Microstructure and mechanical properties of B₄C-NbB₂-SiC ternary eutectic composites by a crucible-free zone melting method

M. Upatov^a, J. Vleugels^b, Y. Koval^a, V. Bolbut^c, I. Bogomol^a

^a National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”, 37, Peremogy Ave., Kyiv 03056, Ukraine

^b KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, B-3001 Heverlee, Belgium

^c Institute of Materials and Joining Technology, Otto-von-Guericke University Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany
e-mail: nikitaupatov@gmail.com

Abstract: Directionally solidified B₄C–NbB₂–SiC ternary composites were prepared by a floating zone method based on crucible-free zone melting of compacted powders. The ternary eutectic composition of B₄C–15NbB₂–35SiC (mol.%) was characterized by a boron carbide matrix, directionally reinforced by lamella-type NbB₂ and SiC phases. NbB₂ and SiC inclusions about 1-2 μm in thickness were uniformly dispersed in B₄C matrix of B₄C–NbB₂–SiC eutectic composite. The Vickers hardness and indentation fracture toughness of the B₄C–NbB₂–SiC ternary eutectic were 35.8 GPa and 6.4 MPa·m^{1/2}, respectively.

Keywords: B₄C–NbB₂–SiC, ternary eutectic, lamellar structure, Vickers hardness, crack propagation.

1. Introduction

Boron carbide (B₄C) has an extremely wide range of properties, such as a low density, high hardness and low thermal conductivity [1-2]. The Vickers hardness of B₄C was reported to be 38 GPa, with a fracture toughness of 3.5 MPa·m^{1/2} [3]. Silicon carbide (SiC) and metal diborides can significantly broaden the application field of boron carbide composites [4]. SiC has a high fracture toughness 3.5-4.1 MPa·m^{1/2} [5], has a good thermal resistance, high temperature strength and oxidation resistance [6]. 47B₄C-53SiC (mol.%) eutectic composites, obtained by the floating zone method, were shown to have a significantly increased oxidation resistance compared to B₄C [7]. B₄C-NbB₂ eutectic composites [8-10] showed an improvement in fracture toughness compared to B₄C, indicating B₄C-NbB₂ eutectic composites could be an interesting engineering material. Demirskyi et al has investigated the SiC-NbB₂ system, revealing that the SiC-39NbB₂ (mol.%) eutectic composite has a flexural strength of 593 ± 12 MPa at 1900 °C [11]. Therefore, B₄C-NbB₂-SiC composites combining the properties of B₄C-NbB₂, B₄C-SiC and SiC-NbB₂ composites might be applied as a high-temperature structural material.

Only few works have been devoted to ternary systems B₄C-NbB₂-SiC. For the first time, an attempt was made to determine the eutectic composition of the B₄C-NbB₂-SiC system by Ordan'yan based on experimental data on the composition and melting points of eutectics in SiC-Me^dB₂ and B₄C-Me^dB₂ quasi-

binary systems [12]. But his theoretical calculations were not supported by practical results. Several composites were processed by crucible-free zone melting in the B_4C - NbB_2 - SiC system, allowing to identify a ternary eutectic with $\sim B_4C$ -(15-20) NbB_2 -(30-35) SiC (mol.%) composition by means of quantitative metallographic analysis [13-14]. The current work is devoted to a study of composites in a selected region of the ternary B_4C - NbB_2 - SiC system in order to determine the exact eutectic composition and grow this directionally solidified ternary eutectic composite with a uniform fine grain structure throughout the sample.

It has been reported that directionally solidified ceramic eutectic composites have superior flexural strength, thermal stability and creep resistance especially at high temperature, and are candidates for high-temperature structural application [15]. However, these materials usually contain structural macro-defects (grain boundaries, colonies, etc.) which are expected to impair their mechanical properties [16-17]. The fabrication of defect-free directionally solidified fully ternary eutectic ceramic composites with uniform fine-grained microstructure allows to improve the mechanical properties [15, 18-20]. Refinements of the eutectic microstructure can be achieved by an increased temperature gradient, increasing the growth rate, and the addition of more components [21].

In this paper, directionally solidified B_4C - NbB_2 - SiC ternary composites with different composition were synthesized by crucible-free zone melting, and their microstructure, hardness, fracture toughness, E-modulus and flexural strength were investigated. For the first time, a B_4C -15 NbB_2 -35 SiC composite with uniform ternary eutectic microstructure without visible structural macro defects was fabricated and the mechanical properties were characterized.

