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

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Directionally solidified B₄C–SiC composites were prepared by a Floating Zone method. The lamellar texture was observed at 53 mol%SiC. The *c*-axis of B₄C phase was tilted 20° to the growth direction. The (102) plane and [1̄21] direction of the B₄C phase were parallel to the (311) plane and [121] direction of the SiC phase, respectively. The thermal conductivity of the composite parallel to the growth direction ($\kappa_{\parallel}$) was about twice as great as that of monolithic B₄C. The anisotropy of electrical conductivity and thermal conductivity were explained by a mixing law using the values of B₄C and SiC. The mass gain due to oxidation was about 1/3 to 1/5 less than that of monolithic B₄C at 1023 K. The surface perpendicular to the growth direction showed slightly better oxidation resistance than that parallel to the growth direction. The microhardness of the composite was almost the same as that of B₄C.

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1. Introduction

Boron carbide (B₄C) has many applications for abrasives and structural materials due to high hardness,^{1,2)} low density and high strength.^{1–3)} If the characteristics of B₄C such as oxidation resistance and thermal shock resistance are improved, B₄C would be applied more widely. Fabricating B₄C-based composites is one method of improving the performance of B₄C. Silicon carbide (SiC) could be a candidate to make composite with B₄C because of its high oxidation resistance,⁴⁾ excellent thermal shock resistance⁴⁾ and particularly good compatibility with B₄C.^{5–7)} Therefore, SiC must be suitable dispersoid to improve the characteristics of B₄C.

Since B₄C significantly accelerates the sintering of SiC, many papers reported on the SiC–B₄C system materials where the B₄C content was less than a few mol%. However, B₄C-based B₄C–SiC composites were not been studied well, because B₄C is hardly sintered even if a relatively large amount of SiC is added as a sintering aid. The melting and solidification process could be applicable for synthesizing fully dense composites. Although SiC does not melt (dissociate at 3100 K) and B₄C has too high melting point (2700 K), the mixture of B₄C and SiC melts congruently due to the eutectic nature between B₄C and SiC.

In the present work, directionally solidified B₄C–SiC eutectic composites were prepared by a floating zone (FZ) method, and the electrical conductivity, thermal conductivity, oxidation resistance and hardness of the composite were investigated.

2. Experimental Procedure

B₄C powder and SiC (β -type) powder were mixed in the composition range of 0 to 55 mol%SiC, 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.

Then the rods were melted and directionally solidified by a FZ method in Ar using a Xe lamp. The solidification rate was controlled at 2.8×10^{-6} , 1.4×10^{-5} and 5.6×10^{-5} ms⁻¹. For comparison, high purity SiC (CVD-SiC, β -type, ADMAP) and single crystalline B₄C prepared by FZ were used.

The lattice parameters and phases were determined by X-ray powder diffraction (XRD). The growth direction and crystal orientation were investigated by pole figure X-ray diffraction and transmission electron microscopy (TEM). The microstructure was observed by scanning electron microscopy (SEM). The electrical conductivity (σ) was measured by a dc four-probe method, and the thermal conductivity (κ) by a laser flash method. The measurements were conducted for specimens parallel and perpendicular to the growth direction in the temperature range between room temperature and 1023 K. The oxidation resistance was evaluated by thermogravimetry at 1023 K in O₂ for 86.4 ks. The Vickers microhardness was measured under the indenter load from 0.245 to 1.96 N.

3. Results and Discussion

3.1 The study of the eutectic structure

Figure 1 shows X-ray powder diffraction pattern of the B₄C–SiC composites (55 mol%SiC in the starting powder) prepared at the growth rate of 1.4×10^{-5} ms⁻¹. The composites consisted of two phases, B₄C and SiC (β -type). It is known that boron carbide has a wide non-stoichiometric range (9–20 at% C),⁸⁾ and the lattice parameters depend on the composition.^{9,10)} The lattice parameters of boron carbide in the B₄C–SiC composites were in agreement with those of stoichiometric B₄C (*i.e.*, $a = 0.561$ nm and $c = 1.209$ nm in hexagonal expression).⁹⁾ The lattice parameter of SiC in the composites was 0.436 nm. This value was also in agreement with literature values of SiC (0.436 nm).¹¹⁾ Therefore, there may be no solid solution between B₄C and SiC in the composites.

The lamellar texture was observed at the composition of

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Fig. 1 X-ray powder diffraction pattern of B_4C -55 mol%SiC composite at the growth rate of $1.4 \times 10^{-5} \text{ ms}^{-1}$.

