Effect of composition and joining parameters on microstructure and mechanical properties of silicon carbide joints

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Powder- and tape-like joining materials composed of SiC with Al–B–C (ABC) or Al–B<sub>4</sub>C–C (ABCC) sintering additives were used for the joining of SiC. The effect of interlayer composition, joining temperature and particle size of SiC on the microstructure and mechanical properties of SiC joints was studied. The results indicated that the tape-like adhesive introduces denser microstructure of interlayer relative to the powder-like one under the same conditions. It was demonstrated that using fine starting SiC powder instead of coarse one enhances the densification process of SiC joints. As joined at 1650°C, the microstructure of interlayer is improved gradually with the increasing Al content from 1 to 6 wt % in composition while slightly affected by the forms of additives, i.e. ABCC additive having the equal action to ABC one on the densification of joints. At higher joining temperature of 1750°C, the microstructure of interlayer containing 3 wt % Al almost does not change while that containing 6 wt % degrades. SiC joints with strength higher than 344 MPa have been produced by using optimized joining variables, where the fracture of bonded SiC generally occurs within the SiC substrate.

Key-words : Silicon carbide, Joints/joining, Microscopy, Mechanical properties

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1. Introduction

Silicon carbide (SiC) is one of the most extensively studied and widely used compounds because of its combination of exceptional properties, such as good mechanical properties (high hardness, strength and elastic modulus), low thermal expansion coupled with high thermal conductivity, superior chemical inertness and so on. Due to the low self-diffusion coefficient and high energy of grain boundaries, however, the densification of SiC is difficult to accomplish if without sintering additives or high external pressure. Many investigations have been done to find appropriate additives for SiC sintering. In the mid-1970’s, Prochazka et al. firstly introduced pressureless solid-state sintering of SiC with boron and carbon sintering-aids. This solid-state sintering process, however, usually results in materials with low fracture toughness and requires high processing temperature (>2100°C) that easily leads to exaggerated grain growth. Instead, a liquid-phase sintering process was developed by adding aluminum to B–C additions to lower densification temperature. It was demonstrated that SiC ceramics can be densified at temperatures lower than 1900°C with Al–B–C additives. The sintered SiC shows improved ambient-temperature fracture toughness and strength, and stable high-temperature toughness/creep behavior at temperatures up to 1300°C. Effect of the forms of sintering additives in Al–B–C system, e.g. AlB<sub>2</sub>–C, Al<sub>4</sub>B<sub>2</sub>C<sub>5</sub> and Al<sub>6</sub>B<sub>4</sub>C, on the microstructure, densification and mechanical properties of sintered SiC were also studied.

Nowadays, SiC parts with small size and simple shape are commercially available. While specific desire for large-sized and complex-shaped SiC components increases with the development of advanced industry. Joining of SiC parts is one of the promising and effective approaches to produce SiC components. For instance, SiC substrates sintered with B–C additions were diffusion bonded at 1950°C with 14 MPa and the bending strength of joints reaches 300 MPa. Other attempts contain the joining of SiC in the green state followed by sintering with or without pressure and prepared SiC joints show strengths up to 323 MPa. Furthermore, it is well known that the mechanical strength of joint depends on the weakest part, mostly the interface between interlayer and substrate. If one wants to produce high strength SiC joints, therefore, the joining interlayer should possess high strength and the thermal mismatch at interface should be minimized. SiC powder mixed with Al–B–C additions is definitely a good choice for the joining of SiC bodies based on abovementioned literatures. In fact, this system has been used for the joining of two dense SiC sintered bodies and bonding strength up to 530 MPa was achieved at hot-processing at a temperature as low as 1650°C for 30 min under 50 MPa pressure. The effect of the composition of additive and the impurities in SiC sintered body on the microstructure and mechanical properties of SiC joints were investigated. These results point to a fact that the powder mixture of SiC with Al–B–C additives is suitable for the joining of SiC-based ceramics.

However, the influences of starting SiC powders, the forms of sintering additives (Al–B–C or Al–B<sub>4</sub>C–C) and the preparation method of joining materials (powder mixtures or tapes) as well as the joining process on the microstructure and properties of bonded SiC are not elaborated in detail. In the present work, therefore, we focus on the relationship between interlayer microstructure and abovementioned influencing factors by conducting SiC joining tests in the temperature range of 1650–1850°C for 30–60 min under mechanical pressure of 12.5–50 MPa, with the objective of producing high-strength SiC joints.

