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

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Directionally solidified B_4C-TiB_2 composites were prepared by a Floating Zone method. TiB₂ phases in a rod shape were continuously connected in the B_4C matrix. The c-axes of TiB₂ and B_4C phases were perpendicular and tilted 22° to the growth direction, respectively. The (101) and (120) planes of the B_4C were in parallel to the (001) and (100) planes of TiB₂, respectively. The electrical conductivity of the composite parallel to the growth direction (σ_{\parallel}) was greater than monolithic B_4C by a factor of 100 to 1000. The thermal conductivity of the composite parallel to the growth direction (κ_{\parallel}) was about one and a half times as high as that of B_4C . The anisotropy of electrical and thermal conductivity were basically explained by a mixing law using the values of B_4C and TiB₂. The microhardness of the composite was almost the same as that of B_4C . The electric discharge machining of the composite was possible owing to the enhancement of electrical conductivity.

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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 provides wide variety of applications for abrasives,⁵⁾ nuclear controlling rods⁵⁾ and thermoelectrics.^{6–13)} However, the high hardness and the low thermal conductivity could be drawbacks for machinability to complicated shapes⁵⁾ and for thermal-shock resistance,^{3,5)} respectively. 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 wellcontrolled texture. The directional solidification is advantageous to control the texture particularly for eutectic composites.^{18–21} In the present work, directionally solidified B_4C – 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

 B_4C and TiB_2 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. Direction-

ally solidified B_4C-TiB_2 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. B_4C and TiB₂ monolithic materials were prepared for comparison. B_4C 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 with 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-



Fig. 1 B_4C -TiB₂ pseudo-binary phase diagram.¹⁷⁾

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Fig. 2 Microstructure of directionally solidified B_4C -TiB₂ composites. (a1) growth rate $2.8 \times 10^{-6} \text{ ms}^{-1}$ (Parallel to growth direction). (a2) growth rate $2.8 \times 10^{-6} \text{ ms}^{-1}$ (Perpendicular to growth direction). (b1) growth rate $1.4 \times 10^{-5} \text{ ms}^{-1}$ (Parallel to growth direction). (b2) growth rate $1.4 \times 10^{-5} \text{ ms}^{-1}$ (Perpendicular to growth direction). (c1) growth rate $5.6 \times 10^{-5} \text{ ms}^{-1}$ (Parallel to growth direction). (c2) growth rate $5.6 \times 10^{-5} \text{ ms}^{-1}$ (Perpendicular to growth direction).

mens (ϕ 8 mm by 2 mm). The measurements were conducted for specimens parallel and perpendicular to the growth direction in the temperature range between room temperature and 1023 K. The Vickers microhardness was measured under the indenter load from 0.245 to 1.96 N. The electric discharge machinability were evaluated for B₄C and B₄C–TiB₂ composite using copper electrodes.

3. Results and Discussion

3.1 Eutectic texture

The B_4C-TiB_2 system is pseudo-binary eutectic¹⁷) as shown in Fig. 1. The typical eutectic texture was observed at the composition of $B_4C-25 \text{ mol}\%\text{TiB}_2$ in this study. Textures of directionally solidified B_4C-TiB_2 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.¹⁸⁾

The spacing between rods decreased with increasing the growth rate as shown in Fig. 2. The time for the diffusion of



Fig. 3 Relationship between rod spacing (λ) and growth rate (V).

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 (λ) for the eutectic growth may be given as follows,²²

$$\lambda^2 V = K \tag{1}$$

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 λ and the reciprocal square root of growth rate *V* for the B₄C–TiB₂ system. The *K* value in this system was 8.6 × 10⁻¹⁷ m³s⁻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–Ni₃Si $(1.0 \times 10^{-16} \text{ m}^3 \text{s}^{-1})^{20}$ 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. TiB₂ 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_4C and TiB_2 . Although B_4C belongs to a rhombohedral unit cell structure, hexagonal expression is often used to indicate the structure of B_4C . The crystal structure of B_4C has a three-atom chain, in which each end atom is bonded to three icosahedra. B_4C 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-B-C- and -C-B-B- chains.^{23,24}) This feature causes the wide-ranged solid solution of B_4C . In spite of the wide non-stoichiometry, the B_4C phase in the B_4C-TiB_2 composite was stoichiometric (*i.e.*, B/C = 4 in atomic ratio) as shown later. TiB₂ has a hexagonal AlB₂-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_4C-TiB_2 composite for the cross section perpendicular to the growth direction. (110) diffraction of TiB₂ appeared at the center of the figure. This indicates that the growth direction of TiB₂ phase was $\langle 110 \rangle$. The angle between (100) or (010) plane and



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



Fig. 5 Crystal structures of B_4C (a) and TiB_2 (b).

(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 TiB₂ 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" stands for hexag-



Fig. 6 Pole figure of B₄C–TiB₂ composite for the cross section perpendicular to growth direction.



