Brazing of pressureless-sintered SiC using Ag–Cu–Ti alloy

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A pressureless-sintered SiC was brazed to itself using Ag–Cu alloy foil to which titanium had been added. The results obtained revealed the following. (i) Increasing the titanium addition to the base metal from 2 to 8 wt% improved the wettability greatly, but the bonding generally became weaker. (ii) With 2 wt% Ti addition, a reaction layer about 1 μm thick was formed, regardless of which brazing temperature was used, while bond strength reached was over linearly with temperature. The maximum room-temperature bend strength reached was over 350 MPa. (iii) In the case of the alloy with only 2 wt% Ti additive, bonding was greatly influenced not only by improvement of the wettability at high temperatures and longer holding times, but also the composition and thickness of the resultant reaction layer.

1. Introduction

Of late some progress has been made in finding ways to join ceramics, especially oxide ceramics to ceramics, or to metals. But work on the joining of non-oxide ceramics like SiC is limited [1–7]. Unlike oxide ceramics, the brazing of non-oxide ceramics to get a good bond is complicated due to the inertness of the surfaces to be bonded. To produce a very strong bond therefore requires careful surface treatment and the use of an active metal incorporated into the alloy. However, over-alloying of the base metal with active metal, or a progressive increase in temperature and contact time, while aiding wetting, may finally cause weakening of the bond [8].

In this work, the effect on bonding of filler metals containing different weight percentages of titanium was investigated to select the best alloy for brazing. The effects of temperature and holding time on the shear and bend strengths of the brazed joints are discussed. The choice of brazing conditions and titanium additions to the alloy were based mainly on our previous work, where a powdered alloy of Ag–Cu/Ti was successfully used in brazing SiC and stainless steel [9], and partly on preliminary experiments. It was thought that instead of the powder form, the use of clad or alloy foils would be much simpler in so far as easy handling and control of interlayer thickness was concerned, and also to avoid contamination during titanium powder processing.

2. Experimental procedure

2.1. Materials

The pressureless-sintered SiC (PLS-SiC) used was manufactured by Kyocera, Kyoto, Japan, and contained 0.7 wt% B and 2.5 wt% free carbon [9]. The pieces to be joined were cut to the required sizes, and their surfaces ground with a 20 μm grit diamond wheel. Three metal alloys (manufactured by Tanaka Kikinzoku, Tokyo, Japan) based on 72 wt% Ag–

28 wt% Cu (eutectic composition) were used as 70 μm thick filler metal foils. The titanium concentrations in them were 2, 4.5 and 8 wt%. The two filler metals with 4.5 and 8 wt% Ti were in the form of sandwiches (Ag–Cu/Ti/Ag–Cu) which the titanium in the third was alloyed with the base metal.

Before the samples were bonded, the materials were cleaned by degreasing in acetone using ultrasonic vibration and dried by passing hot air over them. In the case of the filler metals, a second cleaning by dipping in a 6% H_2SO_4 at about 60 to 80°C for 30 to 60 sec was carried out. They were rinsed in warm distilled water and dried as already described. In all cases the samples thus prepared were used immediately after cleaning to minimize oxidation or contamination of their surfaces.

2.2. Brazing

2.2.1. Effect of titanium addition and brazing temperature

Brazing filler metal of Ag–Cu/Ti foil (6 mm diameter × 0.07 mm thickness) was inserted between the SiC couple to be brazed as shown in Fig. 1a. The top was cylindrical (6 mm diameter × 5 mm) and the bottom, rectangular (10 mm × 10 mm × 4.5 mm). The couple was placed in a graphite holder and the assembly heated in a vacuum using a high-frequency induction furnace.

To improve the brazing atmosphere, the heating chamber together with the empty holder was heated to about 200°C for about 30 min while evacuated and then cooled to about 60°C. It was then filled with argon and the samples quickly inserted. This process of cleaning was repeated each time the firing chamber and holder were found to have been exposed to air for quite a long time.

Brazing was done at three different temperatures, 850, 900 and 950°C. The holding time was 5 min and the vacuum reached was 3 × 10^{-3} Pa. The heating and
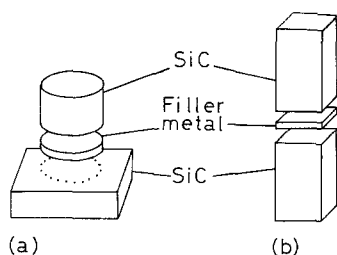
Figure 1 Assembly of brazing couple: (a) for shear test; (b) for bend test.

Figure 3 Effect of brazing temperature and holding time on room temperature shear strength (2 wt % Ti): (O) 900, (□) 850° C.

cooling rates were 40 and $10°\mathrm{C\,min}^{-1}$, respectively. Heating was automatically controlled by a thermocouple and the temperature measured with an optical pyrometer. The brazed samples were inspected for cracks using an optical microscope, and the shear strength tests performed at room temperature using an IS-10T testing machine (Shimadzu Seisakusho Ltd, Kyoto Japan).

