materials is spark plasma sintering (SPS), which ensures maximum densification thanks to the simultaneous application of temperature and pressure. With this method it is possible to reduce both the temperature and sintering time compared to conventional sintering in a resistance furnace or hot pressing. In an earlier work [3], a B_4C ceramic material synthesized by SPS at a maximum temperature of 2000°C and a pressure of 70 MPa exhibited a hardness of 32.6 GPa and a relative density of 99.5%.

One of the promising approaches to modify the properties of boron carbide is the formation of composites by adding refractory transition metal borides such as CrB_2. Monolithic CrB_2 with high relative density (98.4%) was obtained at 1900°C and a uniaxial pressure of 70 MPa, after a holding time of 15 minutes, using the SPS method [4].

The formation of B_4C–CrB_2 composite materials by SPS improves the mechanical properties, in particular the hardness, and produces samples with high relative density.

Experimental

B_4C–CrB_2 ceramic composites were synthesized by spark plasma sintering from a powder mixture of commercial B_4C and CrB_2, additionally homogenized in a planetary ball mill (PM100, Retsch) using a WC vial and WC balls (diameter 10 mm) for 20 min at a speed of 250 rpm. The mass fraction of B_4C was 72%. The homogenized powder mixture was placed into a graphite die with a diameter of 20 mm and sintered using a FAST/SPS system (DSP 507, Dr. Fritsch).

The sample was initially heated to 400°C, and a pressure of 7 MPa was applied for 5 min to establish stable contacts between the powder particles and the graphite die. Subsequently, the temperature was increased to 1800°C at a heating rate of 100°C/min and held for 6 min under vacuum at a pressure of 7 MPa to ensure degassing of the sample. Thereafter, the pressure was increased to 70 MPa while

simultaneously raising the temperature to the maximum values of 1800°C or 1900°C. The sample was held at this temperature for 7 min and then cooled down to room temperature.

The chemical compositions of the starting materials and the synthesized composites were determined using a Tescan Vega 3 LMU scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy system (Oxford Instruments Aztec ONE with an X-Max^{N}20 detector). The images were analyzed using ImageJ software [5], which allowed evaluation of the grain size.

X-ray powder diffraction (XRD) patterns of the synthesized pellets were collected on a Proto AXRD Benchtop powder diffractometer (Cu *K*α-radiation). Structure analyses were performed by Rietveld refinement using the FullProf Suite software [5].

To obtain the relative density, the experimental density of the ceramic was determined by the hydrostatic weighing method and compared with the theoretical density calculated based on the results of the structure refinement on X-ray diffraction data.

The hardness was measured with a diamond pyramidal indenter with an angle at the apex of the pyramid of 136° and a load of 1 kgf (9.807 N) on the sample surface (NOVOTEST TS-MKV1 hardness tester). The hardness value is calculated from the length of the pyramid imprint diagonal.

Results and discussion

The experimental conditions and crystallographic data for the components of the ceramic materials B_4C–CrB_2 are presented in Table 1 and XRD patterns are shown in Fig. 1. For the B_4C–CrB_2 composite synthesized at 1800°C the XRD pattern confirms the existence of a two-phase system consisting of rhombohedral B_4C and hexagonal CrB_2. The phase fractions are 82.2% for B_4C and 17.8% for CrB_2, indicating the preservation of the additive.

For the sample synthesized at 1900°C, a large shift in the phase composition was observed. No new phases were identified but the CrB_2 fraction had decreased to 1.8%. Apparently the CrB_2 phase has participated in the formation of a liquid phase at high temperature. It may be noted that the phase diagram of the Cr–B system has a eutectic at 1830°C / 83 at.% B.

The atomic coordinates, site occupancies, and overall temperature factor for the B_4C phase in both materials are shown in Table 2. There is good agreement with the refinement of the crystal structure of pristine B_4C phase synthesized by spark plasma sintering [3].

According to Pearson's Crystal Data [8], the crystal structure of CrB_2 belongs to the structure type AlB_2 (space group *P6/mmm*, atomic coordinates Cr 1*a* 0; 0; 0, B 2*d* ⅓; ⅔; ½).