Fig. 7 Schematic diagram for twin boundary of B₄C.

onal) of B₄C and the center of the pole figure was about 20°. This indicates that the *c*-axis of B_4C tilted 20° from the growth direction. B₄C had twin boundaries at (101)_H plane (*i.e.*, (100) plane in rhombohedral expression)²⁶⁾ as shown in Fig. 7. The angle between $(101)_{\rm H}$ plane and *c*-axis is 22°. Two $(003)_H$ diffractions of B₄C were symmetrically observed, and each diffraction had an angle of 20° from the center of the pole figure. This suggests the B₄C phase should have twin boundary parallel to the growth direction. Furthermore, two $(003)_{\rm H}$ diffractions of B₄C were symmetric with respect to the horizontal-axis in the pole figure diagram (*i.e.*, the line passing (100) and (010) diffractions of TiB_2). This indicates that the twin boundary of B₄C was parallel to the (001) plane of TiB₂. The schematics of the crystal orientation for B₄C and TiB_2 in the B₄C–TiB₂ eutectic composite are shown in Fig. 8. The $(101)_{\rm H}$ plane of B₄C was parallel to the (001) plane of TiB₂ (shaded planes), and the $(1\overline{2}0)_{H}$ plane of B₄C was parallel to the (100) plane of TiB₂(colored planes). The $(212)_{\rm H}$ direction of B_4C was also parallel to the (010) direction of TiB₂.

Figure 9 shows electron diffraction patterns for the B₄C–



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

TiB₂ composite. Figures 9(a), (b) and (c) are the electron diffraction patterns for single phase region of B_4C and TiB₂, 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 TiB₂ phase, respectively. This result is in agreement with the relationship of the crystal orientations between B_4C and TiB₂ phases obtained by the pole figure shown in Fig. 8.

3.3 Composition

Boron carbide has a wide-ranged solid solution $(9-20 \text{ at}\%\text{C})^{27}$ as indicated in Fig. 10. The lattice parameters change depending on the composition in the single phase region.⁶⁾ The lattice parameters of boron carbide in the B₄C–TiB₂ eutectic composites and monolithic B₄C were in agreement with those of literature value⁶⁾ for boron carbide with 20 at%C ($a_{\rm H} = 0.561 \text{ nm}$ and $c_{\rm H} = 1.209 \text{ nm}$ in hexagonal expression). The B/C atomic ratio of the monolithic B₄C 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 TiB₂ in the composite were $a_{\rm H} = 0.303 \text{ nm}$ and $c_{\rm H} = 0.323 \text{ nm}$. These values were also in agreement with literature values.²⁸)

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.^{7,11} 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 (σ_{\parallel}) was approximately ten times greater than that perpendicular to the growth direction (σ_{\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 B₄C phase and



Fig. 9 TEM diffraction patterns for B_4C matrix (a), TiB_2 phase (b) and B_4C-TiB_2 phase boundary (c).

the TiB₂ phase). The electrical conductivities of the composite parallel to the growth direction (σ_{\parallel}) and perpendicular to the growth direction (σ_{\perp}) may be calculated from a mixing law as given by eqs. (2) and (3).¹⁸⁾

$$\sigma_{\parallel CAL} = (1 - V_B)\sigma_A + V_B\sigma_B \tag{2}$$

$$\sigma_{\perp CAL} = \sigma_{\rm A} (1 - V_{\rm B}^{1/2}) + (\sigma_{\rm A}^{-1} (1 - V_{\rm B}^{1/2}) / V_{\rm B}^{1/2} + \sigma_{\rm B}^{-1})^{-1}$$
(3)

where σ_A and σ_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



Fig. 11 Temperature dependence of electrical conductivity (σ).

simplified as eqs. (4) and (5).

$$\sigma_{\parallel CAL} = V_{\rm B} \sigma_{\rm B} \tag{4}$$

$$\sigma_{\perp CAL} = \sigma_{\rm A} (1 - V_{\rm B}^{1/2}) + \sigma_{\rm A} V_{\rm B}^{1/2} / (1 - V_{\rm B}^{1/2})$$
(5)

Solid and broken lines in Fig. 11 are calculated values of the composite for $\sigma_{\parallel CAL}$ and $\sigma_{\perp CAL}$, respectively. The temperature dependence of σ_{\parallel} 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 σ_{\perp} was intermediate between that of B₄C and TiB₂, being different from that of $\sigma_{\perp CAL}$. 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 (σ_{\parallel}) were almost in agreement with calculated values ($\sigma_{\parallel CAL}$).

The relationships between electrical conductivity and growth rate are depicted in Fig. 12. Both σ_{\parallel} and σ_{\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



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



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

rates for both parallel and perpendicular to the growth direction.

Figure 13 represents the temperature dependence of electrical conductivity for B_4C ,^{6,9–12)} TiB_2 ^{14,15)} and B_4C – TiB_2 composites.⁸⁾ The monolithic B_4C prepared in this study showed slightly greater values than those reported values. The present values were about four times greater than those of hot pressed^{9–11)} and CVD¹²⁾ specimens, and were almost the same as those of arc-melted specimen.⁶⁾ The specimens prepared from melts may have greater conductivity than those



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

from sintering. 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.*⁸⁾ 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 temperature dependence of thermal conductivity for B_4C , TiB_2 and B_4C-TiB_2 composite are shown in Fig. 14. The values of monolithic B_4C and TiB_2 were 20 to $30 \text{ WK}^{-1}\text{m}^{-1}$ and 70 to $80 \text{ WK}^{-1}\text{m}^{-1}$, respectively. They decreased with increasing temperature. The thermal conductivity of the composite parallel to the growth direction (κ_{\parallel}) was greater than that of monolithic B_4C , whereas that perpendicular to the growth direction (κ_{\perp}) was smaller than that of monolithic B_4C .

