Microstructure of ZrB$_2$–ZrN directionally solidified eutectic composite by arc-melting

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ABSTRACT

A ZrB$_2$–ZrN eutectic composite was prepared by arc-melting a mixture of ZrB$_2$ and ZrN powders under a N$_2$ atmosphere. The eutectic composition was 48ZrB$_2$–52ZrN (mol%), resulting in a rod-like microstructure comprising hexagonally faceted ZrN single-crystal rods dispersed in a ZrB$_2$ single-crystal matrix. The crystal orientation relationship between the ZrB$_2$ matrix and the ZrN rod was ZrB$_2$ \{1120\} // ZrN[101] and ZrB$_2$ <0001> // ZrN <111>. The rod-like eutectic composite had a Vickers hardness of 16.2 GPa.

1. Introduction

Zirconium diboride (ZrB$_2$) and zirconium nitride (ZrN) are promising ultra-high-temperature ceramic materials owing to their high mechanical strength, electrical conductivity, and chemical stability [1,2]. Sintering of ZrB$_2$ and ZrN is difficult because of their covalent nature and high melting points, 3310 and 3500 K, respectively. Therefore, they have been consolidated via pressure-assisted sintering techniques with sintering additives, such as Ni, Fe, and Cu [3–6]. Using such additives, however, significantly degrades the mechanical and chemical properties, particularly at high temperatures. It is known that ZrB$_2$–ZrN produces a eutectic system under a nitrogen pressure of 1 MPa and a eutectic temperature of 3050 K. With more than 5 mass% of ZrB$_2$, a two-phase composite was identified; the eutectic composition was determined at 44 mol% of ZrB$_2$ [7]. Still, there are few studies on the formation of eutectic microstructures of the ZrB$_2$–ZrN system in the literature.

Recently, the directionally solidified eutectic (DSE) composites have attracted much attention owing to their unique microstructures and excellent properties. DSEs have a lamellar or rod-like microstructure depending mainly on the eutectic compositions, which cannot be obtained from conventional solid state sintering [8]. Although it is difficult to melt monolithic ZrB$_2$ and ZrN, having melting temperatures >3000 K, and they are likely to decompose under an atmospheric pressure, we previously reported the melting and solidification of ZrB$_2$–ZrC and ZrB$_2$–ZrC–ZrN mixture powders using arc-melting, which resulted in ZrB$_2$–ZrC [9] and ZrB$_2$–ZrC$_x$N$_{1-x}$ [10] eutectic composites, respectively. In the present study, ZrB$_2$–ZrN DSE composites were prepared by arc-melting, and the microstructure, hardness, and fracture toughness of the composites were investigated.

2. Experimental procedure

ZrB$_2$ (Japan New Metals Co., Ltd., Japan) and ZrN powder (Kojundo Chemical Laboratory Co., Ltd., Japan) were used as starting materials. The compositions in this study are expressed as nominal molar percentages of ZrB$_2$ and ZrN with respect to the starting materials. The powders were mixed in a polyethylene bottle via ball-milling with ZrO$_2$ balls in a small amount of ethanol for 4 h. The mixed powder slurry was dried at 333 K for 12 h and then isostatically pressed into disk (diameter, 10 mm; thickness, 3 mm) under a pressure of 5 MPa. The disks were arc-melted twice in an arc-melting furnace (MRHS-500 (S-1), Daihen Co.) using a tungsten electrode under an N$_2$ atmosphere at 80 kPa, and solidified in a water-cooled copper hearth. Finally, the specimens were polished using 1 μm diamond slurry. The phase compositions were examined by X-ray diffraction (Ultima-IV, Rigaku, Japan) with Cu-Ka radiation. The microstructures were observed via scanning electron microscopy (SEM; S-3100H, Hitachi, Japan) and transmission electron microscopy (TEM; EM-002B, TOPCON, Japan). The elemental distributions of the microstructure in the eutectic composites were measured with an electron probe microanalyser (EPMA; JXA-8530F, JEOL, Japan). The Vickers hardness ($H_v$) was determined from 10 indentation measurements at an applied load of 5 N. The indentation fracture toughness ($K_{IC}$) was calculated by the Anstis equation [11].
where \( E \) is Young’s modulus, \( H \) is hardness, \( F \) is indentation load, and \( R \) is radial crack length. The Young’s moduli of the \( \text{ZrB}_2-\text{ZrN} \) composites were calculated from the Vegard’s law, considering \( E \) as 496 and 328 GPa for \( \text{ZrB}_2 \) and \( \text{ZrN} \), respectively [12]. Crystal structure illustrations were produced using VESTA software [13].

