Interfacial morphologies between alumina and silver-copper-titanium alloy

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Joints of high-purity Al_2O_3 were made with a $Ag_{57}Cu_{38}Ti_5$ alloy by vacuum brazing at 800 °C and 900 °C for 30 min. The microstructures at the interface between the ceramic and the alloy were examined in cross-section by scanning electron microscope (SEM) and on different planes parallel to the interface layer-by-layer by optical microscope (OM), respectively. The chemical composition of the reaction product was also analysed by energy dispersive X-ray (EDX). A thin reaction layer about 1.0 µm thick was formed on the Al_2O_3 surface at a temperature of 800 °C. This layer had three kinds of morphologies and they were identified as Ag, Cu_2Ti_4O and AlTi, respectively. According to SEM and OM results, there were two distinct layers 4.0 µm thick interfacial reaction layer for sample heated at 900 °C, one layer in the vicinity of the ceramic consisting mainly of Ti_2O and TiO and the other layer near the alloy was $CuTi_2$. A transition layer structure composed of $Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + CuTi_2/CuTi_2/Ag$–Cu was formed at the interface. The Al concentration at the interface was relatively high and confirmed that the reduction of Al_2O_3 by Ti occurred, which was consistent with the result of a thermodynamic analysis.

1. Introduction

The interfacial characteristic between the ceramic and the filler metal has a strong influence on the bonding strength for oxide ceramics and therefore has been the subject of many experimental studies [1–12]. The efforts have been focused mainly in three areas. First there have been some nascent efforts at first-principle calculations of adhesive forces. For example, Johnson *et al.* [1] calculated the binding energies of Fe, Ni, Cu, and Ag on sapphire using a molecular orbital approach involving Al_2O_3-metal clusters that included second-nearest-neighbour interactions. Such calculations are helpful, but they have been made for only a few simple systems. Secondly, the relative interfacial energies and the wetting ability of a liquid drop on a solid surface have been determined from sessile-drop experiments [2–6]. If the formation of an interface between the liquid and the solid lowers the overall free energy of the system, wetting of the liquid on the solid surface occurs and a thermodynamically stable interface between two dissimilar materials is formed. However, many metals, including those commonly used as base alloys for brazing filler metal (e.g. silver, gold, copper, nickel) do not wet oxides very well. The results have also shown that when a liquid metal forms a more stable oxide than the solid on which it is melted, then dynamic wetting or spreading of the liquid occurs due to the thermodynamical reduction of the solid substrates by elements in the liquid metals. Titanium or zirconium have been shown to be particularly effective at wetting various oxides and this behaviour has been attributed to the high stability of titanium or zirconium oxides. Thirdly, the interfacial reaction between the ceramic and the filler metal has been investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as well as X-ray diffraction (XRD) [7–12]. In our previous work [12], the reaction products at the interface between alumina ceramic and Ag–Cu–Ti alloy have been analysed by XRD layer-by-layer on the planes parallel to the interface. In this paper, the aim is to observe and analyse the morphologies of the interfacial reaction layer formed during the brazing of Al_2O_3 with a Ag–Cu–Ti alloy using an optical microscope (OM).

2. Experimental procedure

The alumina ceramic used, was a 99% pure bar of $5 \times 5 \times 10$ mm. The filler metal was $Ag_{57}Cu_{38}Ti_5$ alloy and its thickness was about 0.7 mm. The contact surfaces of the two materials were polished mechanically and then were cleaned carefully in acetone prior to brazing. A piece of filler metal with the same area as the ceramic was placed on the surface of the Al_2O_3 ceramic and then heated in a vacuum of about 7×10^{-3} Pa to temperatures of 800 °C and 900 °C for 30 min. Each sample then was cut perpendicular to the joining interface into two pieces, one was used for SEM observation of the interfacial microstructures and one for OM analysis of the interfacial morphologies layer-by-layer on different planes parallel to the interface.

3. Results and discussion
3.1. SEM microstructures of the interface
SEM micrographic observations made on perpendicular sections to the interfaces which had been heated at 800 °C and 900 °C are shown in Fig. 1. It can be seen that an interfacial reaction layer between the ceramic and the filler metal was found for both samples. The interfacial reaction layer at 800 °C was discontinuous and its thickness was about 1.0 μm and thinner than that at 900 °C (about 4.0 μm).