The initial mixture of powders and the resulting B_4C–CrB_2 ceramic material were analyzed by scanning electron microscopy. On the SEM-images of the ceramics synthesized at 1800°C Fig. 2 (*a*) and 1900°C (Fig. 2 (*b*)) the light phase is CrB_2 and the dark phase B_4C. The image of the sample sintered at 1900°C shows numerous relatively large pores. Elemental mapping of the ceramic materials B_4C–CrB_2 is shown in Fig. 3.

The analysis of the SEM image of the B_4C–CrB_2 composite synthesized at 1800°C made it possible to quantitatively evaluate the particle size. The average size of the B_4C grains, as well as of the CrB_2 grains before sintering was 1.2 μm; the size of the CrB_2 grains after sintering was 7.7 μm.

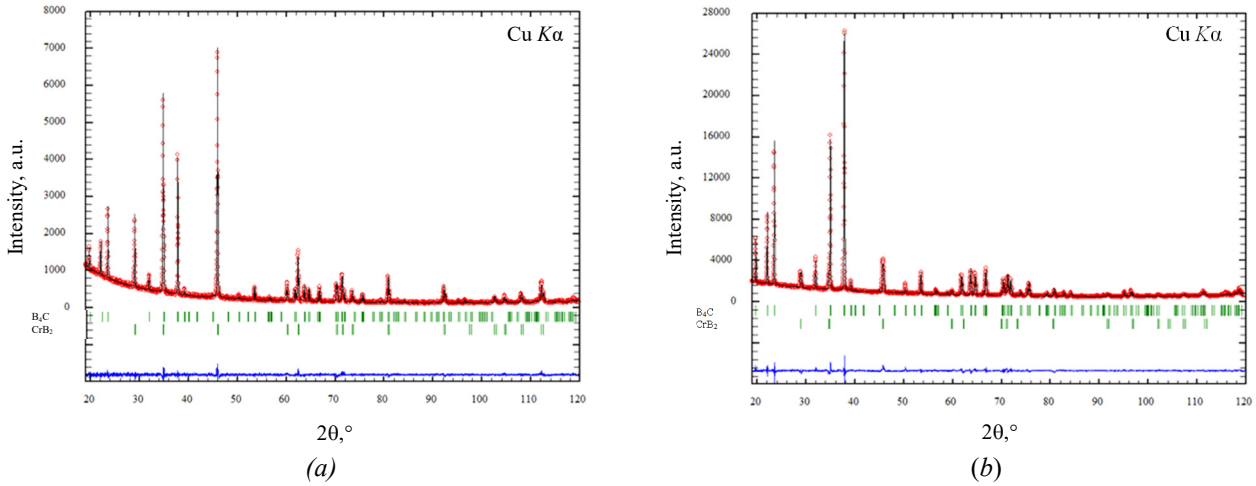


Fig. 1 Observed, calculated, and difference XRD pattern (Cu *K*α-radiation) of the ceramic materials B_4C–CrB_2 synthesized at (*a*) 1800°C and (*b*) 1900°C. The positions of the reflections from B_4C and CrB_2 are indicated by bars.

Table 1 Experimental conditions and results of the refinements of the crystal structures of the components of the B_4C-CrB_2 ceramics.

B_4C–CrB_2 ceramic synthesized at 1800°C		
Composition	$B_{13.12(2)}C_{1.766(10)}$	CrB_2
Structure type	$B_{13}C_2$	AlB_2
Pearson symbol	*hR*51	*hP*3
Space group	*R*-3*m*	*P*6/*mmm*
Cell parameters, Å	a = 5.59897(8), c = 12.0750(2)	a = 2.97477(3), c = 3.07389(4)
Cell volume V, Å^3	327.819(9)	23.557(1)
Formula units per cell Z	3	1
Density D, g·cm^{-3}	2.477	5.189
Mass fraction, %	82.2(10)	17.8(2)
R_B, %	6.35	2.92
Profile reliability factors	R_p = 4.58%, R_{wp} = 6.05%	
B_4C–CrB_2 ceramic synthesized at 1900°C		
Composition	$B_{13.120(6)}C_{1.760(4)}$	CrB_2
Structure type	$B_{13}C_2$	AlB_2
Pearson symbol	*hR*51	*hP*3
Space group	*R*-3*m*	*P*6/*mmm*
Cell parameters, Å	a = 5.60019(5), c = 12.08126(15)	a = 2.98519(18), c = 3.0923(2)
Cell volume V, Å^3	328.132(6)	23.864(3)
Formula units per cell Z	3	1
Density D, g·cm^{-3}	2.474	5.123
Mass fraction, %	98.2(5)	1.8(1)
R_B, %	4.58	10.6
Profile reliability factors	R_p = 3.84%, R_{wp} = 5.02%	

