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High-resolution electron microscopy of a SiC/SiC joint brazed by a Ag–Cu–Ti alloy

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A high-resolution electron microscope observation (HREM) was performed on the joined portion of a brazed polycrystalline or single crystal SiC to itself with (Ag–28 wt% Cu) + 2 wt% Ti alloy foil. The brazing was done under vacuum at temperatures of 800° C to 950° C with a holding period of up to 30 min. Reaction products formed at the joined interface were found to be mainly TiC. In the specimen brazed at 800° C with the holding time of 0 min, reaction product TiC formed itself into small crystallites with a diameter of less than 20 nm, and an amorphous like layer was found between SiC and TiC. On the other hand, TiC was formed as a layer along the joined interface for the specimen brazed at 950° C for the holding time of 30 min. Lattice matching of SiC to TiC crystals appeared to be good so the high bonding strength of the joint was attributed to the formation of this epitaxial interface between SiC and TiC.

1. Introduction

Silicon carbide (SiC) has a lot of merits for use as a high temperature structural material, because of its high temperature strength and low oxidation property.

We have found previously that a high bonding strength brazing of SiC to itself or to a stainless steel with Ag–28 wt % Cu alloy was realized by adding 1.5–2 wt % of Ti to the braze metal [1–3]. However, the bonding mechanism has not yet become clear. There have been several recent reports with respect to the joining interface of ceramics by use of transmission electron microscope (TEM) [4–10]. The identification of reaction products formed between the ceramics and brazing metals seems to be an attractive method of understanding the bonding mechanism. In this respect, an inspection by high resolution electron microscope (HREM) could give us detailed knowledge of both the crystal orientation of products and the lattice matching between products and base materials.

In this paper, a possible mechanism is studied to explain the previously found high-bending strength of the SiC/Ag–Cu–Ti/SiC joint. An HREM observation was applied to the inspection of the joint of two polycrystalline SiC blocks with an intermediate (Ag–28 wt % Cu) + 2 wt % Ti alloy foil. In the same manner, a joint of two single-crystal SiC wafers was investigated, in order to check a simplified joining model. Finally, we studied how the bonding strength of the SiC joints was affected by the interfacial lattice matching.

2. Preparation of samples and HREM inspection

Pressureless sintered SiC (SC-201; 10 × 10 × 18 mm^3: Kyocera Corp., Kyoto Japan) was brazed to itself using Ag–28 wt % Cu alloy foil containing 2 wt % Ti (Tanaka Kikinzoku Kogyo Co. Ltd., Tokyo Japan). Simultaneously, single crystal SiC (Showa Denko Co. Ltd., Tokyo Japan: mainly 6 H polytype) was also joined to itself in the same way as polycrystalline SiC. In the latter case the (0 0 0 1) face of the specimen was placed parallel to the joining interface, as shown in Fig. 1. These joinings were performed in vacuum (3×10^{-3} Pa) at 950° C for 30 min or at 800° C for 0 min as detailed in reference [3].

In preparation for TEM observation, specimens were sliced with a diamond saw into 0.2 mm thickness perpendicular to the interface. In the case of single crystal SiC, the cutting cross section was perpendicular to [0 0 0 1]. Then they were polished with a diamond polishing wheel to 20 μm in thickness. Finally, they were thinned by an argon ion milling machine to the proper condition. TEM observation was performed with Hitachi H-1250S operated in the accelerating voltage of 1000 kV. The magnification of each micrograph was calibrated using the well known lattice spacing of a SiC crystal.

3. Observation results of joined interfaces

Fig. 2 shows an example of the low magnification electron micrograph of a polycrystalline SiC–braze metal interface. A reaction layer was observed between SiC and the braze metal which contrasted with the surroundings. Specimens were further milled by ion milling machine for HREM inspection as described above. The thinning rate of the reaction layer was slower than that of SiC or the braze metal, this fact showed that the composition of the reaction layer is somewhat different from the surroundings.