2. Experimental procedure

Directionally solidified B_4C - NbB_2 - SiC composites were prepared by crucible-free zone melting of compacted powders [22]. B_4C , NbB_2 and SiC powders (purity 98 wt%, average grain size 1-5 μm , Reaktiv Co Donetsk, Ukraine) were used as starting materials. The powders were mixed by shifting them ten times through a 50 μm mesh. Three composites (mol%) were investigated, i.e. B_4C -20 NbB_2 -30 SiC , B_4C -18 NbB_2 -33 SiC and B_4C -15 NbB_2 -35 SiC . 2.5 wt% polyvinyl alcohol was added as a plasticizer. Green rods with a diameter of 10 mm and length of 145 mm were obtained by compacting the powder mixture in a hydraulic press at 100 MPa. They were subsequently dried in a vacuum oven for 12 h at 100°C. The samples were placed in a modified crystal-growth apparatus “Crystal 206” (Russia) equipped with an induction heater. Zone melting was carried out in helium at a pressure of 1 atm and a growth rate of 2 mm/min.

The microstructure of the composites was studied by scanning electron microscopy (SEM; REM 106Y and TESCAN VEGA3). Wavelength dispersive spectroscopy (WDS) analysis and elemental mapping

was performed using electron probe microanalysis (JXA-8530F, Jeol, Japan). The crystalline phases were investigated by X-ray diffraction (XRD, Rigaku Ultima IV) using Cu-K α radiation. The Lotgering factor, a semi-quantitative technique to evaluate the degree of texture, was calculated. The Lotgering factor f is defined as [23]:

$$f = \frac{P - P_0}{1 - P_0} \quad (1)$$

where $P = I_{hkl}^{max} / \sum I_{(hkl)}$, with I_{hkl}^{max} the maximum intensity for a preferred crystallographic phase orientation. P_0 , representing a random crystallographic orientation, was calculated from the PDF-2 card number for B₄C (01-075-0424), NbB₂ (01-075-9206) and SiC (03-065-0360) according to the same formula. $\sum I_{(hkl)}$ is the sum of the peak intensities of the hkl reflections over a 2 θ range of 20⁰–80⁰.

The Vickers hardness of B₄C-NbB₂-SiC composites was measured by a micro-hardness tester (MHV-1000) with time exposure of 10 s, and averaging 30 measurements under a load of 9.8 N. Since the radial crack pattern revealed 0.25 < l/a < 2.5, the fracture toughness was calculated using Eq. (1) given by Niihara et al. [24] for Palmqvist cracks:

$$K_{1c} = 9.052 \cdot 10^{-3} \cdot H^{3/5} \cdot E^{2/5} \cdot d \cdot l^{-1/2} \quad (2)$$

where H is the Vickers hardness GPa, d is the average diagonal line length of the indentation, l is the average length of the cracks, E is the elastic modulus of the composite calculated assuming a mixture rule ($E_{B_4C} = 460$ [25], $E_{NbB_2} = 637$ [26] and $E_{SiC} = 414$ [27] GPa).

The elastic E -modulus of the B₄C-NbB₂-SiC composites was measured on 5 rectangular bars by the resonance frequency method [28]. The resonance frequency was measured by the impulse excitation technique (Grindosonic BVBA, Leuven, Belgium).

The flexural strength was measured by three-point bending using a Deben Microtester for 4 rectangular bar (Woolpit, UK) with a span of 15 mm and maximum load of 500 N. The experiments were carried out in air at room temperature with a crosshead speed of 0.5 mm/min and a pre-load of 2 N. The flexural strength was determined using Eq. (3):

$$\sigma_u = \frac{3Pl}{2bh^2} \quad (3)$$

where P is the axial fracture load; l , the length of the support span; b , the sample width; h , the sample thickness.

3. Results and discussion

Fig.1 shows the XRD patterns of the cross-section perpendicular to the growth direction of (a) B₄C-18NbB₂-33SiC and (b) B₄C-20NbB₂-30SiC, which resemble the XRD pattern of the (c) B₄C-30NbB₂-38SiC

composite obtained in [14]. The phases of the composites were B_4C , NbB_2 and SiC , and no other phase was detected out. Detailed analysis of composites XRD patterns showed SiC phase as polytype 3C in contrast to powder XRD pattern. The relative peak intensities of B_4C , NbB_2 and SiC evolve according to the B_4C , NbB_2 and SiC content in the composites.