3. Results and discussion

Figure 1 depicts the surface microstructures of the \( \text{ZrB}_2-\text{ZrN} \) composites prepared by arc-melting. In 30\%\text{ZrB}_2–70\%\text{ZrN}, the primary phase was round-shaped \( \text{ZrN} \) (grey phase) surrounded by \( \text{ZrB}_2-\text{ZrN} \) eutectic phases, as shown in Figure 1(a). The surface and cross-sectional images of the 48\%\text{ZrB}_2–52\%\text{ZrN} composite are shown in Figure 1(b) and (c). Blunt hexagonal \( \text{ZrN} \) phases, with a grey contrast, were uniformly dispersed in the \( \text{ZrB}_2 \) matrix, with black contrast, as shown in Figure 1(b). The grey \( \text{ZrN} \) phase was elongated toward the growth direction forming a rod-like eutectic structure, as shown in Figure 1(c). The composition calculated from the volume fraction of the grey \( \text{ZrN} \) phase in Figure 1(c) was 47 vol\% (49 mol\%), which was almost in agreement with the nominal molar ratio of \( \text{ZrN} \) (52 mol\%). Figure 1(d) depicts the surface microstructure of the 70\%\text{ZrB}_2–30\%\text{ZrN} composite. The \( \text{ZrB}_2 \) (black) phase was plate-like, and the \( \text{ZrB}_2-\text{ZrN} \) eutectic phases were alternately formed. The \( \text{ZrB}_2 \) phase in the \( \text{ZrB}_2-\text{ZrN} \) eutectic phases was a partially elongated rod-like structure. Figure 1(e) shows the surface microstructure of 80\%\text{ZrB}_2–20\%\text{ZrN}. The \( \text{ZrB}_2 \) (black) phase had a blunt square shape with a small amount of the eutectic phase surrounding it. Figure 2 depicts the EPMA mappings of \( \text{Zr} \), \( \text{B} \), and \( \text{N} \) in the surface of the 48\%\text{ZrB}_2–52\%\text{ZrN} eutectic composite. The matrix and rod-like phases were confirmed to be \( \text{ZrB}_2 \) and \( \text{ZrN} \), respectively. Figure 3(a) shows a bright-field TEM image of the transverse section of the 48\%\text{ZrB}_2–52\%\text{ZrN} rod-like eutectic structure. The corresponding selected area electron diffraction (SAED) patterns are shown in

\[
K = (0.016) \cdot \left( \frac{E}{H} \right)^{1/2} \frac{F}{R^{3/2}}
\]
Figure 3(b–d), for the ZrB$_2$ phase, the ZrN phase and the interface area, respectively. Grain boundaries were not observed in the ZrN rods and in the ZrB$_2$ matrix, as shown in Figure 3(a). The hexagonally faceted ZrN rods were single crystals dispersed in the single-crystalline ZrB$_2$ matrix. The zone axis of ZrN <111> in Figure 3(d) was parallel to that of ZrB$_2$ <0001> in Figure 3(b). At the interfacial region between ZrN and ZrB$_2$, a set of six-fold symmetric diffraction spots of ZrN {022} coincided with that of ZrB$_2$ {1120}, as shown in Figure 3(c). These SAED patterns indicate the formation of a coherent interface between ZrB$_2$ and ZrN with crystal orientation relationships of ZrB$_2$ {1120}//ZrN {022} and ZrB$_2$ <0001>//ZrN <111>. Minford et al. reported that the orientation relationships of directionally oxide eutectics were associated with the minimization of lattice misfit or strain between the two phases at the interface [14]. Figure 4 describes the atomic alignments of the ZrB$_2$ and ZrN planes perpendicular to the growth.

