Characterization of Directionally Solidified B₄C–TiB₂ Composites Prepared by a Floating Zone Method

Itaru Gunjishima *, Takaya Akashi and Takashi Goto

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Directionally solidified B₄C–TiB₂ composites were prepared by a Floating Zone method. TiB₂ phases in a rod shape were continuously connected in the B₄C matrix. The c-axes of TiB₂ and B₄C phases were perpendicular and tilted 22° to the growth direction, respectively. The (101) and (1̅0̅20) planes of the B₄C were in parallel to the (001) and (100) planes of TiB₂, respectively. The electrical conductivity of the composite parallel to the growth direction (σ∥) was greater than monolithic B₄C by a factor of 100 to 1000. The thermal conductivity of the composite parallel to the growth direction (κ∥) was about one and a half times as high as that of B₄C. The anisotropy of electrical and thermal conductivity were basically explained by a mixing law using the values of B₄C and TiB₂. The microhardness of the composite was almost the same as that of B₄C. The electric discharge machining of the composite was possible owing to the enhancement of electrical conductivity.

(Received December 20, 2001; Accepted February 25, 2002)

Keywords: boron carbide, titanium diboride, eutectic, directional solidification, floating zone, electrical conductivity, thermal conductivity, electric discharge machining, hardness

1. Introduction

Boron carbide (B₄C) has several unique characteristics such as extremely high hardness,¹,² high neutron absorption cross-section³ and abnormally low thermal conductivity.⁴ These features provide wide variety of applications for abrasives,⁵ nuclear controlling rods⁶ and thermoelectrics.⁷⁻¹³ However, the high hardness and the low thermal conductivity could be drawbacks for machinability to complicated shapes⁵ and for thermal-shock resistance.⁵,³ However, by making B₄C-based composites with electrically and thermally conductive ceramics, the application of B₄C would be expanded to wider fields because of the capability of electric discharge machining and the improvement of thermal shock resistance.

Titanium diboride (TiB₂) has high electrical conductivity,¹³⁻¹⁵ thermal conductivity¹⁶ and hardness,¹,¹⁵ being compatible with B₄C because B₄C and TiB₂ form binary eutectic composites.¹⁷ Therefore, TiB₂ would be suitable dispersoid to improve electrical and thermal conductivity of B₄C.

Since the properties of composite are strongly influenced by texture, it is important to fabricate composites with well-controlled texture. The directional solidification is advantageous to control the texture particularly for eutectic composites.¹⁸⁻²¹ In the present work, directionally solidified B₄C–TiB₂ eutectic composites were prepared by a floating zone (FZ) method, and the electrical conductivity, thermal conductivity, hardness and electric discharge machinability were investigated.

2. Experimental Procedure

B₄C and TiB₂ powders were mixed at a composition of 25 mol% TiB₂, and isostatically pressed at 9.8 MPa in a latex tube with 10 mm in diameter. The pressed rods were sintered at 1773 K for 3.6 ks in Ar atmosphere. Directionally solidified B₄C–TiB₂ composites were prepared by the FZ method using the sintered rods in Ar atmosphere. A Xe lamp was used for the heating. The solidification rate was controlled at 2.8 × 10⁻⁶, 1.4 × 10⁻⁵ and 5.6 × 10⁻⁵ ms⁻¹. B₄C and TiB₂ monolithic materials were prepared for comparison. B₄C specimen was fabricated by the FZ method, and TiB₂ specimen was prepared by a spark plasma sintering (SPS) since the melting point of TiB₂ (3500 K) is too high for the FZ method. The density of the sintered TiB₂ was 88%.

The lattice parameters of the specimens were measured by an X-ray powder diffraction method. Pure Si powder was used as a standard material. The growth direction and crystal orientation of B₄C and TiB₂ phases were determined by pole figure X-ray diffraction and transmission electron microscopy (TEM). The microstructure was observed by means of scanning electron microscopy (SEM). The electrical conductivity (σ) was measured by a dc four-probe method for rectangular specimens (6 mm by 1 mm by 1 mm). The thermal conductivity (κ) was measured by a laser flash method using disk speci-
Characterization of Directionally Solidified B₄C–TiB₂ Composites by an FZ Method

Fig. 2 Microstructure of directionally solidified B₄C–TiB₂ composites. (a1) growth rate 2.8 × 10⁻⁶ ms⁻¹ (Parallel to growth direction). (a2) growth rate 2.8 × 10⁻⁶ ms⁻¹ (Perpendicular to growth direction). (b1) growth rate 1.4 × 10⁻⁵ ms⁻¹ (Parallel to growth direction). (b2) growth rate 1.4 × 10⁻⁵ ms⁻¹ (Perpendicular to growth direction). (c1) growth rate 5.6 × 10⁻⁵ ms⁻¹ (Parallel to growth direction). (c2) growth rate 5.6 × 10⁻⁵ ms⁻¹ (Perpendicular to growth direction).