2. Experimental procedure

2.1 Joining materials preparation

The characteristics of used powders, including silicon carbide, aluminum, boron, boron carbide and carbon, were listed in...
Table 1. Characteristics of starting powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Purity (%)</th>
<th>D50 (µm)</th>
<th>S.S.A (m²/g)</th>
<th>Major impurities (elements/ wt %)</th>
<th>Maker</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2 (α-SiC)</td>
<td>98</td>
<td>0.60</td>
<td>12</td>
<td>C/1.0, SiO₂/0.6</td>
<td>Showa Denko, Tokyo, Japan</td>
</tr>
<tr>
<td>A-1 (α-SiC)</td>
<td>97</td>
<td>0.48</td>
<td>17</td>
<td>C/1.4, SiO₂/0.7</td>
<td>Showa Denko, Tokyo, Japan</td>
</tr>
<tr>
<td>β-SiC</td>
<td>99</td>
<td>&lt;ultrfine</td>
<td>—</td>
<td>Si/0.03, Fe₂O₃/0.06</td>
<td>Kojundo Chemical Lab., Japan</td>
</tr>
<tr>
<td>Al</td>
<td>99</td>
<td>20</td>
<td>—</td>
<td>Si/0.1, Fe/0.07</td>
<td>Kojundo Chemical Lab., Japan</td>
</tr>
<tr>
<td>B</td>
<td>99</td>
<td>&lt;45</td>
<td>—</td>
<td>Si/0.1, Fe/0.01</td>
<td>H. C. STARCK, Germany</td>
</tr>
<tr>
<td>B₄C</td>
<td>99.7</td>
<td>0.63</td>
<td>20</td>
<td>Fe/0.1, Ca/0.03</td>
<td>Kojundo Chemical Lab., Japan</td>
</tr>
<tr>
<td>C</td>
<td>99.7</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>— data unknown</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Sample label, composition of sintering additive and joining process of bonded SiC ceramics

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Starting SiC</th>
<th>Amount of additive (wt %)</th>
<th>Joining process (°C/MPa/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1BC65</td>
<td>A-2</td>
<td>1 1 0 1</td>
<td>1650/50/30</td>
</tr>
<tr>
<td>A3BC65</td>
<td>A-2</td>
<td>3 0 0 0</td>
<td>1650/50/30</td>
</tr>
<tr>
<td>A6BC65</td>
<td>A-2</td>
<td>6 1 0 1</td>
<td>1650/50/30</td>
</tr>
<tr>
<td>A3BC75</td>
<td>A-2</td>
<td>3 1 0 1</td>
<td>1750/12.5/30</td>
</tr>
<tr>
<td>A6BC75</td>
<td>A-2</td>
<td>6 1 0 1</td>
<td>1750/12.5/30</td>
</tr>
<tr>
<td>T-A6BC75*</td>
<td>A-2</td>
<td>6 1 0 1</td>
<td>1750/12.5/30</td>
</tr>
<tr>
<td>T-A6BC80*</td>
<td>A-2</td>
<td>6 1 0 1</td>
<td>1800/12.5/30</td>
</tr>
<tr>
<td>A6BC55</td>
<td>A-2</td>
<td>6 1 1.3 0.7</td>
<td>1650/50/30</td>
</tr>
<tr>
<td>α-A6BC55</td>
<td>A-1</td>
<td>6 0 1.3 0.7</td>
<td>1650/50/30</td>
</tr>
<tr>
<td>β-A6BC85</td>
<td>β-SiC</td>
<td>6 0 1.3 0.7</td>
<td>1650/50/30</td>
</tr>
</tbody>
</table>

*Joining materials were prepared using tape casting method.

2.3 Microstructure characterization

The joined SiC samples were sectioned perpendicular to the interlayer and polished to 0.5 µm diamond suspensions. Microstructure observations on the polished surfaces were conducted via SEM (JSM-5600, JEOL, Japan).