In contrast to the reference diffractograms, the composite XRD patterns have the most intensive peaks for the NbB_2 (100), B_4C (104) and SiC (111) crystallographic orientation, indicating a preferred crystallographic phase orientation in the composites. The same crystallographic orientations were observed for the B_4C - TiB_2 - SiC ternary eutectic composition [29].

Fig. 2. shows the WDS element distribution maps of niobium (Nb), boron (B), carbon (C) and silicon (Si) in the B_4C -15 NbB_2 -35 SiC (mol%) composite. Comparing the backscattered electron image (CP) with the distribution of elements allows to identify the phases that make up the microstructure of the composite. Since no phase interaction was identified by XRD analysis, we can identify the white phase as NbB_2 , the grey phase as SiC and the black phase as B_4C .

Figure 3 shows typical backscattering electron microstructures of B_4C - NbB_2 - SiC composites on the cross-section perpendicular to the growth direction, where the black phase is B_4C , the white phase is NbB_2 and the grey phase is SiC . The microstructure of B_4C -20 NbB_2 -30 SiC (mol.%) consisted of large NbB_2 dendrites and B_4C - NbB_2 - SiC ternary eutectic phase (TE) as shown in Fig. 3(a). NbB_2 dendrites are evenly distributed throughout the entire volume of the composition B_4C -20 NbB_2 -30 SiC (mol.%).

The microstructure of the B_4C -18 NbB_2 -33 SiC (mol.%) composition includes large TE areas, with some NbB_2 dendrites located mainly in a certain zone of the specimens and closer to the periphery as shown in Fig.3 (b). For compositions of B_4C -20 NbB_2 -30 SiC and B_4C -18 NbB_2 -33 SiC , NbB_2 is the first crystalline phase (NbB_2 primary phase field) to appear on cooling. Then finally the three phases (B_4C , NbB_2 , SiC) are precipitated as TE.

In contrast to the structure of the composites described above, the structure of the B_4C -30 NbB_2 -38 SiC composite in Fig. 3 (c) has certain differences. B_4C -30 NbB_2 -38 SiC represents large NbB_2 dendrites, NbB_2 - SiC binary eutectic (BE1) and TE, implying a SiC - and NbB_2 -richer composition compared to TE. The composition of B_4C -30 NbB_2 -38 SiC is inside the NbB_2 -TE-BE1 triangle, which is NbB_2 primary phase field. NbB_2 is the first crystalline phase to appear on cooling. With precipitating NbB_2 , the composition of liquid leads to BE1-TE line precipitating NbB_2 - SiC , and finally three phases are precipitated as TE [14].

The B_4C - NbB_2 - SiC eutectic composition is determined to be composition of B_4C -15 NbB_2 -35 SiC (mol.%), where uniform eutectic structure is obtained, in which the lamellar eutectic structure was observed. Fig. 4 shows the SEM photographs of the B_4C -15 NbB_2 -35 SiC (mol.%) eutectic composite for the cross-section perpendicular (Fig. 4(a) and (b)) and parallel (Fig. 4(c) and (d)) to the growth direction.

Fig.5 (a,b) shows the XRD pattern of the transverse and longitudinal direction of the B₄C-15NbB₂-35SiC (mol.%) ternary eutectic composite. The most intense peaks in the transverse direction are NbB₂ (100) (hexagonal), SiC (111) (cubic) and B₄C (104) (hexagonal). For the longitudinal direction, the peak of B₄C (104) disappeared, and the most intense peaks are observed for NbB₂ (101) (hexagonal), SiC (111) (cubic).

The results of the Lotgering factor analysis for these crystallographic planes are shown in Table 1. The SiC phase in transverse direction has high Lotgering factor (0.75) and moderate-good value (0.56) in longitudinal directions according to [23]. The value for the B₄C phase is slightly less (0.52). For the NbB₂ the Lotgering factor has moderate values in both directions (0.46 and 0.21). High values of the Lotgering factor for SiC in comparison with other phases are associated with the morphology of NbB₂ and B₄C phases in the ternary directionally solidified composite (Fig. 5c). It is clear from the microstructure that the most oriented phase is SiC. NbB₂ and B₄C phases have a more extensive morphology, which is shown in the XRD patterns (Fig. 5 (a,b)). This behavior is associated with the features of crystallization in the multicomponent B-Nb-Si-C system, which are quite complex and require of additional research. The lamellar eutectic BSE electron contrast microstructure was composed of 1-2 μ m thick lamella white NbB₂ and grey SiC phases, dispersed in a black B₄C matrix, as shown in Fig.5 (c).

