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Relationship Between Wettability and Interfacial Reaction for Sn10Ag4Ti on Al_2O_3 and SiC Substrates

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Abstract: Sn10Ag4Ti filler metal possesses the advantage of low thermal stress for active brazing of ceramics. In order to clarify its brazing mechanism, the wettability and interfacial reactions for such an active filler metal on Al_2O_3 and SiC ceramics substrates were evaluated. It was shown that the contact angle of Sn10Ag4Ti on both ceramics decreased with the increase of temperature and heating time. The wettability of Sn10Ag4Ti on SiC substrate was superior to that on Al_2O_3 substrate. For all cases with better wettability, Ti was also found to aggregate more strongly at the brazing interface. In summarizing these results, it can be concluded that the wetting tendency of Sn10Ag4Ti on Al_2O_3 and SiC ceramics is decided by the interfacial reaction of Ti in the filler metal with the ceramic substrates. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

The advancement of engineering technology to meet future requirements in automotive, aerospace and electronic industrial applications requires the development of ceramic materials. However, for the potential of these materials to be fully realised, it is necessary that reliable joining techniques be available. For mass production, brazing is a preferred joining technique for engineering materials. The principal requirement for ceramics brazing is wetting of their surfaces by the filler metal. It has been shown that the addition of active element in filler metals can effectively improve the wettability of ceramics by reducing the solid–liquid surface free energy and formation of the required subsequent chemical reaction between both ceramic surfaces or between ceramics and metal surfaces.[1,2] In comparison with the widely used Ag-Cu-based active filler metals, the newly developed Sn-based active filler metals possess a melting range below 300°C and have superior properties that can relax the thermal stresses in the ceramic–metal joint.[3] However, brazing with low melting filler metals is always conducted at elevated temperatures owing to a decent thermodynamic activation.[4] This implies that the wetting temperatures for this kind of filler metal on ceramics are far above their melting points. Kapoor *et al.* have shown that a low melting Sn-based filler metal containing titanium exhibited excellent wettability on silicon-nitride ceramic substrates at 900°C.[5] Okamoto *et al.*[6] indicated in a review paper that interfacial reactions are unavoidable in most metal–ceramic joining. The formation of interfacial structures and morphologies affects the wetting process and the joining strength of brazed ceramic components. However, Chung[7] demonstrated that joining could be accomplished by adsorption of Ti on the interface, regardless of whether or not an interfacial reaction layer was formed. For this purpose, the effort of this work is concerned with the wetting behaviour of a Sn10Ag4Ti filler metal on SiC and Al_2O_3 ceramics and its relation to the interfacial reaction.

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2 EXPERIMENTAL PROCEDURE

The bulk alumina ceramic in this study was fabricated by pressure casting and sintered at 1600°C after drying. The silicon carbide was manufactured by H. C. Starck, Germany. The specimen to be joined was cut from these bulk ceramics to a size of 3×4×20 mm, and the surfaces to be joined were polished using a diamond paste of 0.3 μm Ra. Some of the characteristics of the ceramic materials are given in Table 1. The active filler metal included in this study was foil type with a thickness of 0.025 mm supplied by the Degussa Co. The chemical composition is also given in Table 1. In order to evaluate the wettability of the active filler on the ceramic surface, the sessile drop method was used to measure the contact angles between them. The standard deviation of contact angle measurements was about 10°. The wetting atmosphere was 1×10^{-4} *torr* vacuum. For interfacial analyses, two ceramic plates were brazed with filler metal foil in sandwich form. The brazing process was conducted in a vacuum resistance furnace of 1×10^{-4} *torr*. The interfacial structures and elemental distributions of the brazed specimens were analyzed with electron probe microanalyzer (EPMA). In order to confirm the interfacial reactions, differential thermal analyses (DTA) were also employed. For the DTA experiments, the powder form of Ti and ceramics were used to increase the reaction area, which could enhance the peaks of interfacial reactions.