Fig. 2 B_4C -SiC pseudo-binary phase diagram.^{5-7,9)}

B_4C -55 mol%SiC in the starting powder. The eutectic composition calculated from volume ratio of these two phases was B_4C -53 mol%SiC. This value was almost in agreement with the starting composition. The eutectic composition obtained in the present work was compared with reported values^{5-7,9)} in Fig. 2. The composition in the present work was almost in agreement with that obtained from composites by arc melting,⁹⁾ but greater than those of Shaffer,⁵⁾ Secrist⁶⁾ and Kieffer *et al.*⁷⁾ They melted the specimens using carbon crucibles. This might have yielded the B_4C -SiC-C ternary system, whose eutectic composition may be different from that of the B_4C -SiC binary system.

The effect of growth rate on the textures of B_4C -SiC composites are summarized in Fig. 3. The typical lamellar texture was observed, where the white phase was SiC, and the black

Fig. 3 Effect of growth rate (V) on the microstructure of B_4C -SiC composites. (a1): $V = 2.8 \times 10^{-6} \text{ ms}^{-1}$ (Parallel to growth direction) (a2): $V = 2.8 \times 10^{-6} \text{ ms}^{-1}$ (Perpendicular to growth direction) (b1): $V = 1.4 \times 10^{-5} \text{ ms}^{-1}$ (Parallel to growth direction) (b2): $V = 1.4 \times 10^{-5} \text{ ms}^{-1}$ (Perpendicular to growth direction) (c1): $V = 5.6 \times 10^{-5} \text{ ms}^{-1}$ (Parallel to growth direction) (c2): $V = 5.6 \times 10^{-5} \text{ ms}^{-1}$ (Perpendicular to growth direction).

phase was B_4C . It is known that the texture of eutectic composites changes mainly depending on the volume fractions of phases.^{12,13)} In case each phase is more than 30 vol%, the lamellar texture would appear. When one of the two phases is smaller than 30 vol%, one phase would grow in a rod shape.

Fig. 4 Relationship between lamellar spacing and growth rate.

This trend was in agreement with the present work, where the B₄C and SiC phases were 60 and 40 vol%, respectively. We have reported the rod-shape texture in the B₄C–TiB₂ eutectic composite, where the TiB₂ phase was 20 vol%.¹⁴⁾

The spacing between lamellae decreased with increasing the growth rate. 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 lamellae. The relationship between growth rate (V) and lamellar spacing (λ) in the eutectic composites may be given by eq. (1),^{12, 13, 15, 16)}

$$\lambda^2 V = K \quad (1)$$

where K is a constant.

Figure 4 shows the relationship between average λ and $V^{-1/2}$ for the B₄C–SiC composites. The K value in the present study was $4.7 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$, which was almost the same magnitude as those reported for Sn–Se ($1.4 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$),¹⁵⁾ Ni–Ni₃Si ($1.0 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$)¹³⁾ and Mn–MnBi eutectic composites ($1.3 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$).¹⁶⁾

3.2 Crystal orientation

Figure 5(a) shows an X-ray pole figure of the B₄C–SiC composite ($V = 5.6 \times 10^{-5} \text{ ms}^{-1}$) for the cross section perpendicular to the growth direction. One diffraction was observed from (003) plane in hexagonal expression of B₄C. The angle between the (003) diffraction and the center of the pole figure was about 20°, indicating that the c -axis of the B₄C phase tilted 20° from the growth direction. Two (111) diffractions and one (220) diffraction from the SiC phase were measured. The angles between two (111) diffractions and between (220) and (111) diffractions were about 40° and 35°, respectively. β -SiC has often twin boundaries in (111) planes as shown in Fig. 5(b). The angle between two (111) planes of the twin boundary is 39° as shown in Fig. 5(b). Therefore, the SiC phase in the B₄C–SiC composite has twin boundaries in the (111) plane which are almost parallel to the growth direction.

Figure 6 shows electron diffraction patterns of the B₄C–SiC composite shown in Fig. 5. Figures 6(a), (b) and (c) are the electron diffraction patterns for the regions of B₄C,

SiC and B₄C/SiC interface, respectively. The (012) plane of B₄C phase was parallel to the ($3\bar{1}1$) plane of SiC phase. The schematics of the crystal orientation for B₄C and SiC in the B₄C–SiC composite are shown in Fig. 7. The $[\bar{1}21]$ direction of B₄C is parallel to the $[12\bar{1}]$ direction of SiC, and the twin boundary of SiC is parallel to the growth direction.