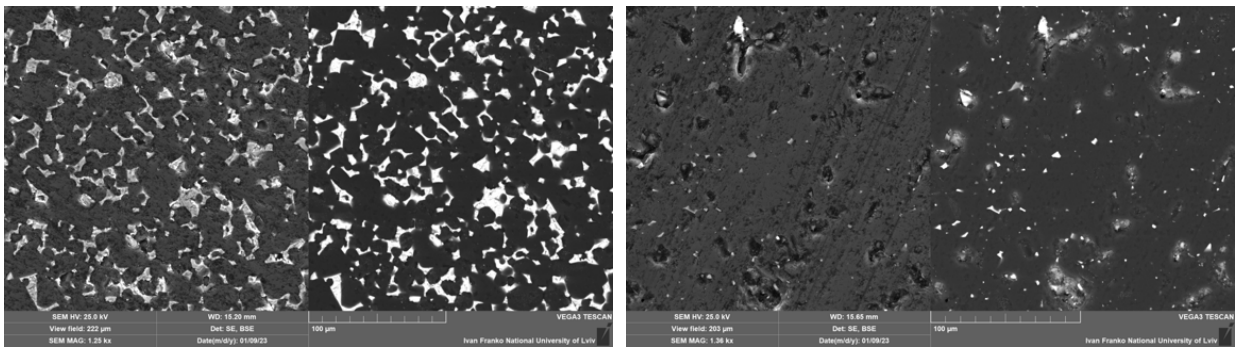
Table 2 Atomic coordinates, site occupancies, and overall temperature factor for the B_4C phase, space group *R*-3*m*.

Site	Wyckoff position	x	y	z	B_{ov}, Å^2	Occupancy[1]
B_4C-CrB_2 ceramic synthesized at 1800°C						
B1	18*h*	0.4405(2)	0.5595(2)	0.0510(2)		1
B2	18*h*	0.5040(3)	0.4960(3)	0.1927(3)		1
C	6*c*	0	0	0.1221(4)	1.28(5)	0.883(5)
B3	6*c*	0	0	0.103(3)		0.117(5)
B4	3*a*	0	0	0		0.883(5)
B_4C-CrB_2 ceramic synthesized at 1900°C						
B1	18*h*	0.44036(8)	0.55964(8)	0.05154(9)		1
B2	18*h*	0.50428(9)	0.49572(9)	0.19166(12)		1
C	6*c*	0	0	0.12255(16)	1.334(19)	0.880(2)
B3	6*c*	0	0	0.0995(11)		0.120(2)
B4	3*a*	0	0	0		0.880(2)

[1] constrain: occ(C) = occ(B4) = 1 – occ(B3)

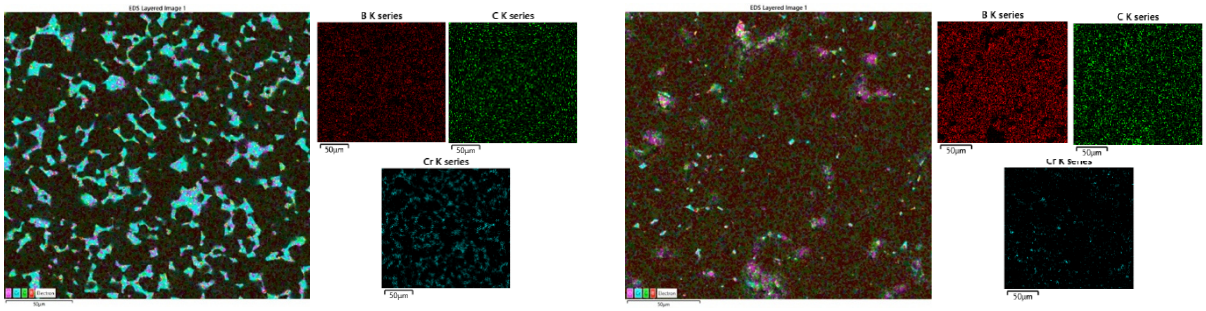
The B_4C ceramic material synthesized by spark plasma sintering at a maximum temperature of 2000°C and a pressure of 70 MPa exhibited a hardness of 32.6 GPa at a relative density of 99.5% [3], indicating near full densification and the formation of a dense, low-porosity microstructure. Monolithic CrB_2, obtained by spark plasma sintering at a maximum temperature of 1900°C and a pressure of 70 MPa also had a high relative density (98.4%) [4]. However, the hardness (15.89 ± 1.3 GPa) was significantly lower than that of B_4C, in agreement with the expectations. CrB_2 undergoes a three-stage densification mechanism, with a sharp increase in density above 1300°C.