3 RESULTS AND DISCUSSION

Sn10Ag4Ti possesses a melting point between 221 and 300°C. However, it adhered to the ceramic substrate surface above 600°C. The contact angles decreased with the increase of temperature as shown in Fig. 1. It can be seen that the Sn10Ag4Ti filler metal wet the Al_2O_3 substrate at temperatures above 700°C for 20 min, but that the contact angle remained about 70° as the temperature was further increased. On the other hand, the Sn10Ag4Ti filler metal wet the SiC substrate at about 680°C for 20 min, and the contact angle decreased to about 0° rapidly with increasing temperature. Increasing the heating time from 20 min to 60 min, the contact angles for both ceramics decreased further. It was also found that the critical wetting temperatures, which are defined as the temperature for a contact angle smaller than 90°, declined from 700 to 620°C and from 680 to 610°C for Al_2O_3 and SiC, respectively. A contracted solidified drop was clearly formed as the heated Sn10Ag4Ti filler metal melted on the ceramic substrate. This phenomenon is different from the case of conventional brazing filler metals in which they are normally spread on the substrate. It is suggested that at about 300°C the filler metal melted but it did not wet the ceramic substrate. The surface tension thus forced the liquid drop to form into an elliptical shape, and the contact area between the filler and the substrate to contract (Fig. 2(b)). Further heating above 700°C of the Sn10Ag4Ti filler metal could lead to wetting

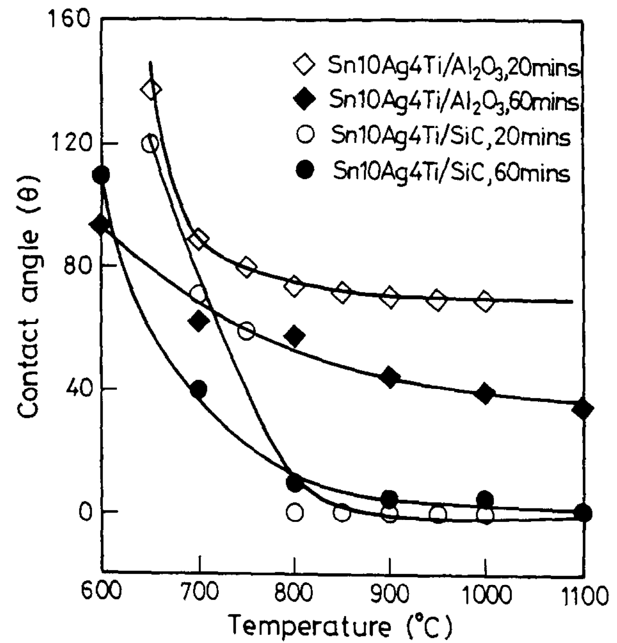


Fig. 1. The contact angle of the Sn10Ag4Ti filler metal on Al_2O_3 and SiC ceramic.

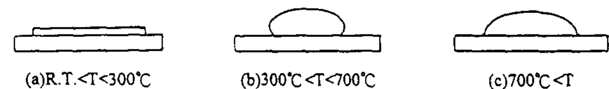


Fig. 2. A schematic diagram of the Sn10Ag4Ti liquid drops on the ceramic substrate during the melting process. (a) R.T. < T < 300°C; (b) 300°C < T < 700°C; (c) 700°C < T.

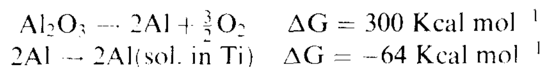
Table 1. (a) The properties of the alumina and SiC; (b) the composition of the filler metal

Material	Melting point (K)	Density ($Mg\ m^{-3}$)	Coefficient of thermal expansion ($10^{-6}K^{-1}$)	Strength (MPa)	Young's modulus (GPa)
(a) SiC	2970	3.1	4.9	315	440
Alumina	2323	4.0	7.9	457	388
(b) Filler metal	Composition (wt%)		Melting range (°C)	Brazing range (°C)	
Degussa CSI	Sn86-Ag10-Ti4		221–300	850–950	

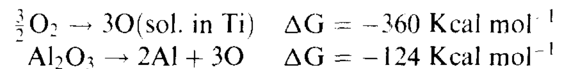
of the ceramic substrate, which resulted in spreading of the liquid drop as shown in Fig. 2(c). The finally solidified contact area was, therefore, smaller than that of the original filler foil.

Kapoor and Eagar[5] have shown that the melting range of Sn-Ti active filler metal is between 400°C and 600°C, and described the wetting steps which occur in the presence of the interfacial reactions between the ceramic surface and filler metals at higher temperatures.