It is notable that there were two distinct layers between the ceramic and the filler metal for the sample heated at 900 °C: one layer appeared dark in colour at the contact with the ceramic and there was a grey colour layer near the filler metal.
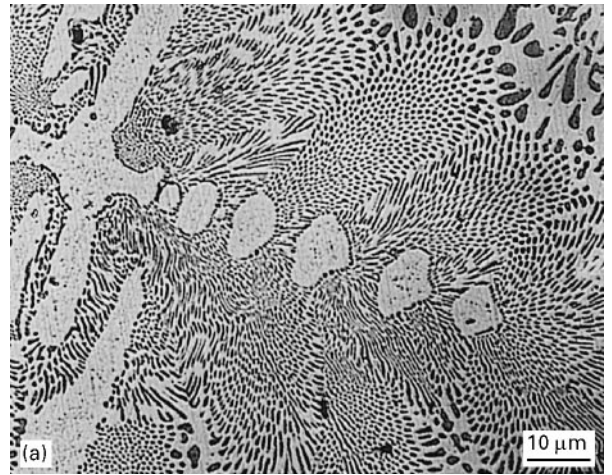
3.2. OM morphologies of the interface
In order to analyse the morphologies and distributions of the reaction products at the interfacial reaction layer, the interfacial reaction layer was polished mechanically and observed sequentially by OM on different planes parallel to the interface, which was similar to the XRD analysis method in our previous work [12].

Fig. 2 shows the results of OM observations for the sample heated at 800 °C. When removing the Ag–Cu eutectic layer (Fig. 2a) by mechanical polishing, three kinds of morphologies in different colours immedi-
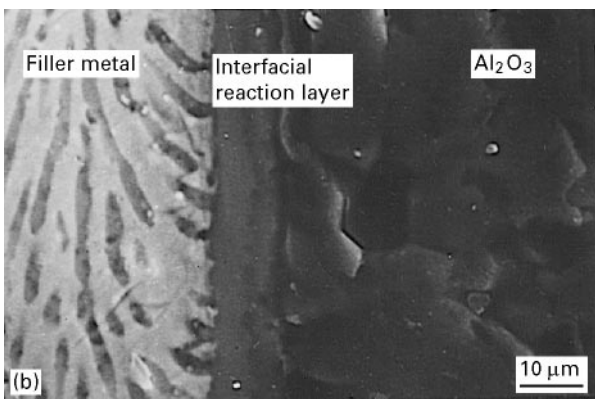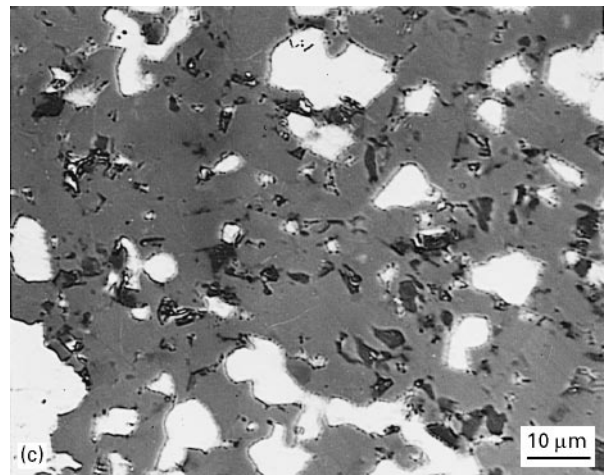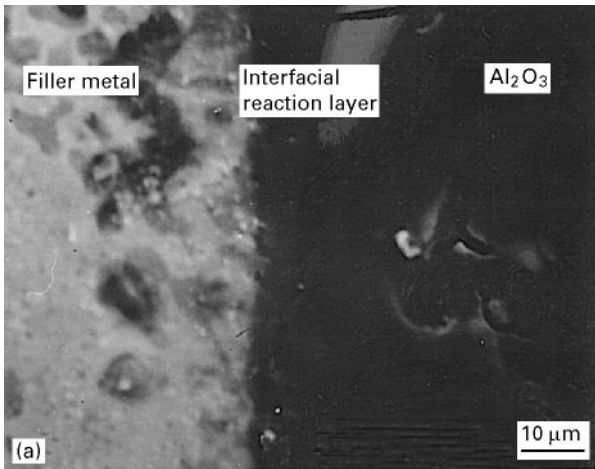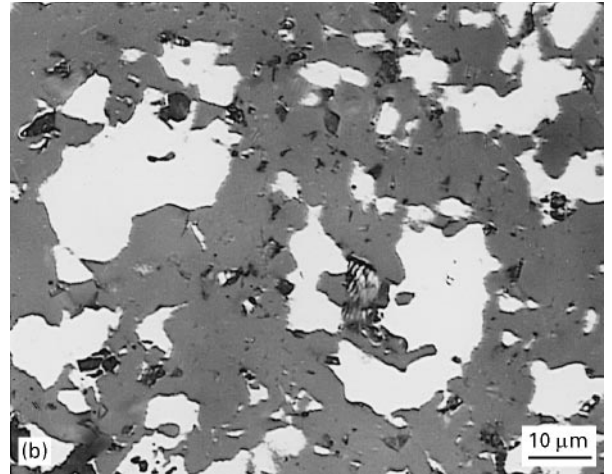