2.4 Mechanical properties measurements

Room temperature 4-point bending strength was measured on 4 × 3 × 40 mm beams with outer and inner span of 30 and 10 mm, respectively, at a crosshead speed of 0.5 mm/min. The tensile surface was polished down to 0.5 µm diamond suspension and the edges of tested specimens were beveled. At least five specimens were used for each strength determination.

3. Results and discussion

3.1 Al–B–C system

3.1.1 Effect of the composition of sintering additive on the microstructure of SiC interlayer

0.2 g powder mixtures of α-SiC (A-2) and Al–B–C additives with 1, 3 and 6 wt% Al (i.e. A1BC, A3BC and A6BC) were firstly used as joining materials. The joining process was conducted at 1650°C for 30 min under 50 MPa, referring to that used by Isekii et al. The SEM images of polished cross-sections of bonded SiC are presented in Fig. 1(a) through (c), from which it is clear that the microstructure of interlayer improves greatly from A1BC to A3BC and further increasing the Al content in sintering additives has slight influence on the microstructure of interlayer.

The formation of a second phase Al₃B₁₂C₁₇ is considered to be contributed to lower sintering temperature and a coexisted liquid phase with Al₃B₁₂C₁₇ enhances the densification of SiC. If assuming the formation of Al₃B₁₂C₁₇ in interlayer, Al₂C contains excess boron and carbon while A3BC and A6BC consist of excess aluminum and boron that form a liquid phase and accelerate the densification process.

3.1.2 Lowering the joining pressure by increasing joining temperatures

To decrease the joining pressure required for good joint microstructure, we adjust the joining temperature from 1650 to 1750°C and simultaneously lower the pressure to 12.5 MPa. The SEM micrographs of A3BC and A6BC cross-sections are shown in Fig. 2(a) and (b). It is found that the microstructure of interlayer in A3BC improves slightly with the joining temperature. In contrary, degraded microstructure of interlayer is observed in A6BC, in which the amount and the size of pores in interlayer increase significantly as joined at 1750°C.

Undoubtedly, the more the Al content and the more the quantity of liquid phase formed from excess aluminum and boron. When the amount of liquid phase is relatively low (A3BC), the interlayer would be further densified at higher...
joining temperature. When the liquid-phase content is too high (A6BC), however, the grain growth will compete with and prevail over the densification of SiC interlayer at higher temperature (1750°C), because the grains grow rapidly and form a rigid skeleton that retards further densification.11)

3.1.3 Comparison between powder- and tape-like A6BC joining materials for the joining of SiC

To compare with the powder-like A6BC and decrease the interlayer thickness, tape-like A6BC (T-A6BC) was applied as joining materials for the joining of SiC. At a joining temperature of 1750°C, a denser interlayer is obtained by using T-A6BC (Fig. 3(a)) if compared with that of powder-like A6BC (Fig. 2(b)). As the joining temperature increases to 1800°C, the interlayer density of SiC joint is improved significantly, as shown in Fig. 3(b), in which the pores inside interlayer are diminished greatly and some areas between interlayer and SiC substrate are bonded together.

For the joining of SiC, several kinds of interlayer materials prepared by using tape casting method have been described13-25) and uniform interlayer was obtained by optimizing the tape casting process and joining variables. In present study, the good joint microstructure is believed to be mainly attributed to the uniform and thin joining materials. Additionally, a small amount of residual carbon left after debinding process could also affect the composition of sintering additives and subsequently the joining process. Similar phenomenon was observed and elaborately investigated for the sintering of tape-cast AlN,26,27) in which the residual carbon from binder burnout shows correlation with the sintering behavior, the composition and distribution of secondary phases and grain-boundary composition of AlN samples.

3.2 Al–B$_4$C–C system

3.2.1 Using SiC powder mixture with Al–B$_4$C–C additives for the joining of SiC

Note that the particle size of boron in Al–B–C system is apparently coarser than that of aluminum and carbon. A new system of Al–B$_4$C–C using finer and cheaper B$_4$C instead of B was applied for the SiC joining. The selected composition of sintering additive is Al:B$_4$C:C = 6:1:3:0:7, i.e. sample A6BCC, which has the same composition to A6BC (Al:B:C = 6:1:1). The polished cross-section of sample A6BCC is displayed in Fig. 4, from which we can see that the interlayer of A6BCC shows similar microstructure to that of A6BC (Fig. 1(c)), suggesting

Fig. 1. SEM images of the polished cross-sections of SiC joints (a) A1BC65, (b) A3BC65 and (c) A6BC65. Joining materials: α-SiC (A-2) with Al–B–C additives; joining process: at 1650°C for 30 min under 50 MPa.

