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Spark plasma sintering of a mixture of B_4C and $TiSi_2$ powders

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A mixture of B_4C and $TiSi_2$ (30 wt.%) powders prepared in a planetary ball mill was sintered at a temperature of 1900°C and a pressure of 70 MPa under argon atmosphere by the spark plasma sintering method. X-ray powder diffraction was used to determine the composition. The obtained material contained four phases: B_4C (75 wt.%), TiB_2 (15 wt.%), SiC (9.5 wt.%), and Si (0.5 wt.%). The average grain size was calculated from images obtained using a scanning electron microscope: B_4C – 1.2 μm, $TiSi_2$ – 1.8 μm, TiB_2 – 11.2 μm. For the ceramic material, a Vickers hardness of 43.9 GPa was achieved at a relative density of 99.5%.

Boron carbide / X-ray diffraction / Crystal structure / Hardness

Introduction

Boron carbide (B_4C) is one of the hardest known materials, ranking just below diamond and cubic boron nitride. Due to its properties, such as low density (2.5 g·cm^{-3}), high hardness (25.5 GPa) [1], high melting point, and excellent chemical stability, B_4C is widely used in armor systems, cutting tools, and abrasives [2].

Among various synthesis methods, spark plasma sintering (SPS) is a very effective method for producing ceramics at relatively low temperatures and in short processing times, compared to hot pressing (HP) and resistance furnace sintering. SPS promotes rapid heating and uniform temperature distribution, which can improve the relative density of the ceramics.

Previous studies [3] describe the study of dense ceramics based on boron carbide, manufactured by spark plasma sintering of B_4C powder at 2000°C submitted to a pressure of 70 MPa in vacuum. The product had a relative density of 99.5% and a hardness of 32.6 GPa (by Vickers method).

Modification of B_4C by introducing additional components to form composite materials can affect the sintering behavior and densification of the material, leading to changes in mechanical properties.

Y. Wang *et al.* [4] synthesized B_4C-based materials by SPS at a temperature of 1800°C and a pressure of 40 MPa, adding from 0 to 16 wt.% of $TiSi_2$ and observed changes in relative density and mechanical properties.

Experimental

The ceramic material studied here was synthesized from high-purity B_4C and $TiSi_2$ powders. The initial content of $TiSi_2$ in the powder mixture B_4C+$TiSi_2$ was 30 wt.% (~40 mol.%). The powders were homogenized in a planetary ball mill (PM100, Retsch) in a WC jar with WC balls (diameter 10 mm) for 20 min at a speed of 250 rpm. Ceramic composites were prepared by spark plasma sintering at a maximum temperature of 1900°C and a pressure of 70 MPa in argon atmosphere. The SPS method and the equipment used here have been described in details elsewhere [3].

X-ray powder diffraction (XRD) patterns from the surface of the synthesized pellets were collected on an HZG-4 powder diffractometer (Cu *K*α-radiation). Structure analyses were performed by Rietveld refinement using the FullProf Suite software [5].

The compositions of the powder mixture and ceramic material were analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope (SEM) TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with an X-Max^{N}20 detector. The grain size was evaluated using ImageJ software [6].

The density of the ceramic material was determined by hydrostatic weighing according to Archimedes' principle using analytical electronic balances.

Hardness was measured by the Vickers method with a square-based diamond pyramidal indenter and a load of 9.807 N (1 kg) into the surface of the sample (Novotest TS-MKV1).

Results and discussion

Experimental conditions and results of the refinements of the crystal structure of the ceramic material prepared from B_4C and $TiSi_2$ powders are presented in Table 1 and an XRD pattern is shown in Fig. 1. The sample contained four phases: B_4C, TiB_2, SiC, and Si. The relative amounts obtained from the Rietveld refinement were: 75(3) wt.% (49.4 mol.%) for $B_{13.17}C_{1.66}$, 14.8(4) wt.% (22.8 mol.%) for TiB_2, 9.5 wt.% (25.6 mol.%) for SiC, and 0.53(6) wt.% (2.2 mol.%) for Si.

The crystal structure of B_4C synthesized by spark plasma sintering is reported in [3]. The atomic coordinates, isotropic displacement and site occupancies for $B_{13.17(1)}C_{1.66(3)}$ (prepared here from a mixture of B_4C and $TiSi_2$ powders) are shown in Table 2. According to Pearson's Crystal Data [7] the crystal structure of TiB_2 belongs to the structure type AlB_2 (space group *P*6/*mmm*, atomic coordinates Ti 1*a* 0; 0; 0, B 2*d* ⅓; ⅔; ½); the SiC modification observed here to the structure type ZnS (space group *F*-43*m*, atomic coordinates Si 4*a* 0; 0; 0, C 4*c* ¼; ¼; ¼); and Si to the structure type diamond (space group *Fd*-3*m*, atomic coordinates Si 8*a* ⅛; ⅛; ⅛).