Figure 4. Schematic illustration of the crystal structures on the ZrB$_2$ (0001) and ZrN (111) planes.
direction. ZrB₂ has a hexagonal AlB₂-type crystal structure with alternating layers of B atoms as two-dimensional graphite-like six-membered rings and close-packed Zr atoms [1], whereas ZrN has a NaCl-type structure [15]. In both crystal structures, Zr atoms on the ZrN (111) and ZrB₂ (0001) planes are hexagonally close-packed. The interplanar distance between the (0210) planes in ZrB₂ is 0.317 nm, which is close to that of the (022) planes in ZrN (0.325 nm). The lattice matching between ZrB₂ and ZrN and their similar atomic arrangements could have resulted in the reduction of the strain at the interface of the two phases and the formation of the hexagonal facets of the ZrN rods, as seen in Figures 1(b), 3(a). Cheng et al. reported a similar atomic arrangement on the TiCₜNₓ₋ₓ (111) and the TiB₂ (0001) planes with crystal orientation relationships of TiB₂ \{12\overline{1}0\}/TiCₜNₓ₋ₓ \{02\} and TiB₂ <0001>/TiCₜNₓ₋ₓ <1\overline{1}1> in TiB₂–TiCₜNₓ₋ₓ rod-like eutectic composites prepared by arc-melting [16,17]. Similar crystal orientation relationships of TiB₂ \{000\}/TiCₜNₓ₋ₓ \{1\overline{1}1\} and TiB₂ \{1\overline{2}\overline{2}0\}/TiN <1\overline{1}0> were also observed in TiB₂–TiN nano-multilayers synthesized by magnetron sputtering [18]. Two single crystal phases in eutectics often grow preferentially along well-defined crystallographic directions, which correspond to structures with minimum interfacial energy [19]. The crystal orientation relationships with faceted microstructure in the non-oxide eutectics between zirconium (titanium) diborides with hexagonal lattices and carbides (nitrides) with cubic lattices would be attributed to structures lowering the interfacial energy.

It is known that eutectic composites change from a rod-like microstructure at less than 30 vol % of the second (dispersed) phase to lamellar-like microstructure at more than 30 vol% [20]. However, in the ZrB₂–ZrN eutectic composite, the rod-like microstructure was formed at 47 vol% (49 mol%) of ZrN. The TiB₂–TiCₜNₓ₋ₓ eutectic composite prepared by arc-melting also showed rod-like microstructure at 63 vol% of the dispersed phase [16]. This might be caused by strong interactions between the hexagonal (0001)-oriented TiB₂ matrix and the cubic (111)-oriented TiCₜNₓ₋ₓ dispersoids. The d-spacings of TiB₂ \{12\overline{1}0\} and TiCₜNₓ₋ₓ \{02\} in the TiB₂–TiCₜNₓ₋ₓ eutectic composite were very similar to each other; 0.263 and 0.260–0.264 nm, respectively. The cubic (111)-oriented TiCₜNₓ₋ₓ dispersed phase could be constrained to align with the hexagonal (0001)-oriented TiB₂ matrix phase. The d-spacings of ZrB₂ \{12\overline{1}0\} and ZrN \{02\} in ZrB₂–ZrN eutectic were also close to each other, 0.317 and 0.325 nm, respectively. The slight difference in these d-spacings might have yield the blunt hexagonal shape of the ZrN phase in the ZrB₂–ZrN eutectic composite.

