Low-temperature joining of boron carbide ceramics

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Low-temperature joining of boron carbide (B$_4$C) ceramics using an Al sheet was investigated in the temperature range of 600–1200°C for 2 h in vacuum (10$^{-2}$–10$^{-4}$ Pa). Successful joining and high bending strength close to that of the B$_4$C base were achieved in the samples joined at 700–1100°C. Different techniques including scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and transmission electron microscopy (TEM) were used to characterize the high-strength B$_4$C joints. SEM observations suggested the dense interlayer and the crack-free interface as well as the penetration of Al into the surface microcracks of B$_4$C base. Further TEM examinations revealed that B$_4$C and Al joined directly. EPMA analysis demonstrated the existence of several reaction products within interlayer, including AlB$_2$ and Al$_3$BC, which resulted in the development of high-strength composite interlayer.

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1. Introduction

Boron carbide (B$_4$C) ceramics are an important type of non-oxide ceramics that have high hardness, high elastic modulus, and low density. Therefore, B$_4$C ceramics have been worthy of remark as high performance structural materials. Nowadays, large-sized B$_4$C ceramics are required for stages and table of steppers, which are one of the semiconductor manufacturing equipments. Steppers are an essential part of the semiconductor manufacturing process, called photolithography, which creates millions of microscopic circuit elements on the surface of tiny chips of Si. The stepper operates at a very high speed. Stages and tables in steppers are used as a stand of Si wafer, and ceramics, such as Al$_2$O$_3$ or SiC, are used as the component material of a stage or table instead of metals because of their high elastic modulus and low weight. In the near future, higher elastic modulus, lower density and larger-sized ceramic materials for stages and tables are expected due to finer electronic circuit, higher throughput and larger size Si wafer. B$_4$C ceramics have higher elastic modulus and lower density than Al$_2$O$_3$ and SiC. Therefore, B$_4$C ceramics are the desirable materials for stages and tables in steppers, which are one of the semiconductor manufacturing processes.

In this study, we investigated the low-temperature joining of B$_4$C using Al sheet at 600–1200°C in vacuum on the basis of the theoretical density and a room-temperature bending strength of 240 ± 14 MPa. The B$_4$C plate (25 mm × 5 mm) was ground using #200 diamond wheel, and the average roughness, Ra, of the joining face was measured to be 0.2–0.4 μm. An Al sheet (thickness: 10 μm; purity: >99.0%; Nilaco, Tokyo, Japan) was sandwiched between the metal foils such as Ti and Mo foils for high-temperature applications. He tested the joining of B$_4$C at 1500°C for 10 h under a pressure of 18.6 MPa using various foils and their microstructural observations indicated that Al was the most suitable bonding material for B$_4$C joining. On the other hand, for low-temperature applications, such as the manufacture of Si wafers that is usually operated at room temperature, low-melting-point metal phase can instead be used to realize lower joining temperatures for saving the energy. However, rare studies have been done on the joining of B$_4$C at low temperatures. It is well known that Al has a low melting point of 660°C, and sintering of B$_4$C using Al additive was studied. Kuwashima et al. reported that B$_4$C compacts were pressureless sintered using Al gas and Si compound gas derived from SiC. Miyazaki et al. studied the microstructure of B$_4$C pressureless sintered in an Ar atmosphere containing gaseous. They concluded that Al is an effective sintering additive for the preparation of B$_4$C ceramics. Meanwhile, the wetting of B$_4$C substrate by liquid Al and the reactions between them have been studied extensively for their composite applications.

In this study, we investigated the low-temperature joining of B$_4$C using Al sheet at 600–1200°C in vacuum on the basis of phase analyses, microstructure examinations and mechanical strength measurements. The reasons responsible for the high joint strength were also discussed in details.