The thermal conductivities parallel (κ_{\parallel}) and perpendicular to the growth direction (κ_{\perp}) of the composite may be given by a mixing law as eqs. (6) and (7).^{18,29)}

$$\kappa_{\parallel CAL} = (1 - V_{\rm B})\kappa_{\rm A} + V_{\rm B}\kappa_{\rm B} \tag{6}$$

$$\kappa_{\perp CAL} = \kappa_{\rm A} \{ 1 - V_{\rm B}^{1/2} \} + \{ \kappa_{\rm A}^{-1} (1 - V_{\rm B}^{1/2}) / V_{\rm B}^{1/2} + \kappa_{\rm B}^{-1} \}^{-1}$$
(7)

where κ_A and κ_B are the thermal conductivities of the matrix and the second phase, respectively. V_B is the volume ratio of the second phase. A solid and broken lines in Fig. 14 are calculated $\kappa_{\parallel CAL}$ and $\kappa_{\perp CAL}$ for the composite. The experimental values of κ_{\parallel} were slightly smaller than that of $\kappa_{\parallel CAL}$. On the other hand, the experimental values of κ_{\perp} were much smaller than that of $\kappa_{\perp CAL}$. 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.



Fig. 15 Relationship between thermal conductivity (κ) and growth rate (V).

The relationships between thermal conductivity and growth rate are depicted in Fig. 15. Both κ_{\parallel} and κ_{\perp} values at $1.4 \times 10^{-5} \text{ ms}^{-1}$ were slightly greater than those other growth rates. Since the connectivity of TiB₂ rods at $1.4 \times 10^{-5} \text{ ms}^{-1}$ was better than that of other growth rates for both parallel and perpendicular to the growth direction as described in 3.4, the κ_{\parallel} and κ_{\perp} showed the maxima at this growth rate.

The temperature dependence of thermal conductivities for B₄C,^{4,6,30,31}) TiB₂¹⁶) and B₄C-TiB₂ composites⁸) are demonstrated in Fig. 16. The thermal conductivity of the monolithic B₄C in this study was the greatest among the reported values.^{4,6,30,31)} Since the monolithic B₄C 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 TiB₂ sintered body in this study was slightly smaller than the reported value.¹⁶⁾ The density of the sintered TiB₂ in the report is 97% whereas that of the TiB₂ in this study is 88%. Lower density might have caused the smaller thermal conductivity of TiB2 in this study. The thermal conductivity of sintered B₄C-38 mol%TiB₂ 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_4C and TiB_2 , and the B_4C-TiB_2 composite, and the B_4C and TiB_2 phases in the B_4C-TiB_2 composite are shown in Fig. 17. The microhardness of the B_4C and TiB_2 phases in the composite were obtained by indenting only B_4C and TiB_2 phase, respectively. The microhardness of the B_4C-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_4C-TiB_2 composite was independent of the growth rate. The difference of the microhardness





Fig. 17 Relationship between Vickers microhardness (*Hv*) and indenter load.

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 B₄C. 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.²⁾ The B₄C–TiB₂ composite was almost the hardest material particularly at high indenter load.



Fig. 18 Relationship between Vickers microhardness (Hv) and indenter load.



Fig. 19 A hole in B_4C -Ti B_2 eutectic composite made by electric discharge machining.

3.7 Electric discharge machinability

Figure 19 demonstrates the typical example after electric discharge machining for the B_4C –TiB₂ composite (growth rate: 5.6×10^{-5} ms⁻¹). The electric discharge machining was attained for the B_4C –TiB₂ composite.

The work material for the electric discharge machining should be electrically conductive. It is commonly said that the electrical conductivity of the work material should be more than $100 \,\mathrm{Sm^{-1}}^{.32}$ The electrical conductivity of the monolithic B₄C used in this study was about $500 \,\mathrm{Sm^{-1}}$ at room temperature. However, the electric discharge machining of the monolithic B₄C was not possible probably due to the non-conductive oxide layer formation on the B₄C surface. In contrast to the monolithic B₄C, stable electric discharge was observed during the machining of B₄C–TiB₂ composite.

4. Conclusion

Directionally solidified B_4C -Ti B_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_4C .

(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 TiB₂ and B₄C phases were perpendicular and tilted 22° to the growth direction, respectively. The (101) and (120) planes of the B₄C were in parallel to the (001) and (100) planes of the TiB₂, respectively.

(4) The anisotropy of electrical and thermal conductivity were basically explained by a mixing law using the values of B_4C and TiB_2 .

(5) The microhardness of the composite was almost the same as that of B_4C 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.

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