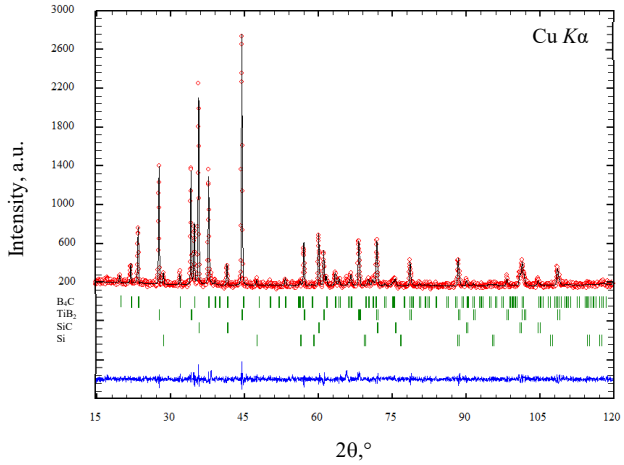


Fig. 1 Observed, calculated, and difference XRD pattern (Cu *K*α-radiation) of the ceramic material prepared from B_4C and $TiSi_2$ powders. The positions of the reflections from B_4C, TiB_2, SiC, and Si are indicated by bars.

Table 1 Experimental conditions and results of the refinements of the crystal structure.

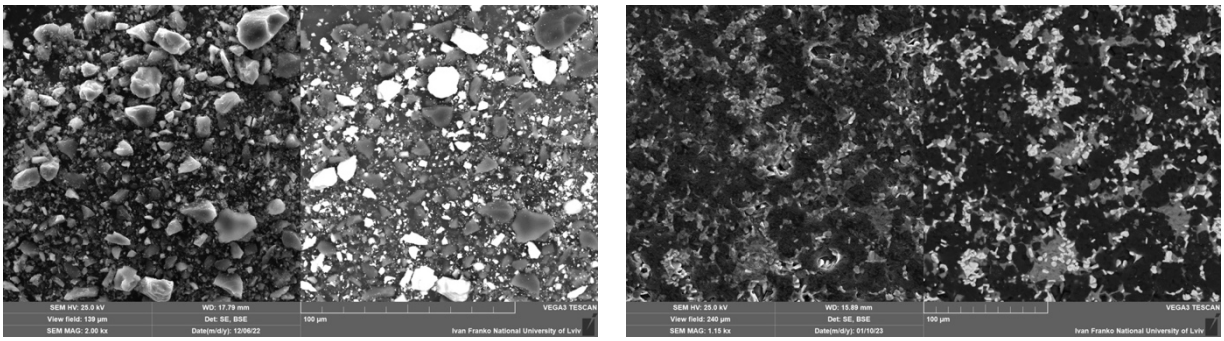
Phase	$B_{13.17(1)}C_{1.66(3)}$	TiB_2	SiC	Si
Structure type	$B_{13}C_2$	AlB_2	ZnS	C
Pearson symbol	*hR*51	*hP*3	*cF*8	*cF*8
Space group	*R*-3*m*	*P*6/*mmm*	*F*-43*m*	*Fd*-3*m*
Cell parameters, Å	*a* = 5.6159(6), *c* = 12.156(2)	*a* = 3.03358(13), *c* = 3.22856(15)	*a* = 4.3552(3)	*a* = 5,419(2)
Cell volume *V*, Å^3	332.01(7)	25.731(2)	82.611(8)	159.11(11)
Formula units per cell *Z*	3	1	4	8
Density *D*, g·cm^{-3}	2.441	4.487	3.224	2.345
Mass fraction, %	75(3)	14.8(4)	9.6(4)	0.6(1)
Reliability factors	$R_B(B_{13.17(1)}C_{1.66(3)})$ = 10.8%, $R_B(TiB_2)$ = 4.01%, R_B(SiC) = 2.87%, R_B(Si) = 11.8%, R_p = 6.01%, R_{wp} = 7.65%			

Table 2 Atomic coordinates, isotropic displacement, and site occupancies for $B_{13.17(1)}C_{1.66(3)}$.

Site	Wyckoff position	*x*	*y*	*z*	$B_{overall}$, Å^2	Occupancy
B1	18*h*	0.4419(6)	0.5581(6)	0.0525(7)		1
B2	18*h*	0.5069(7)	0.4931(7)	0.1938(10)		1
C	6*c*	0	0	0.1154(15)	1.1(2)	0.83(2)
B3	6*c*	0	0	0.102(7)		0.17(2)
B4	3*a*	0	0	0		0.83(2)