The B₄C–TiB₂ system is pseudo-binary eutectic as shown in Fig. 1. The typical eutectic texture was observed at the composition of B₄C–25 mol% TiB₂ in this study. Textures of directionally solidified B₄C–TiB₂ composites at several growth rates are summarized in Fig. 2. Figures 2(a1), (b1) and (c1) show the textures of specimen surface parallel to the growth direction, and Figs. 2(a2), (b2) and (c2) show those of specimen surface perpendicular to the growth direction. The white phase is TiB₂, and the black matrix is B₄C. These pictures show that TiB₂ phases grew as a rod shape in the matrix of B₄C. When the melted B₄C–TiB₂ composite of the eutectic composition is cooled below the solidification temperature, the crystallization of B₄C and TiB₂ would start simultaneously. During this process, a liquid phase rich in Ti might form around B₄C crystallites, and also a liquid phase rich in C might form around TiB₂ crystallites. Then, the excess Ti and C would diffuse to the TiB₂ and B₄C crystallites, respectively. Since a steady-state diffusion of solutes could be maintained in the directional solidification, B₄C and TiB₂ crystallites with constant dimensions could grow parallel to each other depending on the solidification rate.

3. Results and Discussion

3.1 Eutectic texture

The B₄C–TiB₂ system is pseudo-binary eutectic as shown in Fig. 1. The typical eutectic texture was observed at the composition of B₄C–25 mol% TiB₂ in this study. Textures of directionally solidified B₄C–TiB₂ composites at several growth rates are summarized in Fig. 2. Figures 2(a1), (b1) and (c1) show the textures of specimen surface parallel to the growth direction, and Figs. 2(a2), (b2) and (c2) show those of specimen surface perpendicular to the growth direction. The white phase is TiB₂, and the black matrix is B₄C. These pictures show that TiB₂ phases grew as a rod shape in the matrix of B₄C. When the melted B₄C–TiB₂ composite of the eutectic composition is cooled below the solidification temperature, the crystallization of B₄C and TiB₂ would start simultaneously. During this process, a liquid phase rich in Ti might form around B₄C crystallites, and also a liquid phase rich in C might form around TiB₂ crystallites. Then, the excess Ti and C would diffuse to the TiB₂ and B₄C crystallites, respectively. Since a steady-state diffusion of solutes could be maintained in the directional solidification, B₄C and TiB₂ crystallites with constant dimensions could grow parallel to each other depending on the solidification rate.

The spacing between rods decreased with increasing the growth rate as shown in Fig. 2. The time for the diffusion of
solutes around the solid/liquid interface should be short at a high growth rate. This would cause a narrow spacing between rods. The relationship between growth rate \( V \) and rod spacing \( \lambda \) for the eutectic growth may be given as follows,\(^{22}\)

\[
\lambda^2 V = K
\]

where, \( K \) is a constant determined by the eutectic composition and the diffusivity of component atoms near the solid-liquid interface.

Figure 3 shows the relationship between the average \( \lambda \) and the reciprocal square root of growth rate \( V \) for the B\(_4\)C–TiB\(_2\) system. The \( K \) value in this system was \( 8.6 \times 10^{-17} \text{ m}^3\text{s}^{-1} \), being almost the same magnitude as those reported for Sn–Se \((1.4 \times 10^{-17} \text{ m}^3\text{s}^{-1})\),\(^{19}\) Ni–Ni\(_3\)Si \((1.0 \times 10^{-16} \text{ m}^3\text{s}^{-1})\)\(^{20}\) and Mn–MnBi eutectic system \((1.3 \times 10^{-16} \text{ m}^3\text{s}^{-1})\)\(^{21}\). The increase of growth rate caused the formation of colony structure as shown in Fig. 4. TiB\(_2\) phase was aligned nearly parallel to the solidification direction in the central region of colonies, however, the texture was irregular at the boundary.