Based on the results of the tests, the alloy containing 2 wt % Ti was selected and the following experiments performed.

2.2.2. Effect of brazing temperature and holding time

Brazing was carried out at 850 and 900° C under the same conditions as described earlier while the holding times were varied, i.e. 0, 5 and 30 min. "0 min" means that cooling was started immediately the desired temperature was reached. The brazed samples were visually inspected, and the shear strength determined.

For the bend strength tests, SiC blocks (10 mm × 10 mm × 18 mm) were brazed together with the filler metal sandwiched as shown in Fig. 1b. The brazing temperatures were 850, 900 and 950° C, and the holding times, 5 and 30 min. After brazing, test specimens (2 mm × 4 mm × 36 mm) were carefully cut from the block, perpendicular to the interface. The surfaces were ground using a diamond wheel having a grit size of 15 µm and then lapped with a 6 µm diamond paste. The room-temperature bond strength was determined by a four-point bend strength test at a cross-head speed of $0.5\,\mathrm{mm\,min}^{-1}$. The upper and lower spans were 10 and 30 mm, respectively. The brazed joints were analysed using an X-ray diffractometer (Rigaku Denki, Tokyo, Japan), an energy-dispersive X-ray
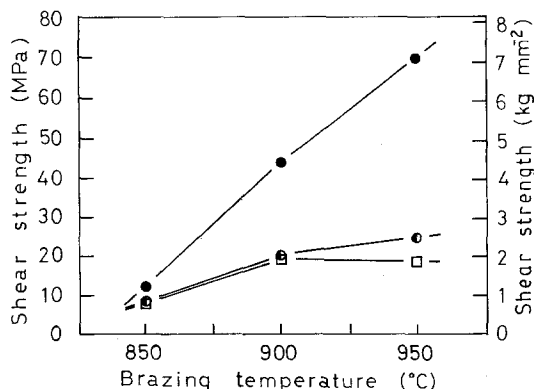
analyser (EDX) System 5000, EG & G Ortec, Oak Ridge USA) and a scanning electron microscope (SEM) (S-450, Hitachi, Japan).

3. Results and discussion
3.1. Effect of titanium addition and temperature

Fig. 2 shows the results of the shear strength tests of samples brazed with various amounts of titanium in the alloy. It can be seen that the lower the titanium concentration, the stronger the bond strength. As the temperature increased, the bond strength of specimens brazed with 2 wt % Ti alloy increased almost linearly, while that of specimens brazed with 4.5 and 8 wt % Ti alloys changed very little.

It was observed that with the higher amounts, 4.5 and 8 wt % Ti, the wettability improved considerably with increasing temperature, whereas with the lowest concentration (2 wt % Ti) the wettability was poorer.

3.2. Effect of temperature and holding time

Fig. 3 shows the results of shear strength tests for specimens brazed with the alloy containing only 2 wt % Ti. There was a marked increase in bond strength with increasing holding time at high temperatures. At 900° C, the strength increased more than three times from 0 to 30 min, while at 850° C the increase was not so significant.

The results of the bend strength tests for specimens brazed with 2 wt % Ti are plotted against brazing temperature and holding time in Fig. 4. Here also the

Figure 2 Effect of titanium addition and brazing temperature on room temperature shear strength (holding time 5 min): (●) 2, (◐) 4.5, (□) 8 wt % Ti.
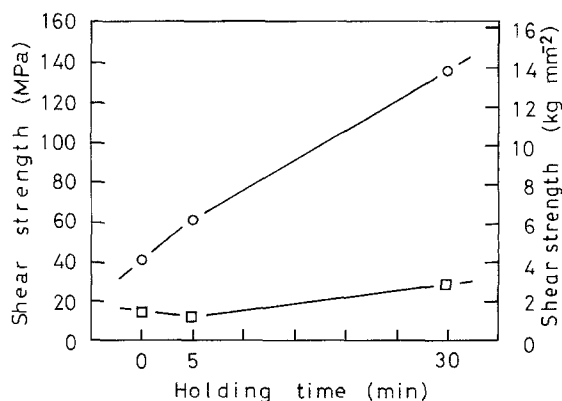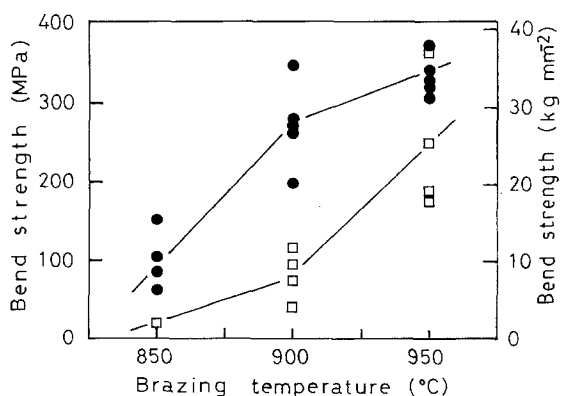