Schematic phase formation diagram of B₄C-NbB₂-SiC composites is presented in Fig. 6. It shows the points of the binary eutectic (BE) of B₄C-NbB₂ [10], B₄C-SiC [30] and SiC-NbB₂ [11] systems, the results of studies in [13] and also the composites investigated in this work.

Fig. 7 (a) shows the Vickers hardness (H_v) of the B₄C-15NbB₂-35SiC, B₄C-18NbB₂-33SiC and B₄C-20NbB₂-30SiC, as measured on the longitudinal and transverse cross-sections. The hardness increased with increased formation of a regular TE eutectic structure throughout the sample. As an example, for the B₄C-20NbB₂-30SiC (mol.%) composite, the indenter entering the areas of large NbB₂ dendrites leaves a larger indent, implying a reduced H_v . The hardness of the B₄C-NbB₂-SiC TE composite was 35.8 GPa at the load of 9.8 N, which might be attributed to the dense and uniform microstructure with the smallest size eutectic domains, as shown in Fig. 4. This is confirmed by the results for eutectic B₄C-TiB₂ composites [19,31,32]. The hardness values are close to the hardness of the B₄C-HfB₂-SiC ternary eutectic composite (35.7 GPa) obtained by Tu et. al. [33]. For the TE composite the hardness values was also calculated by mix rule considering the H_v of individual components: B₄C (38 GPa) [3], SiC (28 GPa) [34] and NbB₂ (21 GPa) [26]. The as obtained value (33,19 GPa) is quite close to the experimental results (Fig. 7a).

Fig. 7 (b) depicts the compositional dependency of the fracture toughness (K_{Ic}) of B₄C-NbB₂-SiC composites, as calculated by Eq. (2). The results show a gradual increase in fracture toughness to formation of a regular TE structure. Fig. 8 shows the radial crack pattern around a Vickers indentation. In the transverse

direction the fracture pattern showed symmetric, well-defined cracks (Fig. 8 (a,b)) and the fracture toughness was estimated from the length of the cracks, the hardness and the elastic modulus of the material.

Similar indentations carried out on the longitudinal cross-sections led to an asymmetric crack pattern (Fig. 8 (c,d)). The cracks parallel to the phase domains were difficult to grow and tended to deviate of straight propagation with followed damping (Fig. 8 (c,d)). The cracks in perpendicular direction are well-defined and propagate mainly through the B_4C matrix phase with some deflections on both SiC and NbB_2 phases (Fig. 8 (c,d)). Crack deflection is a known toughening mechanism in directionally solidified ceramic eutectics [35-36]. This behavior is due to the presence of residual stresses caused by difference in coefficients of thermal expansion in phase components. The difference in fracture behavior in parallel and perpendicular directions could be explained by anisotropy of coefficients of thermal expansion in phase components and texture which lead to difference in values of residual stresses in both directions [36]. Thus the fracture toughness in longitudinal direction was estimated in both directions relative to cracks propagation and their average values were calculated (Fig. 7b). The TE composite has the highest K_{Ic} of $6.4 \text{ MPa}\cdot\text{m}^{1/2}$, which may result from the uniform regular structure with minimum eutectic domain size and also presence of high residual stresses. The fracture toughness values are higher than for the directionally solidified B_4C - TiB_2 -SiC composite (about $4 \text{ MPa}\cdot\text{m}^{1/2}$) [29] and close to the B_4C - HfB_2 -SiC ternary eutectic composite ($6.5 \text{ MPa}\cdot\text{m}^{1/2}$) obtained by Tu et. al. [33].

The H_v and K_{Ic} in the transverse and longitudinal section are slightly different, which is explained by the typical microstructural anisotropy and crystallographic texture as well as the properties of the phase components of the directionally solidified alloys [21].

The E-modulus in the longitudinal direction of the B_4C -15 NbB_2 -35SiC composite was measured to be $462 \pm 3 \text{ GPa}$. This value is slightly lower than the E-modulus of 473 GPa , calculated by the mixture rule, which could be attributed to the microstructural and crystallographic texture.