Fig. 2. SEM micrographs of the polished interlayer of SiC joints (a) A3BC75 and (b) A6BC75. Joining materials: α-SiC (A-2) with Al–B–C additives; joining process: at 1750°C for 30 min under 12.5 MPa.

Fig. 3. SEM micrographs of the polished interlayer of SiC joints (a) A3BC75 and (b) A6BC75. Joining materials: α-SiC (A-2) with Al–B–C additives; joining process: at 1750°C for 30 min under 12.5 MPa.
that $B_4C$ has equivalent effect to that of B and C on the densification of SiC joint.

Studies on the chemical reactions in Al–B$_4$C and Al–B–C systems at temperatures up to 1000°C demonstrate that the phase equilibrium changes with the forms of starting materials even containing same elements.29) In present study, the used sintering additives share the same composition but change the starting forms, which will affect the subsequent reaction dynamic and the intermediate products of grain-boundary phases during the joining process. However, the similar densification effect of A6BC and A6BCC for the joining of SiC suggests that the finally resulting phases of sintering additives play the same role.

3.2.2 Effect of starting SiC powder on the densification of SiC interlayer

To study the effect of starting SiC powder on the microstructure of interlayer, powder mixtures of submicron $\alpha$-SiC (A-1) or $\beta$-SiC with Al–B$_4$C–C additives were used for the joining of SiC (named as $\alpha$-A6BCC or $\beta$-A6BCC, respectively). The composition of sintering additive was maintained to be Al:B$_4$C:C = 6:1.3:0.7 and the joining tests were carried out at 1650°C for 30 min under 50 MPa. The SEM micrographs on polished cross-sections are shown in Fig. 5(a) and (b), from which it is clear that the densification of interlayer improves with decreasing particle size of starting SiC powder at this sintering temperature. This is easy to understand because the powder with finer particle size exhibits greater driving force of densification than the coarser one.29)

3.3 Mechanical properties of SiC joints

Present results suggest that the densification and microstructure of bonded SiC depend on not only the joining parameters (temperature and pressure), but also the composition (constituent of additive and starting SiC powder) and the preparation method of interlayer (power mixture or tapes). To sum up, i) more than 3 wt% Al in sintering additive is beneficial to the densification of interlayer at 1650°C while the interlayer density is degraded at 1750°C if Al content is too high (A6BC in Fig. 2(b)), ii) tape-like joining materials show positive effect on the microstructure of interlayer provided similar joining process, iii) $B_4C$ shows equivalent effect to B and C in sintering additive on the
The measured bending strengths of bonded SiC samples are also listed in Table 3. We find that comparably high strengths of bonded SiC are obtained in both β-5BCC (344 ± 25 MPa) and α-5BCC (364 ± 24 MPa) by the selected joining parameters. The fracture of bonded SiC generally occurs within the SiC substrates, suggesting that the strength of joint is higher than that of host SiC ceramics. Note that the strength of SiC substrate probably degrades after joining process due to the heat cycle at 1850°C and the accompanying grain growth. Iseki et al.[20,21] investigated the joining of two dense SiC sintered bodies with a mixture of β-SiC, Al and B powders by hot-pressing at 1650°C. It was found that the bending strength of bonded SiC at room temperature locates in the range from 200 to 530 MPa, varying with the additive composition. Present maximum joint strength is lower than 530 MPa because the bonding strength is also associated with the properties of SiC substrates. It is therefore reasonable to suppose that higher-strength SiC joint can be produced by using stronger SiC sintered bodies or decreasing joining temperatures. This assumption is solid if referring to the work conducted by Morozumi,[22] in which it was found that the sintering additives and the fabrication process of monolithic SiC used to be joined have important effect on the bonding strength.

