JOURNAL OF MATERIALS SCIENCE 30 (1995) 1233–1239

Interfacial reaction of alumina with Ag–Cu–Ti alloy

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The interfacial reaction of Al_2O_3 and Ag–Cu–Ti alloy was investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively. It was shown that Al_2O_3 ceramic reacted strongly with Ag–Cu–Ti alloy. With the increasing heating temperature and holding time, the reaction layer thickness increased and its growth was mainly controlled by the diffusion of titanium through the reaction layer. The reaction products were Cu_2Ti_4O and AlTi at or below 1123 K. However, there were two distinct layers at the interface at or above 1173 K, one layer in the vicinity of ceramic consisting mainly of Ti_2O and TiO and the other layer near the alloy was $CuTi_2$, a layer transition structures with a $Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + CuTi_2/CuTi_2/Ag–Cu$ formed at the interface according to the SEM and XRD analyses results. A lower or a higher joining temperature and a shorter or a longer holding time were disadvantageous for a stable and high reliable joined interface from the point of view of interfacial microstructures and morphologies.

1. Introduction

One factor of considerable importance in the bonding of ceramics is the reaction which may take place at the interface between the interlayer and the ceramic. Reactions determine the interfacial structures and morphologies. In fact, the formation of these interfacial structures or new phases is dependent mainly on the reaction conditions and will have a large influence on the interface strength of the ceramics and interlayers, and then affect the bond strength of joined ceramic components. Therefore, the investigation of metal–ceramic interfacial reactions is important in the design of the interlayer composition, and it will serve as a guide to the choice of bonding conditions for high-reliability joining of a ceramic to metal or to itself.

As is known, brazing methods have been widely used in joining ceramics. There are many experimental studies on the interfacial reaction of non-oxide ceramics with the filler metals [1–5], and the results indicated that different kinds of reaction products are formed at the different filler metal–ceramic interface, and the interfacial reaction between the ceramic and the filler metal plays an important role in determining the joint strength of the brazed ceramic. However for the ceramic oxides, limited experimental studies have been carried out [7–11], there are different points of view on the interfacial reaction and the reaction mechanism is not clear.

This paper investigates the interfacial reactions of alumina ceramic with Ag–Cu–Ti filler metal, and the factors affecting the interfacial reaction such as temperature and time were also evaluated. Finally, from the point of view of interfacial morphologies, the effects of interfacial reactions on the interfacial strength were analysed.

2. Experimental Procedure

The alumina ceramic (99% purity) used was a bar of dimensions $5 \times 5 \times 15$ mm. The filler metal was Ag57Cu38Ti5 and its thickness was about 0.7 mm.

Before the experiment, the surfaces of the ceramics and the filler metals to be contacted were polished mechanically and then were cleaned carefully in acetone. A piece of filler metal 5×15 mm in area and 0.7 mm in thickness was placed on the surface of a Al_2O_3 ceramic with the same area, and then was heated in a vacuum of about 7×10^{-3} Pa to temperatures of 1073–1323 K for 1.8 ks or at 1123 K for 0–3.6 ks. Each sample then was cut perpendicular to the joining interface into two pieces, one was used for scanning electron microscopy (SEM) observation of the interfacial microstructures and one for X-ray diffraction (XRD) analyses of the interfacial reaction products.

3. Results

3.1. Microstructures of the interface

SEM micrographic observations made on a section perpendicular to the interface which had been heated at several temperatures for 1.8 ks are shown in Fig. 1. Between alumina ceramic and Ag–Cu–Ti filler metal, an interfacial reaction layer was observed in the range of temperatures from 1073 to 1323 K, but the interfacial reaction layer at 1073 K was discontinuous and it was thinner. With an increase in heating temperature, the reaction layer thickness was increased rapidly from 1.2 μm at 1073 K to 4.0 μm at 1173 K and then the rate of increment reduced as shown in Fig. 2.

It is notable that there were two distinct layers between the alumina and the filler metal as the heating temperature was at or above 1173 K: one layer that