A typical example of a high magnification electron micrograph of the joining interface is shown in Fig. 3. In this picture the [0 0 0 1] direction of SiC on the

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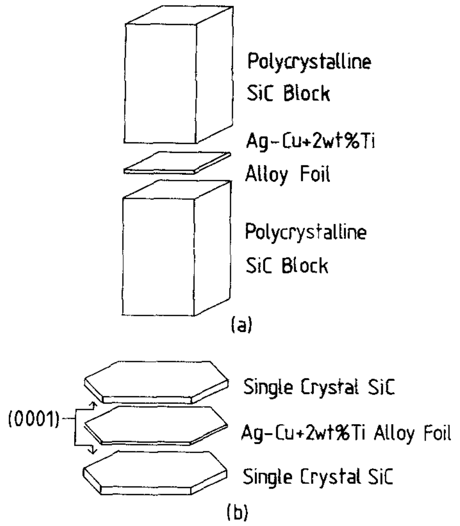

Figure 1 Assembly of the brazing couple (a) polycrystalline SiC, (b) single crystal SiC.

lower side was parallel to the surface of the photograph, thus the contrast of (0 0 0 6) planes of SiC could be seen clearly with a period of 0.252 nm as also indicated. The contrast of the (0 0 0 6) plane of SiC was emphasized in a period of six planes. From the kind of observation shown in Fig. 3, it could be seen that the SiC grain at this joined area had a 6 H polytype. This periodic contrast of every sixth plane gradually decreased at the central area of this figure and finally the 6 H contrast disappeared. From the existence of the macroscopic boundary as observed in Fig. 2, this decrease of 6 H contrast was thought to be caused by the influence of reaction products. In Fig. 3, interface joining SiC to the reaction products was not clear. These reaction products had two lattice planes with the same 0.25 nm spacing, and they intersected at an angle of 70° with each other. This corresponds to the $\{1\,1\,1\}$ planes of TiC (0.250 nm) where the angle of each $\{1\,1\,1\}$ plane of cubic crystal is 70.5°. From this observation, we concluded that this reaction layer should be TiC.

We also observed a specimen of a single crystal SiC joined to itself, because the crystal orientation to the joining interface could be given artificially. Fig. 4 shows a lattice image of the joining interface of single crystal SiC and the brazed metal. This specimen was brazed at 950° C with a holding period of 30 min. This figure reveals that the joining interface between SiC and the reaction products can be seen very clearly. The orientation of the single crystal SiC was selected so that its (0 0 0 1) plane was parallel to the joining interface (Fig. 1). Thus the direction of the incident electron beam in the HREM observation was parallel to $[\bar{1}\,2\,\bar{1}\,0]$ of SiC and also the joining interface. Most of the reaction products that existed near the joining interface were TiC. Although there were some dislocations and distorted regions in TiC, the lattice of SiC and TiC very nearly matched.

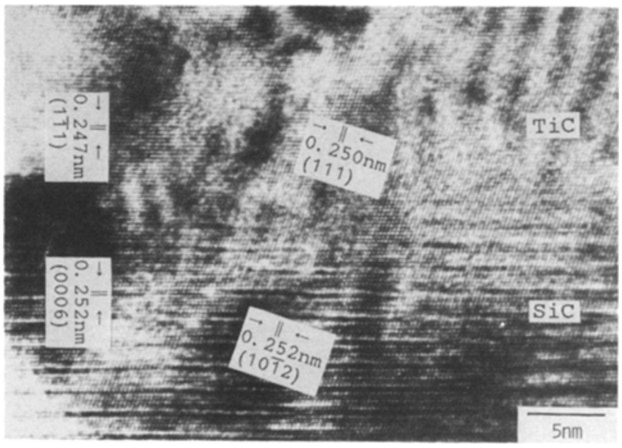

Figure 3 Transmission electron micrograph of joined polycrystalline SiC/braze metal at a high magnification. The brazing condition was the same as that of Fig. 2.

There were a few reaction products with 0.23 nm d-spacing other than TiC, which have not yet been identified. Ti_5Si_3 was not observed at or near the interface, even if it could be seen at an area a little apart from the joining interface (Fig. 5).

The configuration of reaction products for the specimen joined at 800° C should differ from that of the higher temperature joining specimen. Fig. 6 shows a micrograph of the joining interface of a single crystal SiC to braze metal joined at 800° C for 0 min holding. It reveals that there were TiC lattices similar to those of the specimen brazed at 950° C for 30 min, and silver and copper lattices could be also seen near the TiC particles. These reaction products formed themselves

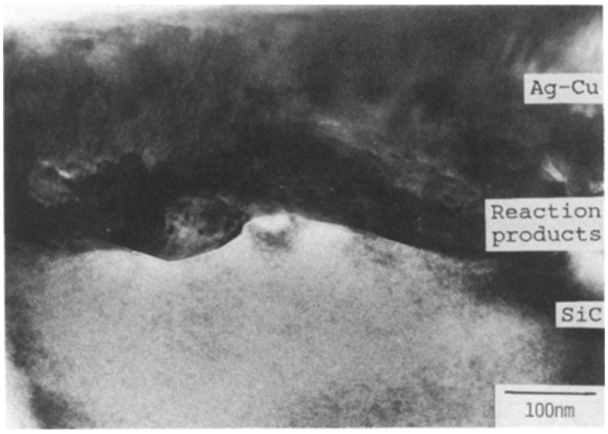

Figure 2 Transmission electron micrograph of joined polycrystalline SiC/braze metal at a low magnification. It was brazed at 950° C for 30 min holding.

