Preparation of TiC-TiB₂-SiC Ternary Eutectic Composites by Arc-Melting and Their Characterizations

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TiC-TiB₂-SiC composites were synthesized by arc-melting using TiC, TiB₂ and SiC powders as starting materials in Ar atmosphere. TiC-TiB₂-SiC system was a ternary eutectic, whose eutectic composition was 34TiC-22TiB₂-44SiC (mol%). The TiC-TiB₂-SiC eutectic composite showed a lamellar texture, where lamellar SiC grains paralleled to lamellar TiC grains. TiB₂ grains had an angle of about 30 to 60° with lamellar SiC and TiC grains. The hardness of TiC-TiB₂-SiC eutectic composite was 25.5 GPa at the load of 1.96 N and increased with increasing TiC content. The electrical conductivity of the eutectic composite was $2.81 \times 10^3 \text{ Sm}^{-1}$ at the room temperature and decreased with increasing temperature. The thermal conductivity of the eutectic composite was 25 to 60 WK⁻¹ m⁻¹ at the room temperature and decreased with increasing temperature. The electrical conductivity of TiC-TiB₂-SiC ternary composites decreased with increasing SiC content, and the thermal conductivity decreased with increasing TiC content.

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1. Introduction

Silicon carbide shows high hardness, excellent oxidation resistance, good thermal shock resistance and high-temperature strength.¹⁻³⁾ Titanium boride (TiB₂) has high hardness, high wear resistance, high thermal conductivity and high electrical conductivity.⁴⁻⁷⁾ Titanium carbide is an engineering material with five independent slip systems allowing the material to be ductile above 1000 K. That is also an useful characteristic as an additive material to improve the performance of SiC and/or TiB₂-based composites.⁸⁻¹⁵⁾ Therefore, TiC-TiB₂-SiC system composites could be an excellent material due to several combined properties of SiC, TiC and TiB₂ such as high hardness and high thermal conductivity.

TiC-TiB₂-SiC composites has been synthesized by hot-pressing and reactive hot-pressing. Mestral *et al.*¹⁶⁾ reported the preparation of TiC-TiB₂-SiC composites with the relative density of 99.8% by hot-pressing at 2473 K. The fracture strength of the TiC-TiB₂-SiC composites obtained was 1070 MPa, and the fracture toughness was 6.7 MPa m^{1/2}. Zhang *et al.*¹⁷⁾ prepared TiC-TiB₂-SiC composites with the relative density of 99.8% by reactive hot-pressing using TiH₂, Si and B₄C as starting materials at 2273 K. The fracture strength of the TiC-TiB₂-SiC composites was 680 MPa, and the fracture toughness was 6.9 MPa m^{1/2}.

On the other hand, the self-assembly of microstructure during the solidification of melted ceramic materials can be a useful technique to develop high-performance composite material. Particularly, an eutectic texture may improve the properties of ceramic composites. Some promising results have been reported for the B₄C-SiC, B₄C-TiB₂ and B₄C-TiB₂-SiC eutectic composites.¹⁸⁻²⁰⁾ However, the study on the TiC-TiB₂-SiC eutectic composite has not been reported. In this study, the TiC-TiB₂-SiC ternary composites were prepared by arc-melting, and the microstructure, hardness, thermal conductivity and electrical conductivity were investigated.

2. Experimental Procedure

TiC, TiB₂ and SiC powders were used as starting materials. The powders were weighed and mixed in an agate mortar by adding a small amount of ethanol. The content of TiC and TiB₂ was changed from 0 to 80 mol% and that of SiC was changed from 0 to 70 mol%. The mixtures of powders were then pressed into disks with 10 mm in diameter and 5 mm in thickness at 30 MPa. The specimens were melted and solidified on water-cooled copper holder for two times by arc-melting in Ar atmosphere of about 60 kPa. Each melting time was fixed at 30 s.