DTA analyses showed that an exothermal peak at 612°C appeared during the heating cycle of the Ti–Al_2O_3 mixture (Fig. 3(a)). This could be attributed to the interfacial reaction between Ti and Al_2O_3. From the point of view of thermodynamics at 1000°C, Moorhead *et al.*[8] have reported that the free energy of oxygen that dissolves in Ti is less than that of Al in Ti. As a result of the following reactions:



$$Al_2O_3 \rightarrow 2Al + \tfrac{3}{2}O_2 \quad \Delta G = 300\ \text{Kcal mol}^{-1}$$
$$2Al \rightarrow 2Al(\text{sol. in Ti}) \quad \Delta G = -64\ \text{Kcal mol}^{-1}$$



$$\tfrac{3}{2}O_2 \rightarrow 3O(\text{sol. in Ti}) \quad \Delta G = -360\ \text{Kcal mol}^{-1}$$
$$Al_2O_3 \rightarrow 2Al + 3O \quad \Delta G = -124\ \text{Kcal mol}^{-1}$$

Ti can react with Al_2O_3 to form titanium oxide at this temperature. In Hongqi's research,[9] it has been reported that the reaction products of Al_2O_3 and Ag-Cu-Ti filler metal are AlTi and Cu_2Ti_4O below 850°C and are Ti_2O, TiO and $CuTi_2$ above 900°C. Moorhead[8] also found a reaction layer of titanium oxide at the joint interface of Al_2O_3 and Ag-Cu-4Sn-4Ti filler metal. Peytour[10] indicated that TiO existed between Al_2O_3 and the Cu-40Ag-5Ti filler metal and promoted wetting.

The DTA curve for the Ti–SiC mixture is shown in Fig. 3(b). The exothermal peak at 615.44°C is considered to be caused by Ti-C reaction. It is interesting to note that the 615.44°C exothermal peak of the Ti–SiC mixture is close to the 612°C of the Ti–Al_2O_3 mixture. This result reveals the fact that the Ti-C reaction temperature of the Ti–SiC mixture is near the Ti-O reaction temperature of the Ti–Al_2O_3 mixture. Figure 3(c) shows the DTA

Fig. 3. (a) The DTA curve of Ti–Al_2O_3; (b) The DTA curve of Ti/SiC; (c) The DTA curve of Sn10Ag4Ti/Al_2O_3; (d) The DTA curve of Sn10Ag4Ti/SiC.

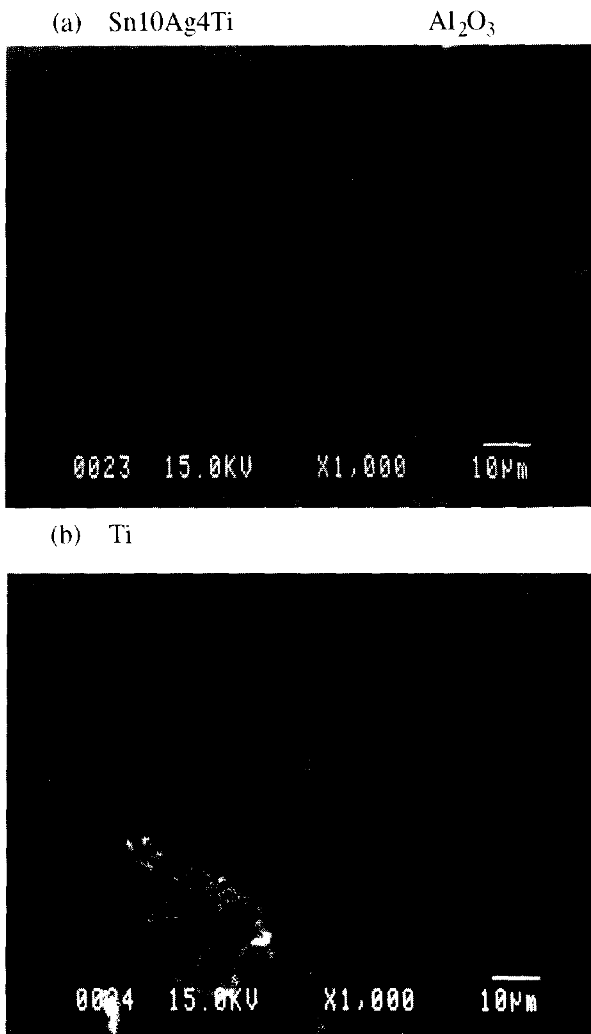


Fig. 4. The micrographs and element distributions of a cross-section of the Sn10Ag4Ti–Al_2O_3 jointed interfaces. (700°C, 20 min).