Figure 2 Microstructures on different polished surfaces parallel to the interface between the ceramic and the filler metal for the sample heated at 800 °C.

Figure 1 SEM microstructures of cross-sections at the interface between the ceramic and the filler metal heated at (a) 800 °C and (b) 900 °C for 30 min.

TABLE I EDX results of the interfacial reaction layer

Phases	Chemical composition (at %)				
	Ti	Cu	Ag	O	Al
Grey	55.15	30.57	1.47	12.23	0.58
Dark	50.14	2.19	0.47	0.35	46.85
White	—	1.74	98.26	—	—
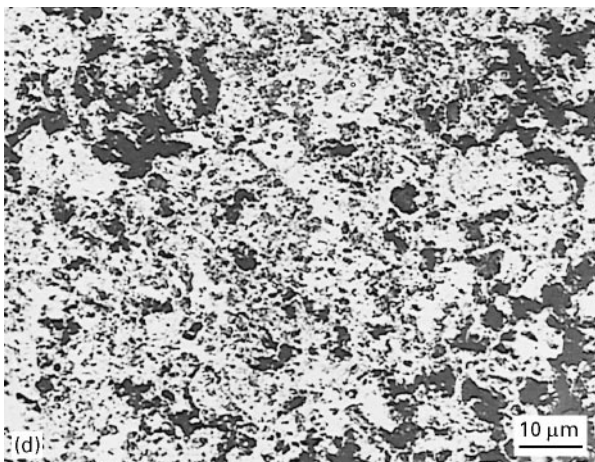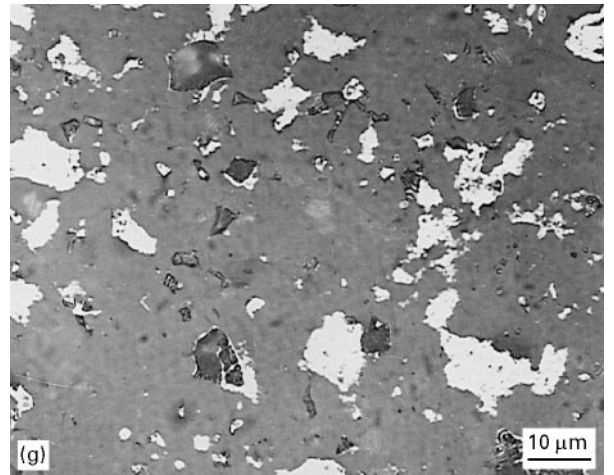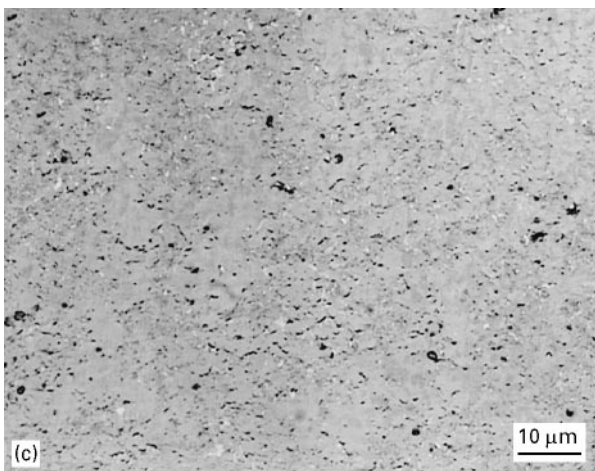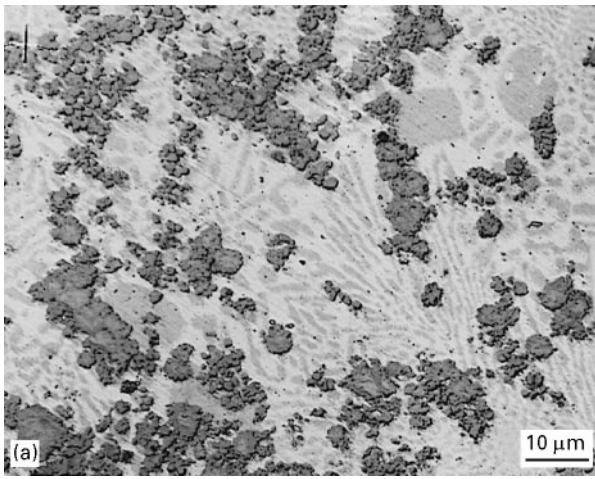
Figure 3 Microstructures on different polished surfaces parallel to the interface between the ceramic and the filler metal for the sample heated at 900 °C.