In our case, the results obtained confirm the efficiency of the spark plasma sintering method for the fabrication of dense B_4C–CrB_2 composites. For the ceramic sintered at 1800°C, a relative density of 97.6% was achieved, indicating effective densification and the formation of a relatively homogeneous microstructure. Under these conditions, CrB_2 acts as a reinforcing



(*a*) (*b*)

Fig. 2 SEM-image (left – SE, right – BSE) of the ceramic materials B_4C–CrB_2 synthesized at (*a*) 1800°C (×1250) and (*b*) 1900°C (×1360).



(*a*) (*b*)

Fig. 3 Elemental mapping of the ceramic materials B_4C–CrB_2 synthesized at (*a*) 1800°C and (*b*) 1900°C.

phase, contributing to the improvement of the mechanical properties of the composite compared to monolithic B_4C. The hardness was 34.1 GPa.

The temperature of 1800°C can be considered as optimal for the preparation of B_4C–CrB_2 composites based on the phase stability, high relative density, and the reinforcing role of CrB_2. Increasing the sintering temperature to 1900°C leads to the formation of a liquid phase at high temperature and loss of Cr. This in turn causes the formation of pores in the ceramic material, and, consequently, a decrease in the relative density. The presence of pores in the microstructure was confirmed by scanning electron microscopy. The hardness was 37.4 GPa.

Conclusions

Ceramic composites B_4C–CrB_2 were fabricated by spark plasma sintering at 1800°C and 1900°C under a uniaxial pressure of 70 MPa. At 1800°C, a two-phase composite with a relative density of 97.6% and a hardness of 34.1 GPa was obtained. Under these conditions, CrB_2 acts as a reinforcing component, contributing to improve the mechanical properties compared to pure B_4C. Sintering at 1900°C led to changes in the phase ratio of the composite due to the partial transformation of CrB_2 into a liquid phase, accompanied by the formation of pores in the ceramic, as confirmed by scanning electron microscopy. These effects led to a decrease in the relative density, however, the hardness increased to 37.4 GPa.

The results show that the sintering temperature plays a crucial role in controlling the phase composition, densification and hardness of the material. The temperature of 1800°C was determined to be optimal for achieving a balance between high density, phase composition, and effective reinforcement in B_4C–CrB_2 composites.

References

[1] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, T. Massalski, H. Okamoto, K. Osaki, A. Prince, *Pauling File. Inorganic Materials Database and Design System. Binaries Edition*. 2001.

[2] I.G. Crouch, *Def. Technol.* 15 (2019) 241-253. https://doi.org/10.1016/j.dt.2019.02.002

[3] A. Ivanushko, R. Gladyshevskii, *Visn. Lviv. Univ. Ser. Khim.* 65 (2024) 102-110. http://dx.doi.org/10.30970/vch.6501.102

[4] B. Mahesh, K. Sairam, J.K. Sonber, T.S.R.Ch. Murthy, G.V.S. Nageswara Rao, T. Srinivasa Rao, J.K. Chakravartty. *Int. J. Refract. Met. Hard Mater.* 52 (2015) 66-69. https://doi.org/10.1016/j.ijrmhm.2015.04.035

[5] W. Rasband, *ImageJ (Version 1.51)*, National Institute of Mental Health, Bethesda, Maryland, USA. https://imagej.net/ij/index.html

[6] J. Rodriguez Carvajal, *Recent Developments of the Program FULLPROF, in Commission on Powder Diffraction (IUCr)*, *Newsletter* 26 (2001) 12-19. http://journals.iucr.org/iucr-top/comm/cpd/Newsletters/

[7] A. Ivanushko, R. Gladyshevskii, *Chem. Met. Alloys* 18(1/2) 17-20. https://doi.org/10.30970/cma18.0451

[8] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park (OH), 2023/2024. https://www.crystalimpact.com/pcd/