Figure 4 Effect of brazing temperature and holding time on the room temperature bend strength (2 wt % Ti): (●) 30 min, (□) 5 min.
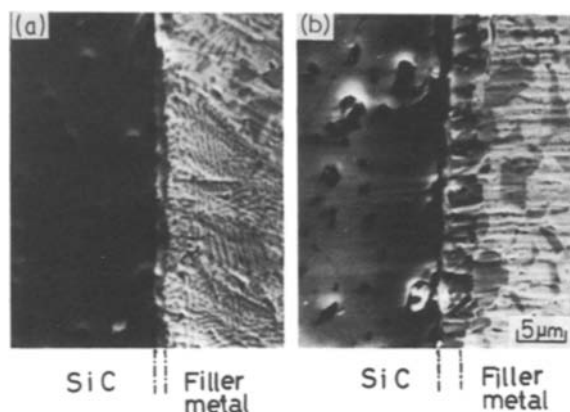
Figure 5 Cross-sectional SEM photographs of brazed joints comparing the reaction layer thicknesses: (a) of 2 wt % Ti alloy; (b) of 8 wt % Ti alloy, at 950° C and a holding time of 5 min.

Figure 6 (a, b) Cross-sectional SEM photographs and (c, d) EDX line scanning of brazed joint with 2 wt % Ti alloy: (a, c) at 850° C; (b, d) at 950° C. Holding time is 30 min in both cases.

results are in the same order as that of the shear strength tests, that is the bond strength increased with temperature and time.

During bend tests, most specimens which were brazed at lower temperatures and shorter holding times fractured at the SiC–metal interface. But as brazing time was prolonged for 30 min at 900° C, fracture occurred through the SiC very close to the interface or sometimes through the filler metal. Almost all the specimens brazed at 950° C fractured through the SiC body away from the interface; an indication of good bonding.

Fig. 5 shows cross-sectional SEM photographs of two specimens, brazed with different alloys at 950° C for 5 min. With 2 wt % Ti additive (Fig. 5a) a very thin reaction layer about 1 μm thick was formed at the interface. The small dark spots in the filler metal matrix were found to be copper-rich Ag–Cu alloy.

In contrast, the braze with a higher titanium content (Fig. 5b) had a thicker, greater than 3 μm reaction layer. This was partly composed of rectangular titanium-alloy crystals which had been precipitated from the solutions during cooling. The filler metal matrix was composed not only of copper-rich but of titanium-rich Ag–Cu–Ti alloy of different compositions. This had also segregated but rather in large pools. Like most of the specimens brazed with higher titanium concentration, the filler metal easily separated from the SiC as can be seen in Fig. 5b. This usually occurred during cutting and polishing of the specimens.

Fig. 6 shows SEM photographs and EDX line scans of the cross-section of the joints brazed with only 2 wt % Ti alloy, at 850° C (Fig. 6a) and 950° C (Fig. 6b). The holding time in both cases was 30 min. The sample brazed at higher temperature seemed to be completely bonded to the filler metal, while in the lower temperature sample some voids could be seen at the interface, probably due to poorer wettability. There were no cracks at any of the interfaces. In both cases the thicknesses of the reaction layers were about 1 μm. But whereas in Fig. 6a there was a single layer, the section in Fig. 6b had a double layer which coincides with the two titanium peaks in the line scan shown in Fig. 6d.

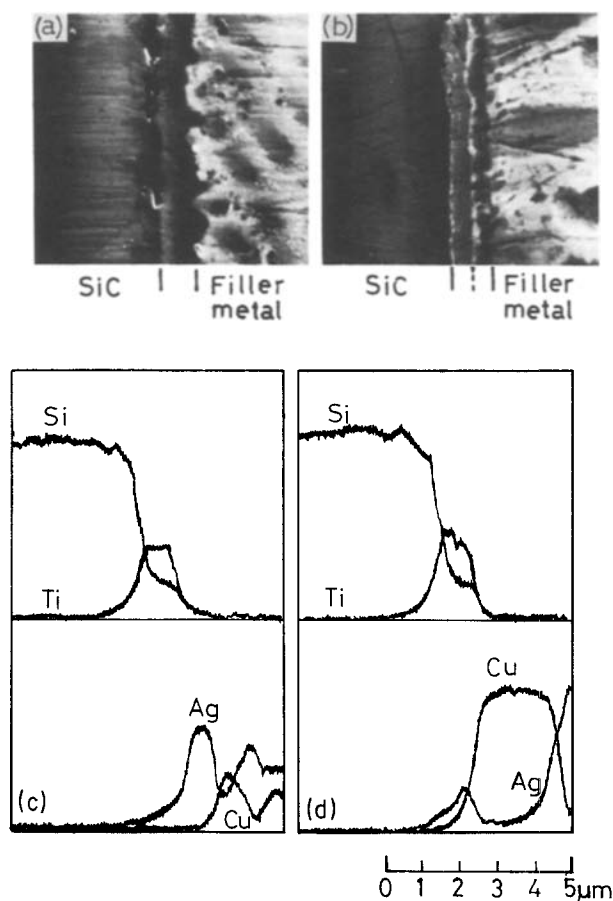X-ray diffraction patterns of the surfaces of the filler