### 3.2 Crystal orientation

Figure 5 shows crystal structures of B\(_4\)C and TiB\(_2\). Although B\(_4\)C belongs to a rhombohedral unit cell structure, hexagonal expression is often used to indicate the structure of B\(_4\)C. The crystal structure of B\(_4\)C has a three-atom chain, in which each end atom is bonded to three icosahedra. B\(_4\)C is constructed from a number of structural unit, including B\(_{12}\), B\(_{11}\)C, B\(_{10}\)C\(_2\) icosahedra (predominantly B\(_{11}\)C), and –C–C–C–, –C–C–C– and –C–B–B– chains.\(^{23,24}\) This feature causes the wide-ranged solid solution of B\(_4\)C. In spite of the wide non-stoichiometry, the B\(_4\)C phase in the B\(_4\)C–TiB\(_2\) composite was stoichiometric \((i.e., B/C = 4 \text{ in atomic ratio})\) as shown later. TiB\(_2\) has a hexagonal AlB\(_2\)-type crystal structure.\(^{25}\) It is characterized by the alternate stacking of hexagonal layers of titanium and boron atoms.

Figure 6 shows an X-ray pole figure of B\(_4\)C–TiB\(_2\) composite for the cross section perpendicular to the growth direction. \((110)\) diffraction of TiB\(_2\) appeared at the center of the figure. This indicates that the growth direction of TiB\(_2\) phase was \((110)\). The angle between \((100)\) or \((010)\) plane and \((110)\) plane is 30° in the hexagonal unit cell. Two diffractions at 30° on the both sides of \((110)\) diffraction are from the \((100)\) and \((010)\) planes. Therefore, the crystal planes of the TiB\(_2\) rods were oriented in parallel with each other since the diffractions from \((100)\) and \((010)\) planes were appeared. The angle between the \((003)_H\) diffraction \("H" \text{ stands for hexag-}

---

**Fig. 3** Relationship between rod spacing \( \lambda \) and growth rate \( V \).

**Fig. 4** Colony structure at the growth rate of \( 5.6 \times 10^{-5} \text{ m}\text{s}^{-1} \). (a) Perpendicular to growth direction, (b) Parallel to growth direction.

**Fig. 5** Crystal structures of B\(_4\)C (a) and TiB\(_2\) (b).
Characterization of Directionally Solidified $B_4C$–$TiB_2$ Composites by an FZ Method

Fig. 6 Pole figure of $B_4C$–$TiB_2$ composite for the cross section perpendicular to growth direction.

Fig. 7 Schematic diagram for twin boundary of $B_4C$.

Fig. 8 Schematics of the crystal orientation for $B_4C$ and $TiB_2$ in $B_4C$–$TiB_2$ eutectic composites.

Fig. 9 Electron diffraction patterns for the $B_4C$–$TiB_2$ composite. Figures 9(a), (b) and (c) are the electron diffraction patterns for single phase region of $B_4C$ and $TiB_2$, and interface region between the two phases, respectively. The (101) and (120) planes of $B_4C$ phase were parallel to the (001) and (100) planes of $TiB_2$ phase, respectively. This result is in agreement with the relationship of the crystal orientations between $B_4C$ and $TiB_2$ phases obtained by the pole figure shown in Fig. 8.

3.3 Composition
Boron carbide has a wide-ranged solid solution (9–20 at% C) as indicated in Fig. 10. The lattice parameters change depending on the composition in the single phase region. The lattice parameters of boron carbide in the $B_4C$–$TiB_2$ eutectic composites and monolithic $B_4C$ were in agreement with those of literature value for boron carbide with 20 at% C ($a_H = 0.561$ nm and $c_H = 1.209$ nm in hexagonal expression). The B/C atomic ratio of the monolithic $B_4C$ measured by chemical analysis was 3.98 ± 0.06, which is in good agreement with the stoichiometric value of 4 (B/C in atomic ratio). The lattice parameters of $TiB_2$ in the composite were $a_H = 0.303$ nm and $c_H = 0.323$ nm. These values were also in agreement with literature values.

3.4 Electrical conductivity
Figure 11 shows the temperature dependence of electrical conductivity for the monolithic $B_4C$ and $TiB_2$, and the $B_4C$–$TiB_2$ eutectic composite. The electrical conductivity of $B_4C$ increased with increasing temperature. This may be mainly resulted from the increase of mobility as reported elsewhere. The electrical conductivity of $TiB_2$ slightly decreased with increasing temperature showing metallic behavior. The electrical conductivity of $B_4C$–$TiB_2$ composite was almost independent of temperature, and was intermediate between those of $B_4C$ and $TiB_2$. The electrical conductivity parallel to the growth direction ($\sigma_\parallel$) was approximately ten times greater than that perpendicular to the growth direction ($\sigma_\perp$).