The crystal phase of composites was investigated by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM). The hardness was measured by a hardness tester (MVK-E) and calculated from the average value of 30 points indented at random. The fracture toughness was calculated from eq. (1):²¹⁾

$$K_{Ic} = 0.0719(P/C^{3/2}) \quad (1)$$

where P is the indentation load (N) and C the half of average cracks length (m). The electrical conductivity was measured by a DC four-probed method for rectangular specimens. The thermal conductivity was measured by a laser flash method using disk specimens in the temperature range between the room temperature and 1023 K.

3. Results and Discussion

3.1 Microstructure of TiC-TiB₂-SiC composites

Figure 1 shows the XRD pattern of composites prepared at the composition of (a) 34TiC-22TiB₂-44SiC, (b) 10TiC-30TiB₂-60SiC, (c) 70TiC-10TiB₂-20SiC and (d) 30TiC-40TiB₂-30SiC (mol%). The phases of the composites were TiC, TiB₂ and SiC, and no other phase appeared. The relative XRD intensities of TiC, TiB₂ and SiC peaks depended on the content of TiC, TiB₂ and SiC in the composites. Figure 2 shows several typical microstructures of TiC-TiB₂-SiC composites for the cross-section perpendicular to the growth

Fig. 1 XRD pattern of composites with the composition of (a) 34TiC-22TiB₂-44SiC, (b) 10TiC-30TiB₂-60SiC, (c) 70TiC-10TiB₂-20SiC and (d) 30TiC-40TiB₂-30SiC (mol%).

Fig. 2 SEM photograph of composites with composition of (a) 9TiC-26TiB₂-65SiC, (b) 10TiC-30TiB₂-60SiC (mol%), (c) 70TiC-10TiB₂-20SiC, (d) 30TiC-40TiB₂-30SiC.

direction, where the white phase is TiC, the gray phase is TiB₂ and the black phase is SiC. The microstructure of 9TiC-26TiB₂-65SiC (mol%) composite was the rod SiC grains co-existing with binary and ternary eutectic textures as shown in Fig. 2(a). TiB₂-SiC binary eutectic and TiC-TiB₂-SiC ternary eutectic textures were observed at the composition of 10TiC-30TiB₂-60SiC (mol%) as shown in Fig. 2(b). The TiB₂-SiC binary eutectic texture (BE1) was surrounded by the TiC-TiB₂-SiC ternary eutectic texture (TE), suggesting that the TiB₂-SiC binary eutectic phase first precipitated and then TiC-TiB₂-SiC ternary eutectic solidified corresponding to the ternary eutectic phase diagram. Figure 3 demonstrates the TiC-TiB₂-SiC ternary phase diagram. The composition of 10TiC-30TiB₂-60SiC (mol%) was on the binary eutectic curve line, as indicated by a dash line in Fig. 3. The ternary

Fig. 3 phase diagram of TiC-TiB₂-SiC composites.

eutectic point can be assumed from the microstructure observation. However, the ternary eutectic point could be indistinguishable due to the similar binary and ternary eutectic textures. We have reported that the ternary eutectic point of B₄C-TiB₂-SiC system can be determined from the microstructures observation for the compositions between ternary eutectic texture and the each end component as marked by dotted lines in Fig. 3. The microstructure at the composition of 70TiC-10TiB₂-20SiC and 30TiC-40TiB₂-30SiC (mol%) were spherical TiC grains and elongated rod TiB₂ grains co-existing with the eutectic texture, respectively, as shown in Figs. 2(c) and 2(d). These composition points were on the lines between the ternary eutectic point and TiB₂ or TiC, respectively. The TiC-TiB₂-SiC ternary eutectic composition was determined as 34TiC-22TiB₂-44SiC (mol%), where no primary phases were observed. A few researchers reported the solid state sintering of the TiC-TiB₂-SiC composites by hot-pressing and measured their mechanical properties.^{16,17} However, no study on the ternary eutectic composite by melt-solidification was reported. The ternary eutectic point was abbreviated as TE, and the binary eutectic points were abbreviated as BE1 for 40TiB₂-60SiC (mol%)²² and BE2 for 28TiB₂-72TiC (mol%).²³ In the TiB₂ primary phase area, the microstructure can be mainly categorized into TiB₂+TE+BE1, TiB₂+TE and TiB₂+TE+TiC. Although TiB₂, BE2 and TE might have been expected near the composition of BE2, no BE2 was identified. However, in our experiments on the TiC-TiB₂ binary system, the typical lamellar texture of TiC-TiB₂ eutectic was observed.²³ The compositions of high content SiC were easily evaporated due to decomposition of SiC. The TiC-SiC binary system might be also an eutectic system and the details will be reported elsewhere. Figure 4 shows that the SEM photographs of the TiC-TiB₂-SiC eutectic composite for the cross-section perpendicular (a) and parallel (b) to the growth direction. The white, gray and black phases were TiC, TiB₂, and SiC grains, respectively. TiC, SiC and TiB₂ grains showed lamellar texture of 3, 3 and 2 μm in thickness, respectively.