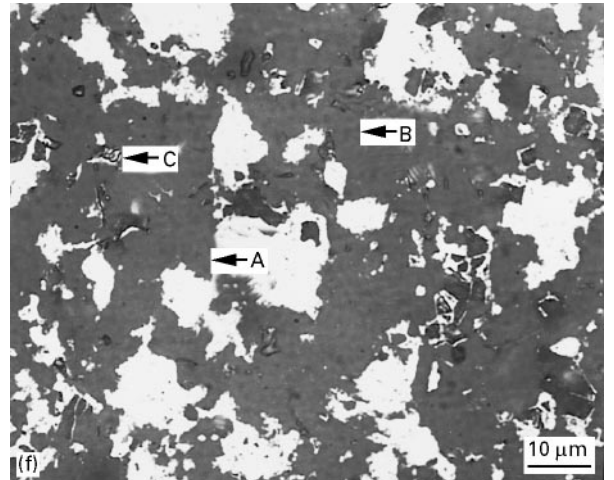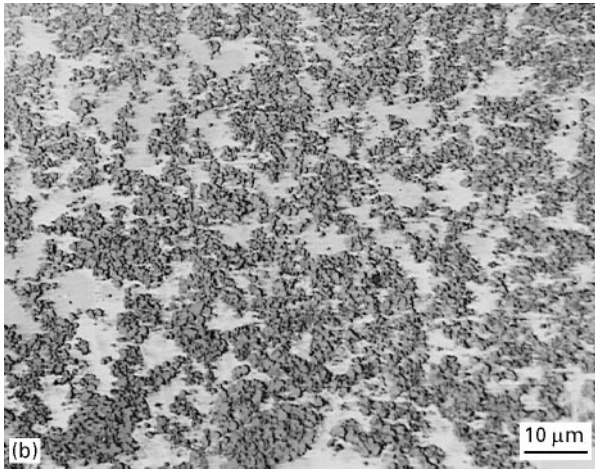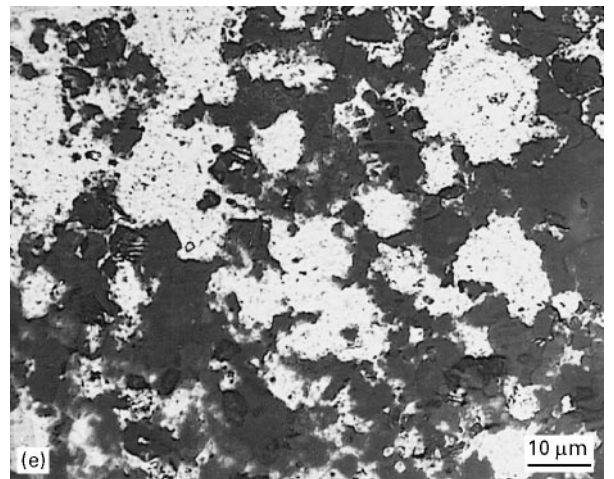ately appeared: one was grey, one dark and one white (Fig. 2b). When removing the reaction layer further, the volume fraction of the grey or dark one increased while that of the white one decreased gradually (Fig. 2c). The EDX result is shown in Table I. It can be seen that the grey one might be a Ti–Cu–O compound and the dark one could be a Ti–Al compound, while the white one was Ag.