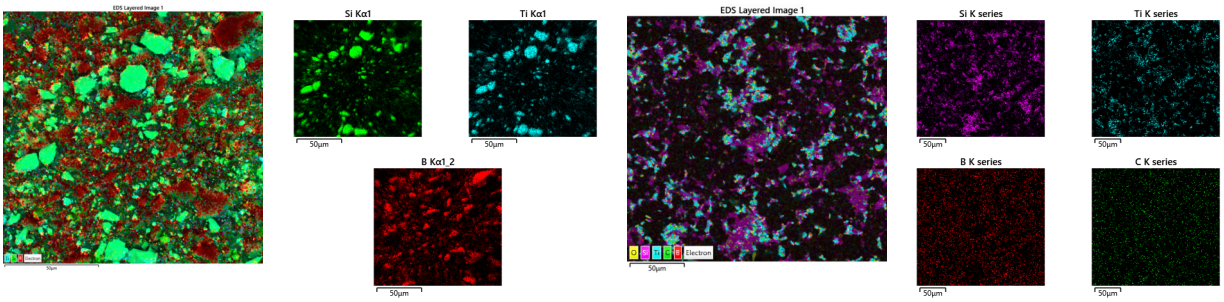
The initial mixture of powders and the resulting ceramic material were analyzed by scanning electron microscopy (Fig. 2). On the SEM-image of the initial mixture (Fig. 2 (*a*)) the light phase is $TiSi_2$, and the dark phase is B_4C. On the SEM-image of the final ceramic (Fig. 2 (*b*)) the lightest phase is TiB_2, the light gray phase SiC, the dark gray phase Si, and the darkest phase B_4C. Elemental mapping of the B_4C+$TiSi_2$ powder mixture and of the ceramic material are shown in Fig. 3.

The average size of the B_4C grains before sintering was 1.2 μm, $TiSi_2$ – 1.8 μm; the size of the TiB_2 grains after sintering was 11.2 μm. The distribution of the TiB_2 grain size in the ceramic material after sintering is shown in Fig. 4.



(*a*) (*b*)

Fig. 2 SEM-image (left – SE, right – BSE) (*a*) of the B_4C+$TiSi_2$ powder mixture and (*b*) of the ceramic material after SPS.



(*a*) (*b*)

Fig. 3 Elemental mapping (*a*) of the B_4C+$TiSi_2$ powder mixture and (*b*) of the ceramic material after sintering.

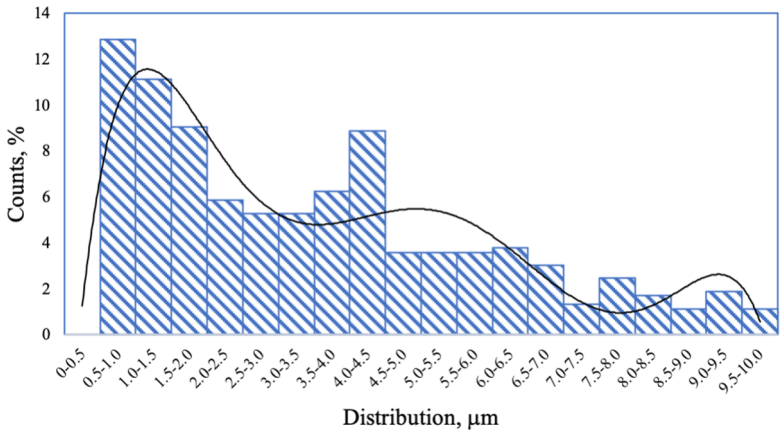


Fig. 4 Grain size distribution of the TiB_2 phase in the ceramic material after sintering.

Sh. Wang *et al.* [8] report that their powders were first pressed in a uniaxial mold under a pressure of 40 MPa and were then isostatically pressed at 215 MPa. After that, the samples were sintered without external pressure in a graphite resistance furnace at temperatures up to 2200°C. As a result, the B_4C-TiB_2-SiC ceramic obtained from the starting powder mixture containing B_4C and 30 wt.% of $TiSi_2$ reached a relative density of 97.2%.

In our case, the ceramic material was prepared from a B_4C and $TiSi_2$ (30 wt.%) powder mixture using the SPS method, during which a pressure of 70 MPa was applied in an argon atmosphere at a temperature of 1900°C. Under these conditions, nearly full densification was achieved, and the material reached a relative density of 99.5%.

The material synthesized here exhibits a Vickers hardness of 43.9 GPa, which is significantly higher than the values reported by Sh. Wang *et al*. [8], where the B_4C-SiC-TiB_2 composite obtained from B_4C and $TiSi_2$ powders did not exceed 33.5 GPa. This notable difference indicates that the synthesis conditions used here minimize residual porosity, promote almost complete densification and provide more effective indentation resistance, thereby increasing the hardness.

Conclusions

A ceramic material was synthesized from a mixture of B_4C and $TiSi_2$ (30 wt.%) powders by spark plasma sintering at a temperature of 1900°C and a pressure of 70 MPa in an argon atmosphere. Analysis of the X-ray diffraction pattern revealed the formation of four phases: B_4C, TiB_2, SiC, and Si. According to the Rietveld refinement, B_4C (refined composition $B_{13.17(1)}C_{1.66(3)}$) remained the dominant component, while the TiB_2, SiC, and Si phases formed as a result of the interaction between B_4C and $TiSi_2$ during sintering. SEM observations showed that the average grain size of the TiB_2 phase reached 11.2 μm, while the grains of the initial B_4C and $TiSi_2$ powders were significantly smaller (1.2 μm and 1.8 μm, respectively).

The ceramic material demonstrated a high relative density of 99.5% and a Vickers hardness of 43.9 GPa. These results show that the SPS conditions applied here provide effective compaction and make it possible to obtain dense, hard composites.

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