Fig. 4 SEM photograph of TiC-TiB₂-SiC eutectic composites for cross-section perpendicular (a) and parallel (b) to the growth direction.

Fig. 5 XRD pattern of TiC-TiB₂-SiC eutectic composite for (a) cross-section perpendicular to the growth direction comparing with (b) its powder XRD pattern.

Lamellar SiC grains paralleled to lamellar TiC grains. TiB₂ layers had an angle of about 30 or 60° with lamellar SiC and TiC grains, which tilted the angle of 5 to 10° to the growth direction (Fig. 4(b)). Figure 5 shows XRD patterns of the TiC-TiB₂-SiC eutectic composite for the cross-section perpendicular to the growth direction compared with the powder XRD pattern. The intensities of TiC(111), TiB₂(100), and SiC(111) peaks in the ternary eutectic composite were strongest (Fig. 5(a)), whereas the strongest peaks of powder samples were TiC(200), TiB₂(101) and SiC(200) as shown in Fig. 5(b), respectively. Therefore, the growth direction of the ternary eutectic composite was almost perpendicular to TiC(111), TiB₂(100), and SiC(111).

3.2 Characterization of TiC-TiB₂-SiC composites

Figure 6 shows the indenter load dependence of Vickers micro hardness of the TiC-TiB₂-SiC composites at the composition of 10TiC-30TiB₂-60SiC, 34TiC-22TiB₂-44SiC, 30TiC-40TiB₂-30SiC and 70TiC-10TiB₂-20SiC (mol%), respectively. The hardness of TiC-TiB₂-SiC composite increased with decreasing indenter load. The hardness of the TiC-TiB₂-SiC eutectic composite was about 25 GPa at the load of 1.96 N, which was close to that of composites sintered by hot-pressing at 2373 K.³⁾ Figure 7 shows the indentation of the TiC-TiB₂-SiC composites at the load of 4.9 N at the

Fig. 6 Indenter load dependence of Vickers micro hardness of TiC-TiB₂-SiC composites.

composition of (a) 10TiC-30TiB₂-60SiC, (b) 34TiC-22TiB₂-44SiC, and (c) 30TiC-40TiB₂-30SiC (mol%). The fracture toughness was calculated as 3, 5 and 4 MPa m^{1/2} at the composition of 10TiC-30TiB₂-60SiC, 34TiC-22TiB₂-44SiC, and 30TiC-40TiB₂-30SiC (mol%), respectively. This result indicates that the eutectic composite has a higher fracture strength. Zhang *et al.* and Mestral *et al.* reported that the fracture toughness of TiC-TiB₂-SiC composites was 4 to 7 depending on the composition, and plotted calculated iso-fracture toughness curves in the ternary system using a second order polynomial model.^{16,17)} From the contour curve, the fracture toughness of 10TiC-30TiB₂-60SiC, 34TiC-22TiB₂-44SiC (TE), and 30TiC-40TiB₂-30SiC (mol%) could be estimated as 5.5, 6.4 and 6.1, respectively. Although our experimental values were slightly lower than the calculated values, the trend was in agreement to the calculation.