The volume fraction of $TiB_2$ phase in the composite was independent of the growth condition. Thus, the difference of electrical conductivity among the composites should be caused by the texture (i.e., arrangement of the $B_4C$ phase and
the TiB₂ phase). The electrical conductivities of the composite parallel to the growth direction ($\sigma_\|$) and perpendicular to the growth direction ($\sigma_\perp$) may be calculated from a mixing law as given by eqs. (2) and (3).

$$\sigma_\|_{\text{CAL}} = (1 - V_B)\sigma_A + V_B\sigma_B \quad (2)$$

$$\sigma_\perp_{\text{CAL}} = \sigma_A (1 - V_B^{1/2}) + \sigma_B (1 - V_B^{1/2}) / (1 - V_B^{1/2})^{-1} \quad (3)$$

where $\sigma_A$ and $\sigma_B$ are the electrical conductivities of the matrix and the second phase, respectively. $V_B$ is the volume fraction of the second phase. Since $\sigma_B \gg \sigma_A$, eqs. (2) and (3) can be simplified as eqs. (4) and (5).

$$\sigma_\|_{\text{CAL}} = V_B\sigma_B \quad (4)$$

$$\sigma_\perp_{\text{CAL}} = \sigma_A (1 - V_B^{1/2}) + \sigma_B V_B^{1/2} / (1 - V_B^{1/2}) \quad (5)$$

Solid and broken lines in Fig. 11 are calculated values of the composite for $\sigma_\|_{\text{CAL}}$ and $\sigma_\perp_{\text{CAL}}$, respectively. The temperature dependence of $\sigma_\|$ was similar to that of TiB₂ because the TiB₂ phases in the rod shape was almost continuously aligned to the growth direction. The temperature dependence of $\sigma_\perp$ was intermediate between that of B₄C and TiB₂, being different from that of $\sigma_\perp_{\text{CAL}}$. This suggests that the TiB₂ rods were also partially connected perpendicular to the growth direction.

At the growth rate of \(1.4 \times 10^{-5} \text{ ms}^{-1}\), the TiB₂ phases could be almost perfectly connected to the growth direction since the experimental values ($\sigma_\|$) were almost in agreement with calculated values ($\sigma_\|_{\text{CAL}}$).

The relationships between electrical conductivity and growth rate are depicted in Fig. 12. Both $\sigma_\|$ and $\sigma_\perp$ showed the maxima at \(1.4 \times 10^{-5} \text{ ms}^{-1}\). At this growth rate, the connectivity of TiB₂ phases could be better than other growth
Characterization of Directionally Solidified B₄C–TiB₂ Composites by an FZ Method

Fig. 12 Relationship between electrical conductivity (σ) and growth rate (V).

Fig. 13 Temperature dependence of electrical conductivity (σ).

Fig. 14 Temperature dependence of thermal conductivity (κ).

The electrical conductivity of the monolithic TiB₂ prepared in this study had nearly the same magnitude as that of literatures.¹⁴,¹⁵ The electrical conductivity of a sintered B₄C–38 mol% TiB₂ composite (density: 99%) was reported by Cai et al.²⁹ The B₄C–TiB₂ eutectic composite in this study showed ten times greater electrical conductivity than the sintered composite in spite of the lower TiB₂ content because the TiB₂ phase was one-directionally connected in this study.

3.5 Thermal conductivity

The thermal conductivity of TiB₂ and B₄C–TiB₂ composite are shown in Fig. 14. The values of monolithic B₄C and TiB₂ were 20 to 30 W K⁻¹ m⁻¹ and 70 to 80 W K⁻¹ m⁻¹, respectively. They decreased with increasing temperature. The thermal conductivity of the composite parallel to the growth direction (κ∥) was greater than that of monolithic B₄C, whereas that perpendicular to the growth direction (κ⊥) was smaller than that of monolithic B₄C.