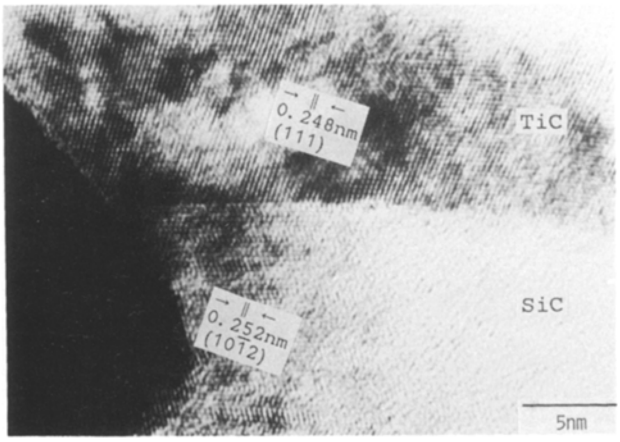

Figure 4 Transmission electron micrograph of joined single crystal SiC/braze metal. The brazing condition was as in Fig. 2.

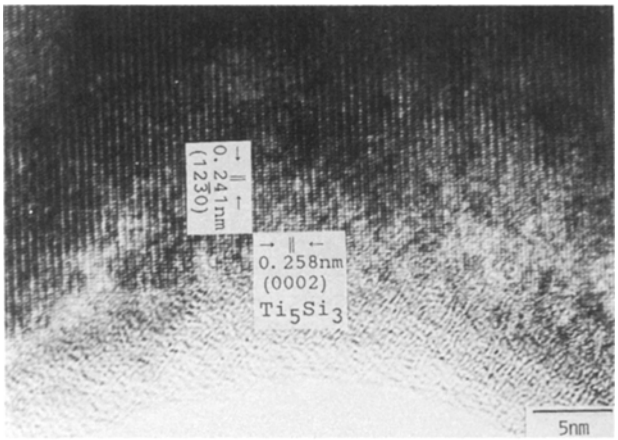

Figure 5 Transmission electron micrograph of Ti_5Si_3 in a reaction products layer. This micrograph was taken of the same specimen as that of Fig. 4, apart from the joining interface.

into crystallites of less than 20 nm in size, which contrasted with the case of layer formation of TiC in the specimen brazed at 950° C for 30 min holding (Fig. 4). Furthermore, there was an amorphous like phase between the reaction products and SiC.

4. Discussion of the tight joining condition

Energy dispersive X-ray analysis (EDX) and X-ray diffraction of reaction products have already been examined in a SiC joint brazed with a Ag–Cu–Ti alloy [3]. Where a 1 μm thick titanium-rich layer was observed on the SiC–braze interface, therefore addition of titanium in a Ag–Cu alloy could be effective for tight joining of SiC. Fig. 7 shows the four-point bending strength of joined SiC plotted against the joining temperature and holding time at that temperature. The bonding strength of the joint is, in general, affected by the following two factors. The residual stress induced by the difference in the thermal expansion coefficients between materials in bonding, and the adhesive contact strength of the interface. Since the braze metal used in this study was a thin foil of thickness less than 70 μm, it appears that the residual stress in the ceramic would be negligible. Therefore, the temperature and holding period dependence of fracture strength should be predominantly influenced by the adhesive contact strength of the interface and what the reaction products were.

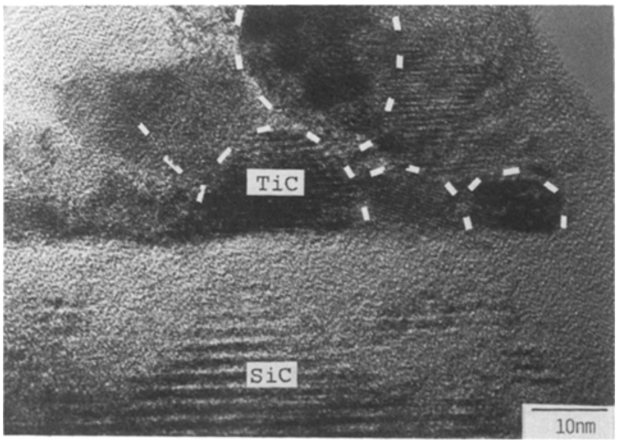

Figure 6 Transmission electron micrograph of joined single crystal SiC/braze metal, brazed at 800° C for 0 min holding.