2. Experimental procedure

B$_4$C ceramic plates having a density of 2.40 g/cm$^3$ (95.2% of the theoretical density) and a room-temperature bending strength of 240 ± 14 MPa were purchased (Mino Ceramic, Nagoya, Japan) and used as base materials (dimensions: 20 mm × 25 mm × 5 mm) for the joining tests. The surface of the B$_4$C plate (25 mm × 5 mm) was ground using #200 diamond wheel, and the average roughness, Ra, of the joining face was measured to be 0.2–0.4 μm. An Al sheet (thickness: 10 μm; purity: >99.0%; Nilaco, Tokyo, Japan) was sandwiched between the
ground B₄C ceramic plates. The B₄C–Al–B₄C sandwich was stabilized using a jig made of carbon (ET-10; Ibiden, Gifu, Japan). Joining was conducted at 600–1200°C for a holding time of 2 h in vacuum (10⁻²–10⁻⁴Pa) in a furnace.

The joined samples were cut into pieces having dimensions of 3 mm × 4 mm × 40 mm, and they were ground using a #400 diamond wheel until the roughness Ra was less than 0.2μm. Their flexural strength was measured using a four-point bending test with an inner and outer span of 10 mm and 30 mm, respectively, at a displacement rate of 0.5 mm s⁻¹ on a universal testing machine (Sintech 10/GL; MTS Systems, USA). Three samples were used for each joining condition. Six samples were tested for the B₄C base material.

Phase identification of the B₄C joint was carried out using XRD with Cu-Kα radiation at 40 kV, 300 mA (RINT 2500HF; Rigaku, Tokyo, Japan). The joint surfaces were polished using a cross-section polisher (SM-09010; JEOL, Tokyo, Japan), and they were then observed by field-emission scanning electron microscopy (FE-SEM) at 7.5 kV (JSM-7000F; JEOL, Tokyo, Japan). The elemental compositions of the interlayers were analyzed using field-emission electron probe microanalysis (FE-EPMA) at 7–10 kV (JXA-8500F; JEOL, Tokyo, Japan). Thin joint specimens were prepared using an ion slicer (EM-09100IS; JEOL, Tokyo, Japan) and observed by transmission electron microscopy (TEM) at 200 kV (JEM-2100F; JEOL, Tokyo, Japan).

3. Results and discussion

3.1 Flexural strength of B₄C joints

Figure 1 shows the relationship between the joining temperature and four-point bending strength of B₄C joints. The strength of B₄C joints varied from 220 to 278 MPa as bonded in the temperature range 700–1000°C in vacuum, suggesting that the joined samples derived high strengths close to that of the base material. In addition, the B₄C joints generally fractured from interlayer on B₄C base material at 700°C and 1000°C, and that of B₄C surface contacted with Al at 1200°C. B₄C was identified at all samples, which originates from B₄C base material. In addition to B₄C phase, Al was present at the joining interlayer at 700°C and 1000°C. However, Al peaks were not observed but AlB₂, Al₃BC and Al₄C₃ were identified at the B₄C surface contacted with Al at 1200°C. XRD analysis on the fracture surface suggested the presence of AlB₂, Al₃BC and Al₄C₃ but the absence of Al, indicating the severe reaction between Al and B₄C, and the possible evaporation of Al at this temperature. This was primarily responsible for the poor joining at high temperature.

3.2 Microstructural observations and phase determination

In present study, the typical B₄C joints bonded with Al at 700°C (joint BCA7) and at 1000°C (joint BCA10) were selected for the following examinations to clarify the phase content and microstructure as well as their effect on the B₄C joint strength in this system.

Figures 3(a) and 3(c) show the interface microstructure of joint BCA7 and BCA10, respectively, in which the fully dense interlayers and the crack-free interfaces can be observed evidently. At higher magnification [Figs. 3(b) and 3(d)], we found that there existed some new phases within interlayer according to their color contrast. Additionally, the microcracks at B₄C surface was permeated and filled by Al phase. The thickness of the joining layer was about 2–5μm, which was thinner than that of the Al sheet (10μm) because of the partial leakage of Al during joining.