The flexural strength was only measured for the B_4C -20 NbB_2 -30SiC composite. The strength is about $313 \pm 14 \text{ MPa}$, which is almost two times higher than for the directional solidified eutectic B_4C - TiB_2 composite and higher than for the B_4C -30 NbB_2 -38SiC composite whose flexural strength is $203\text{--}252 \text{ MPa}$ [14, 22]. The obtained values allow to estimate of the directionally solidified eutectic B_4C - NbB_2 -SiC alloy as a potential structural material for application in wide temperature range. However, the high-temperature mechanical behavior of the composite requires of additional investigations.

Fig. 9 shows the fracture surface and crack propagation path of B_4C -20 NbB_2 -30SiC (mol.%) composite after flexural strength testing at room temperature. The presence of cracks was indirectly indicated by 'zig-zag'-like areas as in [33]. The crack propagation along a zig-zag route is shown in Fig. 9. (b) and (c). The active toughening mechanisms of crack deflection (Fig. 9. (b,c,d)) and crack bridging (Fig.

9. (b)) were observed in the crack propagation path, which prompted the fracture toughness by consuming more fracture energy.

4. Conclusions

The B_4C - NbB_2 - SiC system has a ternary eutectic with B_4C -15 NbB_2 -35 SiC (mol.%) composition with a typical lamellar microstructure. The eutectic microstructure is composed of a B_4C matrix with dispersed NbB_2 grains in SiC lamella. The B_4C - NbB_2 - SiC eutectic composite has a high Vickers H_{V10} micro-hardness of 35.8 ± 1.5 GPa and an indentation fracture toughness of 6.4 ± 0.5 $MPa \cdot m^{1/2}$. The E-modulus of the eutectic B_4C -15 NbB_2 -35 SiC (mol.%) composition in the longitudinal zone molten direction is 462 ± 3 GPa. The results of the X-ray diffraction based Lotgering factor analysis confirm crystallographic texture of all constituent phases in the composites.

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Table 1 Phase characteristics for B_4C -15NbB₂-35SiC (mol%).

Phase	Crystallographic orientation (hkl)	Thickness grain size (μm)	Lotgering factor
transverse direction			
NbB ₂ (hexagonal)	(100)	1-2	0.46
B ₄ C (hexagonal)	(104)	1-2	0.52
SiC (cubic)	(111)	4-5	0.75
longitudinal direction			
NbB ₂ (hexagonal)	(101)	1	0.21
SiC (cubic)	(111)	1-2	0.56

Fig. 1. XRD patterns of the cross-section perpendicular to the growth direction of the B_4C -NbB₂-SiC ternary composites. (a) B_4C -30NbB₂-38SiC, (b) B_4C -20NbB₂-30SiC, and (c) B_4C -18NbB₂-33SiC (mol%).

Fig. 2. WDS elemental maps of the B_4C -15 NbB_2 -35 SiC (mol.%) composite. The elements investigated are: Nb, B, C, Si. (SL-secondary electron image, CP-backscattered electron image of the analyzed area).

Fig. 3. Microstructures of the B_4C - NbB_2 - SiC composites with different compositions (mol.%): (a) B_4C -20 NbB_2 -30 SiC , (b) B_4C -18 NbB_2 -33 SiC , (c) B_4C -30 NbB_2 -38 SiC [14].

Fig. 4. Microstructures of the B_4C -15 NbB_2 -35 SiC (mol%) eutectic composite, cross-sectioned perpendicular (a,b) and parallel (c,d) to the growth direction.

Fig. 5. XRD patterns of transverse (a) and longitudinal (b) directions, and microstructure (c) of B_4C -15 NbB_2 -35 SiC (mol%).

Fig. 6. Schematic phase formation diagram of B_4C - NbB_2 - SiC composites.

Fig. 7. Vickers (9.8N) hardness (a) and fracture toughness (b) of the three B_4C - NbB_2 - SiC composites.

Fig. 8. Radial crack propagation after indentation (9,8 N) in transverse (a,b) and longitudinal (c,d) direction for B_4C -15NbB₂-35SiC (mol%). Microscopy images (a) and (c) were obtained using secondary electrons in the scanning electron microscope.

Fig. 9. SEM images of the fracture surface and crack propagation path in the B_4C -20NbB₂-30SiC (mol.%) composite after flexural strength testing at room temperature.