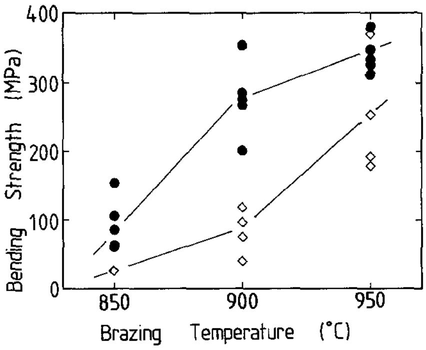

Figure 7 Four-point bending strength of joined polycrystalline SiC using Ag–Cu–Ti braze plotted against brazing temperature and holding period. Note that the highest strength of the joints was obtained for that brazed at 950° C for 30 min holding [3]. (● 30 min, ◇ 5 min).

There were some specimens fractured on the joined interface in bending strength tests. When X-ray diffraction analysis was performed on the fracture surface in such specimens, TiC and SiC were only detected on the surface of the SiC side, while both TiC and Ti_5Si_3 were found, and also silver and copper, on the braze metal side. In this TEM observation, most of the reaction products at the joining interface were TiC, and Ti_5Si_3 was formed apart from the joining interface. Although the field of the TEM image was very restricted in the high magnification observation, the above mentioned results were confirmed by the X-ray diffraction analysis. Therefore, it can be said that the fracture strength of joined SiC depends strongly on the adhesive contact strength between SiC and TiC, and may not be affected much by the existence of Ti_5Si_3 crystals.

The interplanar spacing of (1 1 1) in the TiC crystal differs slightly from part to part. The dispersion of d-spacing in TiC should be caused by change in composition. TiC is capable of having a non-stoichiometric composition and represents TiC_x where the value of x can be taken from 0.5 to 1.0. This change in composition alters the lattice parameter as much as 1% [11]. As the reaction between SiC and Ti seemed not to completely reach the stationary condition, TiC would not be stoichiometric in the reaction layer.

The structure images of Figs 3 and 4 reveal that another plane of TiC could be seen apart from (1 1 1). This plane was (2 0 0) and had 0.208 nm spacing, however (2 0 0) of TiC is known to be 0.216 nm in general. We observed synthesized TiC and found that the d-spacing of (2 0 0) was 0.209 nm and (1 1 1) was 0.246 nm. These d-spacings were similar to those of the TiC found in joined specimens. Although the cause of the difference between observed and calculated d-spacing is not clear, it seems to be affected by the above mentioned dispersion from stoichiometric TiC composition. In this observation, the existence of TiC in the reaction layer was verified.

Figs 3 and 4 reveal that the lattices of SiC and TiC are joined together well. If the lattice matching of different crystals is good, in general, the continuity of atomic

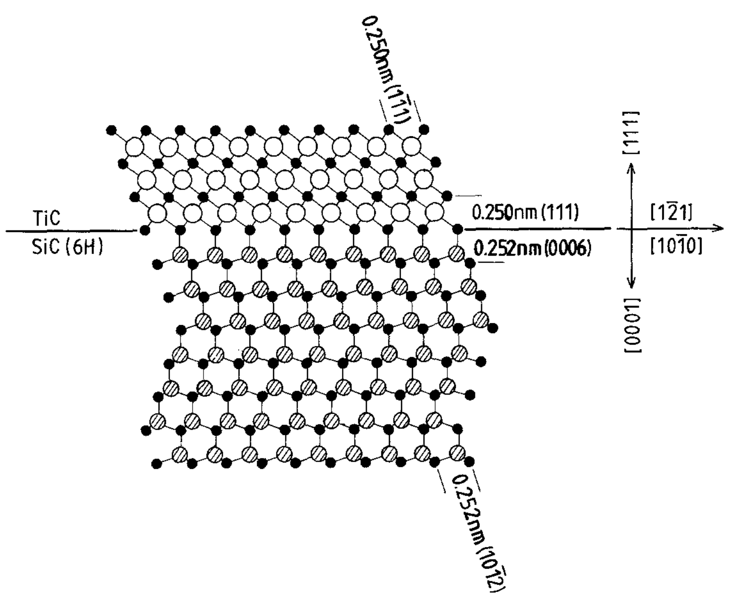

Figure 8 Schematic of the lattice on the SiC–TiC joined interface. (● C, ▨ Si, ○ Ti).