3.3 Electrical conductivity

Figure 8 shows the temperature dependence of electrical conductivity for the monolithic B₄C and SiC, and the B₄C–SiC composite ($V = 1.4 \times 10^{-5} \text{ ms}^{-1}$). The electrical conductivities of all specimens increased with increasing temperature. The electrical conductivity of the B₄C–SiC composite parallel to the growth direction ($\sigma_{\parallel}$) was greater than that perpendicular to the growth direction ($\sigma_{\perp}$), and had almost similar temperature dependence of the monolithic B₄C. The anisotropy of electrical conductivity between $\sigma_{\parallel}$ and $\sigma_{\perp}$ should be caused by the texture, *i.e.*, the arrangement of B₄C and SiC phases. The electrical conductivity of the composite may be calculated from a mixing law. The calculated electrical conductivity (σ_{Cal}) by parallel, series and particle dispersion models may be expressed as eqs. (2) to (4).¹⁷⁾

Parallel model:

$$\sigma_{\text{Cal}}(\text{parallel}) = V_A \sigma_A + V_B \sigma_B \quad (2)$$

Series model:

$$\sigma_{\text{Cal}}(\text{series})^{-1} = V_A \sigma_A^{-1} + V_B \sigma_B^{-1} \quad (3)$$

Particle dispersion model:

$$\sigma_{\text{Cal}}(\text{particle}) = \sigma_A + 3(\sigma_B - \sigma_A) \sigma_A V_B / (2\sigma_A + \sigma_B) \quad (4)$$

where V is volume fraction, and subscribes (A and B) indicate the component of the composite. Calculated results from eqs. (2) to (4) are demonstrated in Fig. 8, where the conductivities of the monolithic B₄C and SiC were used. The experimental $\sigma_{\parallel}$ was in agreement with the $\sigma_{\text{Cal}}(\text{parallel})$. This means that the more conducting phase (B₄C) is continuously connected to the growth direction, which is consistent with the texture observation as shown in Fig. 3(b1). The $\sigma_{\perp}$ was close to $\sigma_{\text{Cal}}(\text{particle})$, but was far different from $\sigma_{\text{Cal}}(\text{series})$. As shown in Fig. 3(b2), the more conducting phase (B₄C) is not completely separated by the less conducting phase (SiC). The texture seems to be analogue to particle dispersion, where SiC phases disperse in B₄C matrix. The $\sigma_{\perp}$ was slightly smaller than $\sigma_{\text{Cal}}(\text{particle})$ in this study. If the shape of particles is assumed to be a long and flat plate, the calculated values, $\sigma_{\text{Cal}}(\text{particle})$, would have been closer to the experimental $\sigma_{\perp}$.

The relationships between electrical conductivity and growth rate are shown in Fig. 9. Both $\sigma_{\parallel}$ and $\sigma_{\perp}$ values at $1.4 \times 10^{-5} \text{ ms}^{-1}$ were greater than those other growth rates. The connectivity of the B₄C phase at this condition may be better than that at other conditions.

3.4 Thermal conductivity

The temperature dependence of thermal conductivity for monolithic B₄C and SiC, and the B₄C–SiC composites are demonstrated in Fig. 10 with reported values.^{18–22)} The thermal conductivity of the B₄C–SiC composites were greater than that of monolithic B₄C, and that parallel to the growth

Fig. 5 Pole figure of the B₄C-SiC composite ($V = 5.6 \times 10^{-5} \text{ ms}^{-1}$) for the cross section perpendicular to growth direction (a), and the schematic of SiC twin boundary (b).

direction ($\kappa_{\parallel}$) was much greater than that perpendicular to the growth direction ($\kappa_{\perp}$).

The thermal conductivity of composites may be also explained from the mixing law. The parallel, series and particle dispersion models for composites may be given by eqs. (5) to (7).¹⁷⁾

Parallel model:

$$\kappa_{\text{Cal}}(\text{parallel}) = V_A \kappa_A + V_B \kappa_B \quad (5)$$

Series model:

$$\kappa_{\text{Cal}}(\text{series})^{-1} = V_A \kappa_A^{-1} + V_B \kappa_B^{-1} \quad (6)$$

Particle dispersion model:

$$\kappa_{\text{Cal}}(\text{particle}) = \kappa_A + 3(\kappa_B - \kappa_A) \kappa_A V_B / (2\kappa_A + \kappa_B) \quad (7)$$

The thermal conductivity of SiC changes significantly by the fabrication method probably due to impurity concentration and microstructure as shown in Fig. 10.^{21,22)} Since the $\sigma_{\parallel}$ was in agreement with $\sigma_{\text{Cal}}(\text{parallel})$, $\kappa_{\parallel}$ can be also explained by the parallel model. Therefore, the thermal conductivity of the SiC phase in the B₄C-SiC composites may be estimated from eq. (5), where the experimental $\kappa_{\parallel}$ should be in agreement with the $\kappa_{\text{Cal}}(\text{parallel})$. The κ_{SiC} in Fig. 10 is the calculated value for the SiC phase in the B₄C-SiC composite. The experimental $\kappa_{\perp}$ was almost in agreement with the $\kappa_{\text{Cal}}(\text{series})$ and $\kappa_{\text{Cal}}(\text{particle})$. Since the experimental $\sigma_{\perp}$ was almost in agreement with the $\sigma_{\text{Cal}}(\text{particle})$, the experimental $\kappa_{\perp}$ could be also explained from the $\kappa_{\text{Cal}}(\text{particle})$.