The thermal conductivities parallel (κ∥) and perpendicular to the growth direction (κ⊥) of the composite may be given by a mixing law as eqs. (6) and (7).¹⁸,²⁹

\[
κ_{\parallel, \text{CAL}} = (1 - V_B)κ_A + V_Bκ_B \tag{6}
\]

\[
κ_{\perp, \text{CAL}} = κ_A \frac{1 - V_B^{1/2}}{V_B} + κ_B \frac{1 - V_B^{1/2}}{V_B} + κ_B^{-1} \tag{7}
\]

where κₐ and κₜ are the thermal conductivities of the matrix and the second phase, respectively. V₁ is the volume ratio of the second phase. A solid and broken lines in Fig. 14 are calculated κ∥CAL and κ⊥CAL for the composite. The experimental values of κ∥ were slightly smaller than that of κ∥CAL. On the other hand, the experimental values of κ⊥ were much smaller than that of κ⊥CAL. The phonon scattering at B₄C/TiB₂ interface may be small when heat flows parallel to the growth direction. When the heat flows perpendicular to the growth direction, the phonon scattering at B₄C/TiB₂ interface may be significant, which might have caused the decrease of thermal conductivity.
The relationships between thermal conductivity and growth rate are depicted in Fig. 15. Both $\kappa_\parallel$ and $\kappa_\perp$ values at $1.4 \times 10^{-5}$ m/s were slightly greater than those other growth rates. Since the connectivity of TiB$_2$ rods at $1.4 \times 10^{-5}$ m/s was better than that of other growth rates for both parallel and perpendicular to the growth direction as described in 3.4, the $\kappa_\parallel$ and $\kappa_\perp$ showed the maxima at this growth rate.

The temperature dependence of thermal conductivities for B$_4$C, 4, 6, 30, 31) TiB$_2$ 16) and B$_4$C–TiB$_2$ composites 8) are demonstrated in Fig. 16. The thermal conductivity of the monolithic B$_4$C in this study was the greatest among the reported values. 4, 6, 30, 31) Since the monolithic B$_4$C in this study is high purity single crystal, 7) there is no phonon scattering at grain boundary or impurity. The thermal conductivity of the monolithic TiB$_2$ sintered body in this study was slightly smaller than the reported value. 16) The density of the sintered TiB$_2$ in the report is 97% whereas that of the TiB$_2$ in this study is 88%. Lower density might have caused the smaller thermal conductivity of TiB$_2$ in this study. The thermal conductivity of sintered B$_4$C–38 mol%TiB$_2$ composite (density: 99%) was reported by Cai et al., 8) being smaller than that of the composite in this study. The directionally solidified texture could cause the greater thermal conductivity than sintered composite in spite of the smaller TiB$_2$ content (25 mol% TiB$_2$).

### 3.6 Hardness

The indenter load dependence of Vickers microhardness of the monolithic B$_4$C and TiB$_2$, and the B$_4$C–TiB$_2$ composite, and the B$_4$C and TiB$_2$ phases in the B$_4$C–TiB$_2$ composite are shown in Fig. 17. The microhardness of the B$_4$C and TiB$_2$ phases in the composite were obtained by indenting only B$_4$C and TiB$_2$ phase, respectively. The microhardness of the B$_4$C–TiB$_2$ composite means the average value of 30 points in the composite indented at random. The hardness commonly increases with decreasing the indenter load. This trend can be generally observed in the measurement for hard materials. 15) The microhardness of the B$_4$C–TiB$_2$ composite was independent of the growth rate. The difference of the microhardness between parallel and perpendicular to the growth direction was not observed. With decreasing the indenter load, the size of indentation became smaller nearly same as the eutectic texture. This caused the relatively large scattering of the microhardness values. The microhardness of the composite measured at high indenter loads showed almost the same value as that of B$_4$C. Figure 18 compares the indenter load dependence of microhardness for several hard materials. The results obtained in this study are shown with values of various ceramics. 5) The B$_4$C–TiB$_2$ composite was almost the hardest material particularly at high indenter load.
Directionally solidified B$_4$C–TiB$_2$ eutectic composite was prepared by an FZ method, and following results were obtained.

1. The composition of the boron carbide in the composite was stoichiometric B$_4$C.
2. The TiB$_2$ phase in a rod shape was continuously connected in the composite matrix. The diameter of the TiB$_2$ rods decreased with increasing the growth rate.
3. The c-axes of TiB$_2$ and B$_4$C phases were perpendicular and tilted 22$^\circ$ to the growth direction, respectively. The (101) and (120) planes of the B$_4$C were in parallel to the (001) and (100) planes of the TiB$_2$, respectively.
4. The anisotropy of electrical and thermal conductivity were basically explained by a mixing law using the values of B$_4$C and TiB$_2$.
5. The microhardness of the composite was almost the same as that of B$_4$C in the indenter load region more than 1 N.
6. The electric discharge machining of the composite was achieved due to the enhancement of electrical conductivity.

Acknowledgments

The authors appreciate the financial support from the Izumi Science and Technology Foundation. This research was mainly conducted by using facilities of Laboratory for Advanced Materials, Institute for Materials Research.

REFERENCES