Fig. 3 shows the OM results for the sample heated at 900 °C. When removing the filler metal layer on the ceramic surface partially by mechanically polishing,

a hard, a grey colour reaction product appeared on the matrices of the Ag–Cu eutectic (Fig. 3a). The volume fraction of the reaction product increased gradually when removing the reaction layer further (Fig. 3b), and in such a position (Fig. 3c), the whole polished surface was composed of the reaction product. When observed by SEM on this polished surface, the grain shape of the grey phase was clear and a white network phase distributed along the grain boundary, as shown in Fig. 4. EDX results showed that the chemical composition of the white phase in Fig. 3b and the network phase in Fig. 4 was the same and contained 98.53% Ag and traces of Cu and Ti. The grey phase in Figs 3b and c was: Ti = 62.17%, Cu = 31.81%, O = 2.63%, Ag = 1.04%, Al = 2.35%. It is clear that the white phase was Ag and the grey phase was a Cu–Ti compound with small amounts of other elements.

When removing the grey reaction layer further, there were at least three kinds of microstructures in shape or colour and they are marked A, B and C in Fig. 3f: a grey one (marked A), a dark one (marked B) which had a circular or a short bar shape and a laminar structure of white and dark, marked C. It can also be seen that the volume fraction of A and B phases was almost equal and obviously greater than that of C on the same polished surface, and the closer the reaction layer was to the ceramic, the greater the volume fraction of A and B phases, but that of C changed little (Figs 3d–g). EDX results for A, B and C morphologies are shown in Table II. It is clear that A and B phases were all the Ti–O compounds but with different amounts of Ti and O, while the laminar
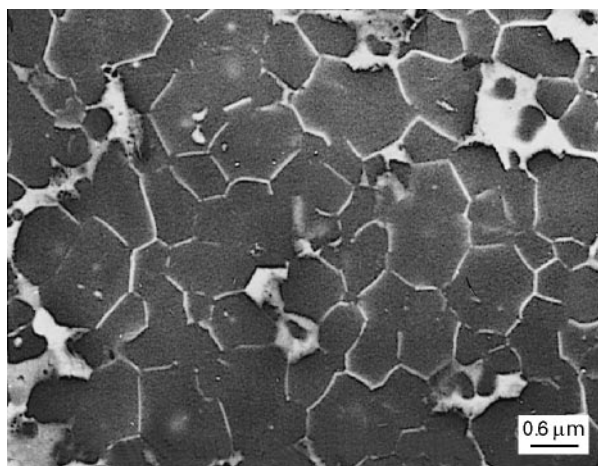

Figure 4 SEM microstructure of the grey phase in Fig. 3c.

TABLE II EDX analysis results of the three kinds of morphologies in Fig. 3f

Morphologies	Chemical composition (at %)				
	Ti	Cu	Ag	O	Al
A	48.25	3.22	0.61	44.14	3.78
B	60.27	3.84	1.15	32.43	2.41
C	38.65	7.13	15.40	34.57	4.35

structure C was very complicated. On the other hand, the Al concentration at the interface was relatively high.

XRD analyses of the interfacial reaction products had been performed sequentially on different planes parallel to the interface in our previous work [12] and the results for the sample heated at 800 °C showed that the interfacial reaction layer was composed mainly of AlTi and Cu_2Ti_4O. The reaction products for the sample heated at 900 °C were different from the sample heated at 800 °C and consisted of Ti_2O, TiO and $CuTi_2$ compounds. The reaction products adjacent to the filler metal were $CuTi_2$, and Ti_2O and TiO at the reaction layer near the ceramic.