The relationships between thermal conductivity and growth rate are depicted in Fig. 11. Both $\kappa_{\parallel}$ and $\kappa_{\perp}$ showed the maxima at $1.4 \times 10^{-5} \text{ ms}^{-1}$. At this growth rate, the B₄C and SiC phases may connect more continuously than those at other growth rates.

3.5 Oxidation resistance

Figure 12 shows the oxidation mass gain of the monolithic B₄C and SiC, and the B₄C-SiC composite ($V = 1.4 \times 10^{-5} \text{ ms}^{-1}$) at 1023 K in O₂. The mass gain of the B₄C was much higher than that of SiC. This agreed with the general trend reported in many papers. The mass gain of the B₄C-SiC

composites was about 1/3 to 1/5 less than that of monolithic B₄C. We have confirmed that the mass loss due to evaporation of B₂O₃ was less than 5% by comparing the mass change with the actual amount of oxide after oxidation experiments.

The oxidation of B₄C-SiC composites prepared by arc-melting was investigated by Narushima *et al.* using raman spectroscopy.²³⁾ They explained that oxide layer consisted of mainly borosilicate glass, and the higher the SiO₂ content in borosilicate, the lower the diffusivity of oxygen in the borosilicate. This caused greater oxidation resistance of the B₄C-SiC composite than monolithic B₄C.

The oxidation resistance of the surface parallel to the growth direction was greater than that perpendicular the growth direction. Since the B₄C phase is easily oxidized, the SiC phase may remain in borosilicate layers during the oxidation as shown in Fig. 13. Since the SiC phases are not continuously connected perpendicularly to the growth direction, the SiC plates may be removed from the composite surface and dispersed in the borosilicate layer. In case the oxidation proceeds along the growth direction as shown in Fig. 13(b), the SiC plates may remain connecting from the composite. These SiC plates remaining on the composite surface might have effectively improved the oxidation resistance of the B₄C-SiC composites.

3.6 Hardness

The indenter load dependence of Vickers microhardness of the monolithic B₄C and SiC, and the B₄C-SiC composite, and the B₄C and SiC phases in the B₄C-SiC composite are shown in Fig. 14. The microhardness of the B₄C and SiC phases in the composite were obtained by indenting relatively large B₄C and SiC phase, respectively. The microhardness of the B₄C-SiC composite means the average value of 30 points in the composite indented at random on B₄C phase, SiC phase and phase boundary. Cracks from the indentation were not observed at this load range. The microhardness value increased with decreasing the indenter load. This trend can be generally observed in the measurement for hard materials.²⁴⁾ The clear growth rate dependence was not observed for the microhardness of B₄C-SiC composite. No difference of the mi-

Fig. 6 TEM diffraction patterns for B₄C phase (a), SiC phase (b) and B₄C/SiC phase boundary (c).

crohardness between parallel and perpendicular to the growth direction was observed. With decreasing the indenter load, the size of indentation became smaller nearly the 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 the monolithic B₄C.

4. Conclusion

Directionally solidified B₄C–SiC eutectic composites were prepared by an FZ method, and following results were obtained.

Fig. 7 Schematics of the crystal orientation for B₄C and SiC in the B₄C–SiC composite.

Fig. 8 Temperature dependence of electrical conductivity.

Fig. 9 Relationship between electrical conductivity and growth rate at 1023 K.

Fig. 10 Temperature dependence of thermal conductivity.

Fig. 11 Relationship between thermal conductivity and growth rate.

Fig. 12 Relationship between mass gain and time.

Fig. 13 Oxidation models for perpendicular to growth direction (a) and parallel to growth direction (b).

Fig. 14 Relationship between Vickers microhardness and load.

(1) The composition of the boron carbide in the composite was stoichiometric B_4C .

(2) The lamellar texture was observed at 53 mol%SiC. The lamellar spacing decreased with increasing the growth rate.

(3) The c-axis of B_4C phase was tilted 20° to the growth direction. The (102) plane and $[\bar{1}21]$ direction of the B_4C phase were parallel to the (311) plane and $[12\bar{1}]$ direction of the SiC phase, respectively.

(4) The anisotropy of electrical conductivity ($\sigma_{||}$ and $\sigma_{\perp}$)

and thermal conductivity ($\kappa_{\parallel}$ and $\kappa_{\perp}$) were explained by a mixing law.

(5) The mass gain due to oxidation was about 1/3 to 1/5 less than that of monolithic B₄C at 1023 K. The B₄C–SiC composite surface perpendicular to the growth direction showed slightly better oxidation resistance than that parallel to the growth direction.

(6) The microhardness of the B₄C–SiC composites was almost the same as that of B₄C in the indenter load region larger than 1 N.

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