The thermal expansion coefficient (CTE) of ZrB₂ (6.66 × 10⁻⁶ K⁻¹ for a-axis and 6.93 × 10⁻⁶ for c-axis K⁻¹ [21]) and ZrN (7.8 × 10⁻⁶ K⁻¹ [22]) are slightly different. However, the ZrB₂ matrix and ZrN dispersoids were both single crystals in a wide area. Since the lattice parameter and CTE of ZrB₂ are close to those of GaN, ZrB₂ single crystals are a promising substrate material for GaN epitaxial films [21]; however, the crystal could hardly be grown by the conventional Czochralski method. Therefore, the ZrB₂–ZrN eutectic single crystalline composite may be used instead of the ZrB₂ single crystals.

Figure 5 depicts the effect of the ZrB₂ content on the Vickers hardness of the ZrB₂–ZrN composite. The Vickers hardness of ZrB₂ and ZrN are 15.8 and 17.3 GPa, respectively. On the whole, the hardness of ZrB₂–ZrN composites slightly increased with increasing the ZrB₂ content because ZrB₂ is harder than ZrN. However, the Vickers hardness value of the 48ZrB₂–52ZrN eutectic composite \((H_v = 16.2\) GPa) was slightly higher than those of ZrB₂–ZrN composites with ZrB₂ contents above and below the eutectic composition (48 mol% ZrB₂). The 48ZrB₂–52ZrN eutectic composite comprised ZrN rods with sizes less than 2 μm in the ZrB₂ matrix (Figure 1(b)), whereas grain sizes of the primary phases of ZrN in 30ZrB₂–70ZrN (Figure 1(a)) and those of ZrB₂ in 70ZrB₂–30ZrN (Figure 1(d)) were larger than 5 μm. According to the Hall–Petch relation, the Vickers hardness decreases with increasing grain size [23,24]. Thereby, the hardness of ZrB₂–ZrN composites with ZrB₂ contents above and below the eutectic composition, which contained large grains of primary phases, could be lower than that of the

![Figure 5](image-url)
48ZrB$_2$–52ZrN eutectic composite with a fine rod-like microstructure.

**Figure 6** depicts the Vickers indentation and cracks in 48ZrB$_2$–52ZrN eutectic (Figure 6(a,b)) and 70ZrB$_2$–30ZrN composites (Figure 6(c,d)). In the 48ZrB$_2$–52ZrN eutectic composite, the crack formed from the four corners, as seen in Figure 6(a), where the terminal of each crack is denoted with white allows in Figure 6(a). The calculated $K_{IC}$ value was 2.7 MPa m$^{1/2}$, which was slightly lower than that of ZrB$_2$ (3.1 MPa m$^{1/2}$) and higher than that of ZrN (2.4 MPa m$^{1/2}$). The cracks partially passed through the ZrN (with a grey contrast) and ZrB$_2$ (with a black contrast) phases and also partially at the ZrB$_2$/ZrN interface, as shown in Figure 6(b). On the contrary, the cracks in the 70ZrB$_2$–30ZrN composite irregularly formed from not only corners but also sides of the indentation, as seen in Figure 6(c,d). Most of the irregular cracks in the 70ZrB$_2$–30ZrN composite was terminated at points closer to the indentation (Figure 6(c)), compared to cracks propagated in the 48ZrB$_2$–52ZrN eutectic composite (Figure 6(a)). Although the $K_{IC}$ for the 70ZrB$_2$–30ZrN composite could not be evaluated from Equation (1), the 70ZrB$_2$–30ZrN composite with shorter crack lengths might be more fracture resistant than the 48ZrB$_2$–52ZrN eutectic composite.

### 4 Conclusions

ZrB$_2$–ZrN eutectic composites were prepared via arc-melting with a mixture of ZrB$_2$ and ZrN powders under an N$_2$ atmosphere. The 48ZrB$_2$–52ZrN eutectic composite showed a rod-like structure, with hexagonally faceted (111)–oriented ZrN single-crystal rods dispersed in a (0001)–oriented ZrB$_2$ single crystal matrix.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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