arrangement should be reserved and high interfacial bonding strength could be expected. In this study, SiC and TiC were joined in the following relation

$$SiC_{(0006)} = 0.252\,\mathrm{nm} \,//\, TiC_{(111)} = 0.244\text{–}0.250\,\mathrm{nm}$$

$$SiC_{[10\bar{1}0]} \,//\, TiC_{[1\bar{2}1]}$$

The corresponding d-spacings of SiC and TiC differed by not more than 3%, hence a significant misfit dislocation network which was often observed on the mismatching joining interface, was not seen in the specimen joined at 950° C. Therefore, it is concluded that SiC and TiC crystals have good lattice matching. Fig. 8 shows a schematic view of the lattice on the interface. This figure indicates that carbon atoms retain almost the same sites after the reaction to produce TiC, and TiC would not tend to be distorted in this reaction.

Morozumi *et al.* have reported on the TEM study done for joined SiC using titanium [6]. They joined SiC to itself using titanium foil by hotpressing at 1400° C, and the reaction products were mainly Ti_3SiC_2. They concluded that the lattice matching between Ti_3SiC_2 and SiC was good enough to join them. In our observation, no Ti_3SiC_2 phases were seen. This would be caused by the difference in joining temperatures, while we joined SiC at 800–950° C due to the low melting point of the braze metal (= 780° C).

The joined interface of the specimen brazed at 800° C for 0 min holding is shown in Fig. 6. It reveals that the reaction products formed small crystallites with a diameter less than 20 nm, and the crystal orientations were different from each other. Although TiC existed near the joining interface, the lattices of SiC and TiC do not come directly into contact and an amorphous-like layer seems to form between SiC and TiC crystals. In the EDX analysis, there were still a lot of titanium particles in the braze metal, and titanium had not sufficiently diffused to the joined interface due to the low temperature and short holding time.

Finally we discuss the brazing mechanism of the SiC and Ag–Cu–Ti alloy. At first, when the specimen is heated to the joining temperature, the titanium would diffuse to the SiC surface, and gradually react with the SiC to form TiC. An interface in this step appears to be like that of Fig. 6. While the specimen is held at such a joining temperature, the TiC layer could be formed epitaxially on the interface as shown in Figs 3 and 4. The formation of an epitaxially grown TiC lattice on that of SiC, as shown in Fig. 8, is considered to be attributed to the higher bonding strength of the specimen. Then the highest bonding strength was obtained for the specimen joined at a temperature of 950° C for 30 min holding as shown in Fig. 7. Thus, the main reason for the observed strength variation is concluded to be due to the lattice matching of the joining interface.

5. Conclusion

The mechanism of the previously observed high strength of the SiC/Ag–Cu–Ti/SiC joint was investigated by HREM and it is concluded that the main reason for the obtained strength is the excellent lattice matching at the joining interface. Reaction products which existed near the joining interface of the joint were identified to be mainly TiC. Ti_5Si_3 was also found a little away from the joined interface, and it did not seem to be the main reaction product for the joined interface. Interplanar spacings of SiC and TiC at the joined interface were observed to be very close to each other, and lattice matching was found to be good. As the joining temperature and holding time progressed, the TiC layer is formed to create the desired high joint strength, where a fine joined interface is formed between SiC and TiC.

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References

1. T. ISEKI, H. MATSUZAKI and J. K. BOADI, *Amer. Ceram. Soc. Bull.* **64** (1985) 322.
2. T. YANO, N. TAKADA and T. ISEKI, *J. Ceram. Soc. Jpn* **95** (1987) 357.

3. J. K. BOADI, T. YANO and T. ISEKI, *J. Mater. Sci.* **22** (1987) 2431.
4. T. ISEKI, T. KAMEDA and T. MARUYAMA, *ibid.* **19** (1984) 1692.
5. S. MOROZUMI, M. KIKUCHI and T. NISHINO *ibid.* **16** (1981) 2137.
6. S. MOROZUMI, M. ENDO, M. KIKUCHI and K. HAMAJIMA, *ibid.* **20** (1985) 3976.
7. M. FLORJANCIC, W. MADER, M. RÜHLE and M. TURWITT, *J. Physique* **46–C4** (1985) C4–129.
8. Y. ISHIDA, *J. Adhesion Soc. Jpn* **12** (1986) 127.
9. Y. ISHIDA, in Proceedings of the 6th Conference on High-Temperature Materials, Shizuoka, October 1986 (Ceramic Society of Japan, Tokyo 1986) p. 1.
10. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI, *ibid.* (1986) p. 37.
11. E. K. STORMS, "The Refractory Carbides" (Academic Press, New York, 1967) p. 10.

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