To identify the compositions of the new phases within interlayer, EPMA analysis was carried out on joint BCA10 and the corresponding results were listed in Table 1. For instance, the gray phase within interlayer [point 3 in Fig. 3(d)] primarily consisted of B and Al elements and the ratio of B/Al was close to 1.
to 2, which was consistent with the AlB$_2$ phase. Similarly, the existence of Al and Al$_3$BC in the joining layer can be known. It is worth to note that Al$_3$B$_4$C$_2$ ($\beta$-AlB$_{12}$) was occasionally observed in joint BCA10 but not in joint BCA7. Viala et al. investigated the reaction products in B$_4$C/Al system in the temperature range of 627–1000°C and reported that Al$_3$BC and AlB$_2$ were formed at temperatures lower than 868°C but the latter phase was replaced by Al$_3$B$_4$C$_2$ ($\beta$-AlB$_{12}$) at higher temperatures. Arslan et al. documented that AlB$_2$ and Al$_3$BC were present at 985–1370°C in B$_4$C/Al composites. The compounds identified in the present study were consistent with previous reports. The reactions occurred at the joining layer resulted in the formation of metal matrix composites like Al–Al$_3$BC–AlB$_2$. Pyzik et al. studied the mechanical properties of B$_4$C/Al composites including four-point bending strength. They reported that the average flexural strength of B$_4$C/Al composites was from 300 MPa to 550 MPa. It is thought that flexural strength of B$_4$C/Al composites tended to be higher than that of B$_4$C base material. In addition, these compounds should be avoided to grow up to large size because they usually lead to low strength for B$_4$C/Al family. Therefore, it is expected that flexural strength of joining interlayer is higher than that of B$_4$C base material. This is why the joined B$_4$C did not fracture from the joining interlayer.

The interface between B$_4$C and Al was important for the low-temperature joining of B$_4$C due to at least the following two facts: (1) the B$_4$C/Al interface was the dominant microstructure feature in the B$_4$C joints and (2) Al can penetrate into and simultaneously heal the surface cracks of B$_4$C substrate. Figures 4 show the representative TEM micrographs on the B$_4$C/Al interface of joint BCA10. From Fig. 4(a), the good bonding between two phases was evident and defects like microcracks and pores were not found around the interface. The high-resolution transmission electron microscope (HRTEM) image (Fig. 4(b)) revealed a high degree of bonding between B$_4$C and Al.

Fig. 3. SEM micrograph (back scattering electronic image) of the polished cross section of B$_4$C joined using Al (a), (b) at 700°C (BCA7) and (c), (d) at 1000°C (BCA10).

Fig. 4. TEM micrograph of B$_4$C/Al joining interface in BCA10 joint (a) low magnification and (b) HRTEM image.
electron microscopy (HRTEM) image in Fig. 4(b) suggested that B$_4$C and Al joined directly. Moreover, there existed some dislocations in Al side [Fig. 4(a)]. The presence of dislocations in Al was related to the relaxing of residual stress, which was due to the lattice mismatch between two phases and their difference in thermal expansion coefficients.

4. Conclusions

Low-temperature joining of B$_4$C ceramics with a 10μm-Al sheet was tested from 600 to 1200°C in vacuum (10$^{-2}–10^{-4}$ Pa). It was found that B$_4$C ceramics can be firmly joined in the temperature range from 700 to 1100°C. The four-point bending strength of B$_4$C joint was close to that of B$_4$C base and the samples usually fractured from B$_4$C substrate instead of the joined part. The fully dense interlayers and the crack-free interfaces were observed in these joints. The surface cracks of B$_4$C substrate were healed by Al penetration. EPMA analysis revealed the presence of reaction-formed compounds within interlayer, including AlB$_2$ and Al$_3$BC, which leaded to the formation of high-strength composite interlayer. TEM examination further confirmed the good bonding at B$_4$C/Al interface and the direct joining between them.

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