curve for the Sn10Ag4Ti–Al_2O_3 mixture. An obvious exothermal peak appears at 577.54°C, which is considered to result from the interfacial reaction of the Ti in Sn10Ag4Ti filler metal with Al_2O_3 powder. This reaction could be reasonably related to the wetting experimental results where in the Sn10Ag4Ti filler could be wetted on the Al_2O_3 ceramic substrate at about 700°C.

Figure 3(d) shows the DTA curve for the Sn10Ag4Ti–SiC mixture, in which the exothermal peak at 589.11°C is suspected to be attributable to the interfacial reaction of the Ti in Sn10Ag4Ti with SiC. A comparison of the 577.54°C exothermal peak in Fig. 3(c) and the 589.11°C exothermal peak in Fig. 3(d) suggests that the interfacial reaction temperature of the Ti in the Sn10Ag4Ti reacting with the Al_2O_3 is very close to the temperature of the Ti in the Sn10Ag4Ti reacting with the SiC. The closeness of the critical wetting temperature for Sn10Ag4Ti on Al_2O_3 and SiC as shown in Fig. 1 can thus be explained by the similar DTA results obtained from both systems. Furthermore, it has been reported by many workers that a strong reaction occurs between the SiC ceramic and transition elements in active fillers at elevated temperatures.[11–13] The superior wettability for Sn10Ag4Ti on SiC over that on Al_2O_3 as the temperature increased above the critical wetting temperature (Fig. 1) can also be understood.

Figure 4 shows the interfacial microstructure and distribution of chemical elements of the Sn10Ag4Ti–Al_2O_3 interface brazed at 700°C and a holding time of 20 min. The distribution of the Ti at interface is not prominent in the elemental mapping. In addition, there were black blocks in the interior of the Sn10Ag4Ti filler metal after joining. They were mainly composed of Sn and Ti from EDX analysis (Fig. 5). Since we also found black blocks in the interior of the as-received Sn10Ag4Ti active filler metal which were clusters of Ti, and the matrix was mainly composed of Sn and Ag (Fig. 6), it is suggested that most of the Ti

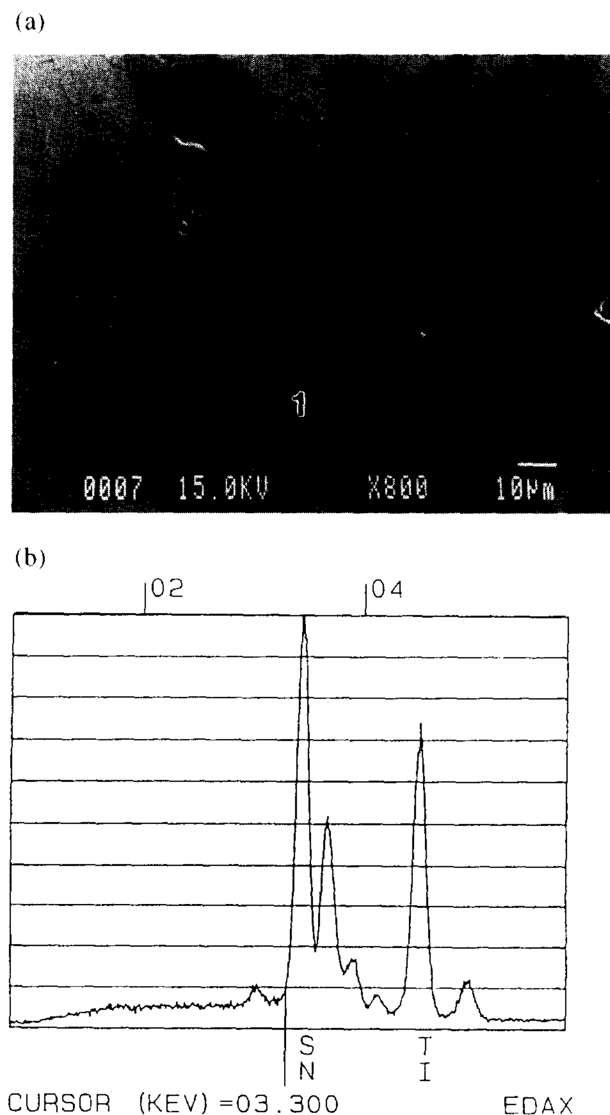


Fig. 5. The micrographs ofthe Sn10Ag4Ti active filler metal after joining (700°C, 20 min). (a) Sn10Ag4Ti active filler metal; (b) EDX analyses (Point 1).