Figure 8 shows the temperature dependence of electrical conductivity of the TiC-TiB₂-SiC composites at the composition of 70TiC-10TiB₂-20SiC, 30TiC-40TiB₂-30SiC, 34TiC-22TiB₂-44SiC and 10TiC-30TiB₂-60SiC (mol%), respectively. The electrical conductivity of TiC-TiB₂-SiC composites decreased with increasing temperature and SiC content. The electrical conductivity of the TiC-TiB₂-SiC eutectic composite was $2.81 \times 10^3 \text{ Sm}^{-1}$ at the room temperature. The electrical conductivity of the TiC-TiB₂-SiC eutectic composite was compared with those simulated by

Fig. 7 Indentation of Vickers micro hardness of the TiC-TiB₂-SiC composites in 4.9 N loading at the composition of (a) 10TiC-30TiB₂-60SiC, (b) 34TiC-22TiB₂-44SiC, (c) 30TiC-40TiB₂-30SiC (mol%).

Fig. 8 Temperature dependence of electrical conductivity of TiC-TiB₂-SiC composites.

parallel, series and effective medium approximation models (EMA) expressed as eqs. (2), (3) and (4), respectively.²⁴⁾

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

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

$$\begin{aligned} \frac{\sigma_{\text{cal(EMA)}} - \sigma_A}{2\sigma_{\text{cal(EMA)}} + \sigma_A} V_A + \frac{\sigma_{\text{cal(EMA)}} - \sigma_B}{2\sigma_{\text{cal(EMA)}} + \sigma_B} V_B \\ + \frac{\sigma_{\text{cal(EMA)}} - \sigma_C}{2\sigma_{\text{cal(EMA)}} + \sigma_C} V_C = 0 \end{aligned} \quad (4)$$

where σ is the electrical conductivity, V is a volume fraction, and subscripts (A, B and C) indicate the component of the composite. The experimental values for eutectic composite (closed square) were inbetween $\sigma_{\text{cal (parallel)}}$ and $\sigma_{\text{cal (series)}}$. This result is consistent with the eutectic microstructure observation by SEM. Figure 9 shows the temperature dependence of thermal conductivity of TiC-TiB₂-SiC composites at the composition of 70TiC-10TiB₂-20SiC, 10TiC-30TiB₂-60SiC, 34TiC-22TiB₂-44SiC and 30TiC-40TiB₂-30SiC (mol%).

Fig. 9 Temperature dependence of thermal conductivity of TiC-TiB₂-SiC composites.

The thermal conductivity of TiC-TiB₂-SiC composite decreased with increasing temperature, and decreased with increasing TiC content. The thermal conductivity of the eutectic composite was about 56 WK⁻¹ m⁻¹ at the room temperature. The thermal conductivity was also compared with those simulated by the parallel, series and EMA models as expressed in eqs. (2) to (4),²⁴⁾ where σ should be substituted by thermal conductivity (κ). The experimental values were closer to the $\kappa_{\text{cal (EMA)}}$ than $\kappa_{\text{cal (series)}}$ and $\kappa_{\text{cal (parallel)}}$. The phonon scattering at the phase boundaries might affect the decrease of κ values. The impurity in the SiC phase such as Ti and B could also reduce the κ value of the eutectic composite. The reference κ value of SiC might be also slightly too large for the calculation of κ values. Under these consideration, both experimental σ and κ values were well explained by the same model.

4. Conclusions

TiC-TiB₂-SiC was a ternary eutectic system. The eutectic composition was 34TiC-22TiB₂-44SiC (mol%), and had a typical lamellar texture. TiC (111), SiC (111) and TiB₂ (100)

of the eutectic composite were perpendicular to the growth direction. The hardness of TiC-TiB₂-SiC composites increased with increasing TiC content. The hardness of the eutectic composite was 25.5 GPa. The electrical conductivity decreased with increasing SiC content. The electrical conductivity of the eutectic composite was $2.81 \times 10^3 \text{ Sm}^{-1}$ at the room temperature. The thermal conductivity decreased with increasing TiC content. The thermal conductivity of the eutectic composite was about 25 to 60 WK⁻¹ m⁻¹.

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