metal showed that the reaction layers in both specimens were composed of compounds of Ti_5Si_3 and TiC. The appearance of Ti_5Si_3 and TiC reaction products in the reaction layer is in agreement with the finding of Snide *et al.* [10], who reported finding the same reaction products between SiC and titanium.

It was found that before the filler metal reached the melt state, a large proportion of the titanium in it diffused and quickly reacted at the SiC surface, forming silicides containing some amount of carbon. The remaining titanium formed compounds with the Ag–Cu alloy in various proportions, and also migrated close to the SiC surface as temperature and time increased.

With the higher-titanium alloy, the weakness of the bonds at all temperatures might have been due to the thickening of the reaction layer or the formation of more brittle reaction products because of excess titanium. With 2 wt % Ti it is thought that, although there was the formation of similar products, the quantity of titanium was such that the thickness of the reaction layer was limited and probably optimum.

As the temperatures and holding times progressed it is thought that other reaction products or layers probably formed such as Ti_3SiC_2, reported by Morozumi *et al.* [7], who found that Ti_3SiC_2 had a good atomic matching with that of SiC. Martineau *et al.* [11] also identified $Ti_5Si_3(C)$, TiC_{1-x} and Ti_3SiC_2 formed between Ti and SiC at 950° C with a holding time of several hours. The formation of these other reaction products could partly explain why there are two

titanium peaks appearing in the line scanning shown in Fig. 6b.

Preliminary tests had shown that above 950°C there was too much evaporation of silver from the alloy, which caused voids and unbonded areas at the interface.

4. Conclusions

PLS-SiC can be brazed to itself using Ag–Cu–Ti alloys. With higher titanium contents the wettability was quite good, but the resultant reaction layer increased in thickness due to the excess titanium, which caused continuous interaction with silicon. This, coupled with the formation of too much of intermetallic compounds with increasing temperature and time, probably caused weakening of the bonds.

The smaller the titanium content in the alloy, the poorer the wettability at lower temperatures, but this improved as temperature and time progressed. The thickness of the reaction layer remained almost unchanged at all the brazing temperatures, and a surprisingly high bond strength was obtained when the holding time was extended to 30 min at 950°C.

The formation of the reaction products, their composition, the order in which they appeared, together with their overall thickness, played a major role in the bonding of PLS-SiC.

Acknowledgement

References

1. R. W. RICE, "Advances in Joining Technology" (Brook Hill, Massachusetts, 1976) p. 69.
2. T. ISEKI, K. YAMASHITA and H. SUZUKI, Proc. Br. Ceram. Soc. No. 31 (1981) 1.
3. T. ISEKI, K. ARAKAWA and H. SUZUKI, J. Mater. Sci. 15 (1980) 1049.
4. T. ISEKI, T. KAMEDA and T. MARUYAMA, ibid 19 (1984) 1692.
5. G. ELSSNER, W. DIEM and J. S. WALLANE, "Surface and Interface in Ceramic and Ceramic Metal System" (Plenum, New York, 1981) p. 629.
6. S. YAJIMA, K. OKAMURA, T. SHISHIDO, Y. HASEGAWA and T. MATSUZAWA, Amer. Ceram. Soc. Bull. 60 (1981) 253.
7. S. MOROZUMI, M. ENDO and M. KIKUCHI, J. Mater. Sci. 20 (1985) 3976.
8. P. M. SCOTT, M. G. NICHOLAS and B. DEWAR, ibid. 10 (1975) 1833.
9. T. ISEKI, H. MATSUZAKI and J. K. BOADI, Amer. Ceram. Soc. Bull. 64 (1985) 322.
10. J. A. SNIDE, F. A. ASHDOWN and J. R. MYERS, Fibre Sci. Technol. 5 (1972) 61.
11. P. MARTINEAU, R. PAILLER, M. LAHAYE and R. NASLAIN, J. Mater. Sci. 19 (1984) 2749.