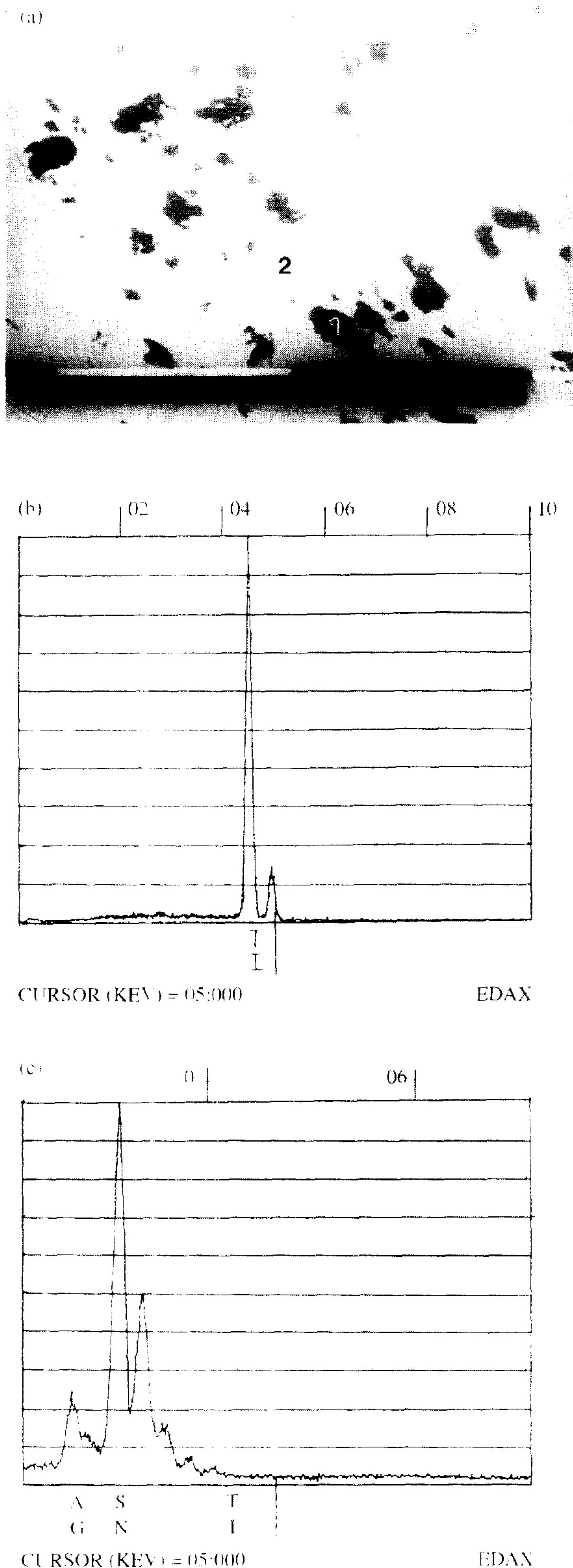


Fig. 6. The micrographs of the as-received Sn10Ag4Ti active filler metal. (a) Secondary electron image; (b) EDX analyses (Point 1); (c) EDX analyses (Point 2).

in the Sn10Ag4Ti active filler metal reacted with the Sn to form the (Ti,Sn) compound during joining. Only a small amount of Ti aggregated at the interface of ceramic–active filler metal to promote