Finally, it is worth to emphasize the most important aspects of present work as follows: firstly, a new sintering additive Al–B–C–C is found to be feasible for the joining of SiC and shows comparable effect with Al–B–C additive that has been widely used to assist the densification of bulk SiC[20,21,22] and its joining.[20,21] Secondly, the tape-like joining materials show some advantages, such as formation of thin and dense interlayer, for the joining of SiC as compared with the powder-like. Tailoring the mechanical properties of SiC joints can be reached by controlling the fabrication of tapes. Most important, high strength of bonded SiC (>344 MPa) is achieved on the basis of an optimized joining parameter, suggesting that present joining method gives a candidate for the production of engineering components and structures.

At this time, we have investigated the effect of several important factors on the microstructure and properties of SiC joints. However, the effect of polypeptide transformation at high temperatures as starting from β-SiC powders and detailed tape-casting process on the microstructure of interlayer and the mechanical properties of SiC joints are not clear yet. From the points of view of energy saving and practical applications, low pressure or even pressureless joining are promising directions for the joining of SiC. Accordingly, following work will focus on these issues.

### 4. Conclusion

Joining tests of commercially available SiC ceramics by using powder- and tape-like joining materials that consist of SiC powder and Al–B–C or Al–B–C–C sintering additives were conducted in the temperature range of 1650–1850°C for 30–60 min under a mechanical pressure of 12.5–50 MPa. SEM observations on the polished cross-sections of SiC joints

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**Table 3. Composition of joining materials and the mechanical properties of SiC joints using optimized joining parameters**

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Starting SiC</th>
<th>Composition of additive (wt %)</th>
<th>Joining parameters (°C/MPa/min)</th>
<th>Interlayer thickness (μm)</th>
<th>Bending strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-5BCC*</td>
<td>β-SiC</td>
<td>Al 5 0 12.8 C 1.72</td>
<td>1850/15/60</td>
<td>33</td>
<td>344 ± 25</td>
</tr>
<tr>
<td>α-5BCC*</td>
<td>A-1</td>
<td>Al 5 0 12.8 C 1.72</td>
<td>1850/15/60</td>
<td>29</td>
<td>364 ± 24</td>
</tr>
</tbody>
</table>

*Tape-like joining materials

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Fig. 6. Backscattered SEM images on the interlayer of (a) α-5BCC and (b) β-5BCC started from α-SiC (A-1) and β-SiC with Al–B–C–C additives (composition of Al:B:Si:C = 6:1.3:1.7) and joined at 1850°C for 60 min under 15 MPa.

densification of SiC interlayer and iv) fine starting SiC powder readily produces dense interlayer for the joining of SiC.

Based on these rules, we conducted a joining test at 1850°C that starts from tape-like joining material consisting of fine SiC (β-SiC) and Al–B–C–C additive (Table 3). The selected composition of Al:Si:B:C = 5:1.3:1.7, corresponding to that of Al:Si:B:C = 5:1.2, is based on above experiments and follows the chemical stoichiometry of AlB4C7 that is usually formed during the sintering of SiC[20,21,22] aiming to decrease the amount of residual liquid phase after joining. The joining temperature is chosen for the crystallizing of grain-boundary phase.[23] For comparison, another tape-like joining material starting from α-SiC powder was also used for the joining of SiC. As a result, we obtain nearly full dense SiC joints. The backscattered SEM images of the interlayer are shown in Fig. 6(a) and (b), where the gray SiC phase and the dark pores (indicated by dot white arrows) coexist with some dark gray phases (marked by solid white arrows) that distribute uniformly in the interlayer. The latter phase is most likely aluminum boron carbide in a formula of Al3B2C7.[21,22]

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demonstrate that i) the microstructure of interlayer is improved with the increasing Al content in ABC at 1650°C while degraded in sample A6BC at 1750°C, ii) tape-like joining materials is favorable for diminishing the pores inside interlayer, iii) sintering additive Al–B4C–C is found to be feasible for the joining of SiC and shows comparable effect with additive Al–B–C and iv) fine星空SiC powder readily results in dense interlayer for the joining of SiC. By using an optimized joining process, a nearly full dense SiC joints is obtained and high strength over 344 MPa is achieved.

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References