From the results of EDX and XRD, it can be confirmed that the grey and the dark phases in Figs 2b and c are consistent with Cu_2Ti_4O and AlTi compounds, respectively. The grey phase in Figs 3b and c corresponds to $CuTi_2$ compound, and the A and B phases to TiO and Ti_2O compounds, respectively. The volume fraction of C is too small to be determined by XRD, it is also difficult to identify its phase structure merely by EDX results. It therefore needs to be analysed further. It is also notable that, according to the results of OM observations on different polished surfaces, a transition layer structure with a Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + $CuTi_2/CuTi_2/Ag$–Cu composition was formed at the interfacial reaction layer for the sample heated at 900 °C, which was consistent with the results of SEM observations (Fig. 1).

From the above results, the relatively high Al concentration in the reaction layer confirmed that reduction of the Al_2O_3 surface occurred during the brazing process because the filler metal originally contained no Al, which is consistent with the result from thermodynamic analysis [12]. The reaction of Al_2O_3 with Ti can be presented by the following equation:

$$1/3 \ Al_2O_3 + (Ti) \rightarrow TiO + 2/3 \ (Al)$$
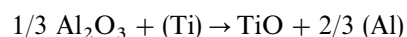
$$\Delta G^0 = -120.030 + 0.086T \ (kJ \ mole^{-1})$$

It is clear that Al_2O_3 can be reduced by Ti in the alloy and form TiO below a temperature of 1123 °C.

There are some other reaction products for Al_2O_3 and Ti-containing alloy systems. Kritsalis *et al.* [7] found in an analysis of reactive wetting in the $CuTi/Al_2O_3$ system that there were two distinct layers between the Al_2O_3 and the alloy according to the micrographic observations and the microprobe line scans of composition. The layer near the Al_2O_3 was $TiO_{1 \pm x}$, with $x = 0.05$, another layer near the alloy corresponded to the compound Cu_2Ti_2O. Naidich *et al.* [8] reported the formation of the metallic-type oxide TiO continuous layer at the Cu/Al_2O_3 interface. Cho and Jin Yu [9] found δ-TiO and γ-TiO present at the interface of Al_2O_3/Ag–Cu–0.5Ti joints. Santella *et al.* [10] reported γ-TiO and Cu_3Ti_3O present in the Al_2O_3/Ag–Cu–Sn–2Ti system. Naka *et al.* [11] found $(Al, Ti)_2O_3$ was formed at the interface of $Al_2O_3/CuTi$ joints. Some of the reaction products mentioned above were not found in the present study possibly

because the reaction conditions were different or the amounts of the reaction products were too small to be found.

4. Conclusion

The interfacial morphologies between alumina ceramic and the Ag–Cu–Ti filler alloy brazed at 800 °C and 900 °C were analysed by optical microscopy and scanning electron microscopy. It is shown that 1.0 μm and a 4.0 μm thick reaction layers were formed at the interface between the ceramic and the alloy when heated at 800 °C and 900 °C, respectively. There were three kinds of microstructures at the interface for the sample heated at 800 °C: white, grey and dark in colour. According to EDX and XRD results, they were identified as Ag, Cu_2Ti_4O and AlTi, respectively. There were two distinct layers at the interface for the sample heated at 900 °C: one layer at the contact with the alloy consisted of a grey product which appeared equaxial in shape and a network of Ag distributed along the grain boundary. The grey phase was indentified as $CuTi_2$. The other layer in the vicinity of the ceramic has at least three kinds of microstructures in colour or shape. A grey one corresponded to TiO and a dark one corresponding to Ti_2O. The phase structure of the laminar structure of white and dark, which mainly contained Ti, Ag and O elements, was not clear because quantities were too small to be identified by XRD. A transition layer structure with a Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + $CuTi_2/CuTi_2/Ag$–Cu composition was formed at the interface for the sample heated at 900 °C. The Al concentration at the interface was relatively high and confirmed that reduction of Al_2O_3 by Ti in the alloy occurred which was consistent with the result of a thermodynamic analysis.

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