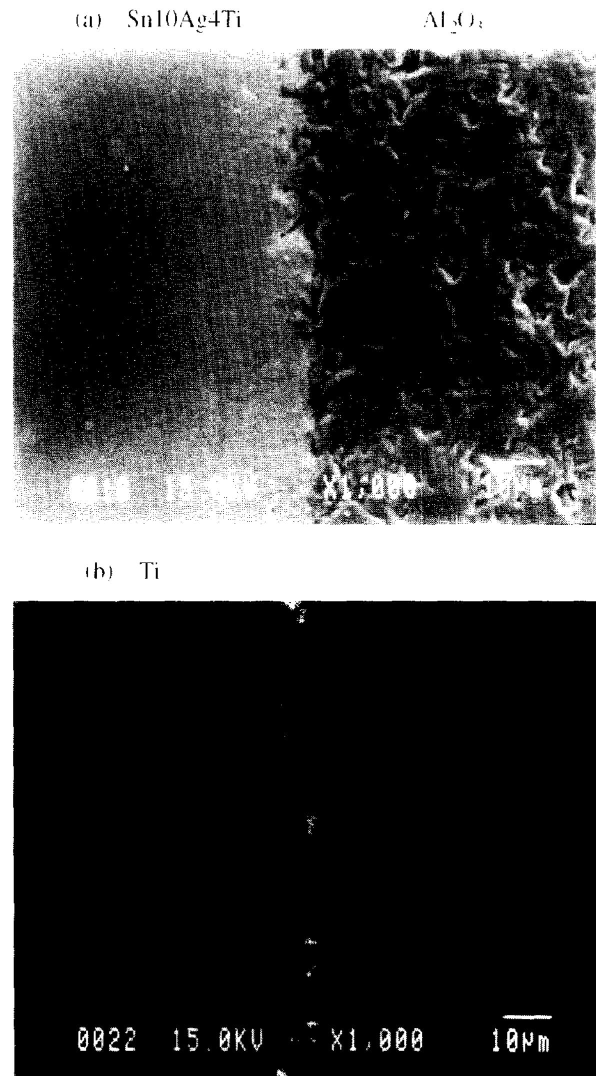


Fig. 7. The micrographs and element distributions of a cross-section of the Sn10Ag4Ti–Al_2O_3 jointed interfaces. (700°C, 60 min).

joining of the ceramic and active filler metal. Increasing the brazing time from 20 min to 60 min for Sn10Ag4Ti–Al_2O_3 joints, the aggregation of Ti at the interface becomes obvious (Fig. 7). This is consistent with the decrease of contact angle during the wetting experiment as the heating time increased (Fig. 1).

Figure 8 shows the microstructure and elemental distribution at the interface of the Sn10Ag4Ti–SiC joint after brazing at 700°C for 20 min. In comparison with the Sn10Ag4Ti–Al_2O_3 joint with a brazing time of 20 min (Fig. 4(b)), Ti aggregated much more strongly along the Sn10Ag4Ti–SiC interface of the Sn10Ag4Ti–SiC joint. Correlating this result with that of contact angle measurements in Fig. 1, it is evident that the stronger aggregation tendency of the Ti along the Sn10Ag4Ti–SiC joining interface causes the superior wettability to that of the Sn10Ag4Ti–Al_2O_3. It is also believed that the higher Ti aggregation tendency is attributed to

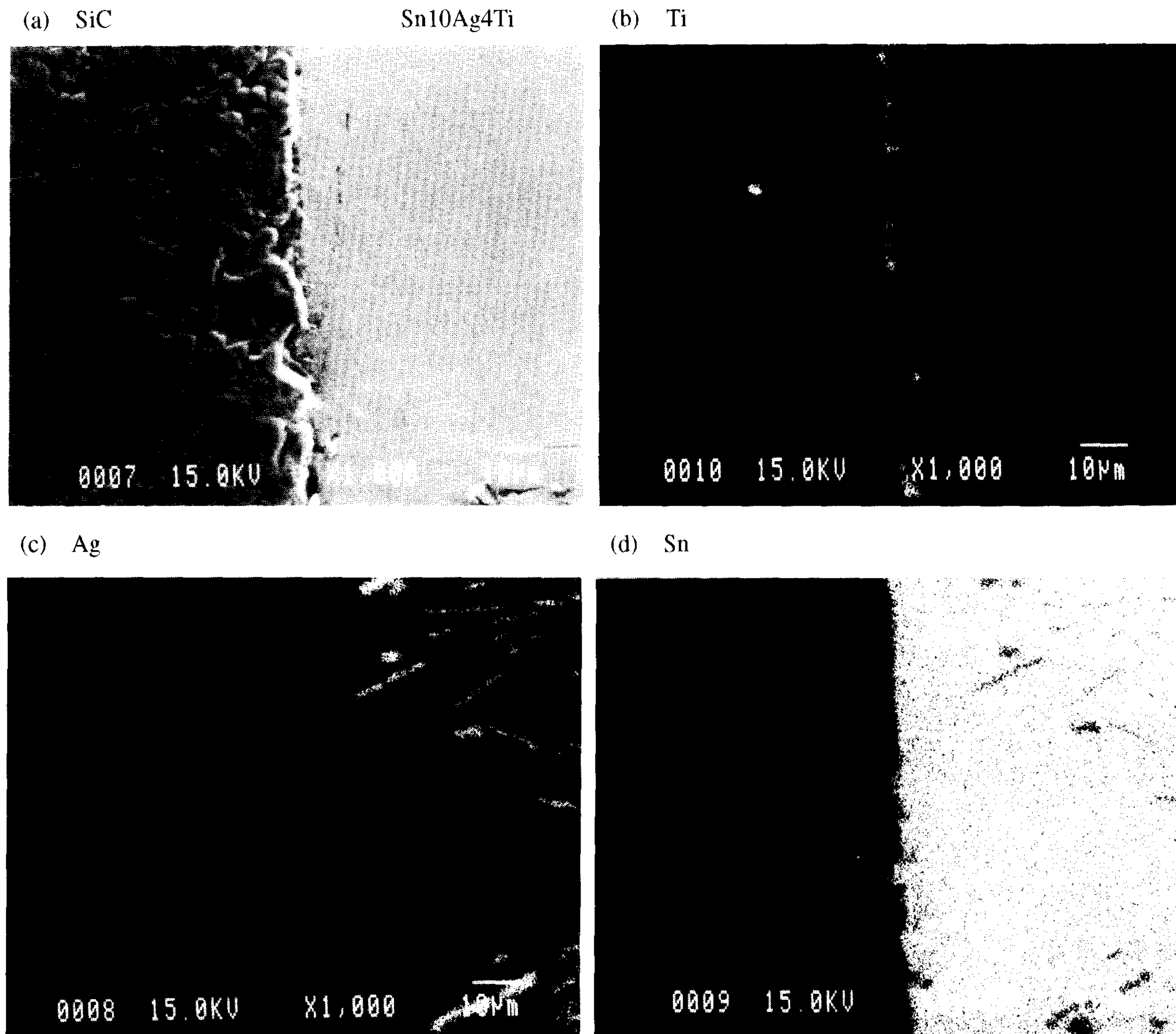


Fig. 8. The micrographs and element distributions of a cross-section of the Sn10Ag4Ti–SiC jointed interfaces. (700°C, 20 min).

the strong interfacial reaction between Ti and SiC as reported by many workers.[11–13]

4 CONCLUSIONS

The contact angle of the Sn10Ag4Ti filler metal on Al_2O_3 and SiC ceramic substrate decreased with the increase of temperature and heating time. Sn10Ag4Ti filler metal on SiC substrate possessed superior wettability to that on Al_2O_3 substrate. The contact angle of the Sn10Ag4Ti filler metal on Al_2O_3 ceramic remained 70° and 40° at temperatures above 700°C for heating times of 20 min and 60 min, respectively, and that of the Sn10Ag4Ti filler metal on SiC ceramic decreased almost to 0° rapidly as the temperature was raised above 680°C for both heating times of 20 min and 60 min. The interfacial reaction temperature of the Sn10Ag4Ti active filler metal on ceramics could be roughly estimated by the temperature of the exothermal peaks in DTA curves. Ti aggregated strongly at the Sn10Ag4Ti–SiC interface after brazing at 700°C for 20 min, while this was not prominent at the Sn10Ag4Ti–Al_2O_3 interface under the same brazing conditions. Increasing the brazing time to 60 min, the aggregation of Ti at Sn10Ag4Ti–Al_2O_3 becomes obvious. The better wettability of Sn10Ag4Ti on SiC than that on Al_2O_3 is attributable to the stronger interfacial reaction of Sn10Ag4Ti–SiC as compared with Sn10Ag4Ti–Al_2O_3.

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