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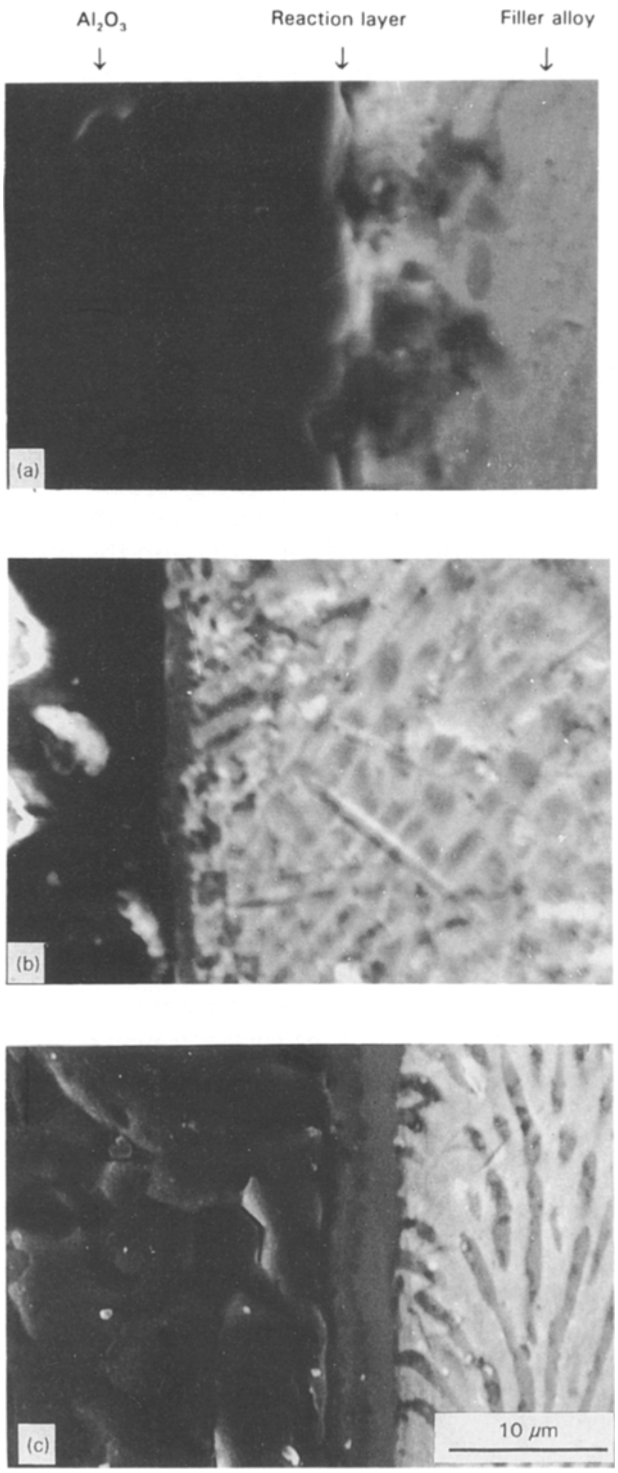


Figure 1. SEM micrographic changes of cross section at the interface at the temperatures of (a) 1073 K, (b) 1123 K and (c) 1173 K for 1.8 ks.

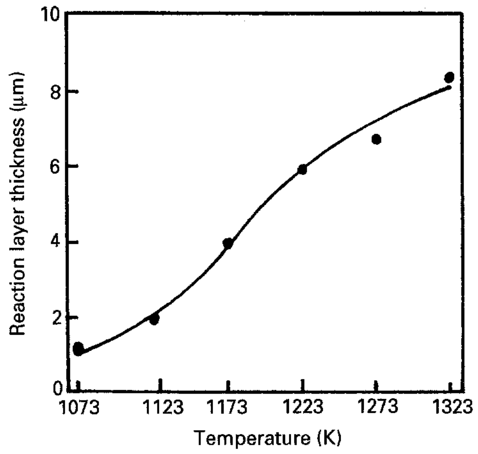


Figure 2. The effects of heating temperature on the reaction layer thickness at the Al_2O_3/Ag–Cu–Ti joint interface heating for 1.8 ks.

appeared darker in colour at the contact with the alumina and a grey layer near the filler metal. Furthermore, cracks parallel to the interface were observed at the interface of the reaction layer and Al_2O_3 at the heating temperature of 1173 K or above as shown in Fig. 1c. These cracks might be caused by differences in thermal expansion coefficients between the interface and the ceramic in the temperature range from bonding to room temperature.

The holding time has also some effects on the microstructures of the interfacial layer, as shown in Fig. 3 and Fig. 4. It can be seen that with the increase in holding time, the interface layer became continuous, and its thickness was gradually increased, but the effect of holding time was little in comparison with the temperature. When the holding time was 2.7 ks or 3.6 ks, cracks parallel to the interface were observed, which was similar to that in Fig. 1c.

3.2. The elemental distribution at the interface

The results of elemental distribution analysed by energy dispersive X-ray (EDX) revealed that titanium was the most active of the four elements (Ag, Cu, Ti and Al). The distribution of titanium showed a large variation with increment of the heating temperature. When the heating temperature was low, such as at 1073 K, only a small amount of titanium diffused from the filler metal into the interface. However, when the heating temperature was 1123 K or above, almost all of the titanium was concentrated at the interface; the interface reaction layer thickness increased gradually with the increase of titanium content at the interface.

The evidence for the existence of two layers at the interface was obtained from EDX results. Fig. 5 presents a group of typical images of SEM and AlK_α, AgK_α, TiK_α and CuK_α X-rays heated at 1173 K for 1.8 ks. It was obvious that almost all titanium in the filler metal concentrated at the interface, the reaction layer near the ceramic was high in titanium and near the filler metal was high in titanium and copper. The holding time has some influence on the elemental distribution especially on titanium, but its effect was not as large as the heating temperature. Titanium was gradually concentrated at the interface with the lengthening of holding time.

3.3. XRD results of reaction product analyses

XRD analyses of interfacial reaction products were performed on different planes parallel to the interface one after another. When the reaction layer is thick, it is possible to analyse in this way, but when the reaction

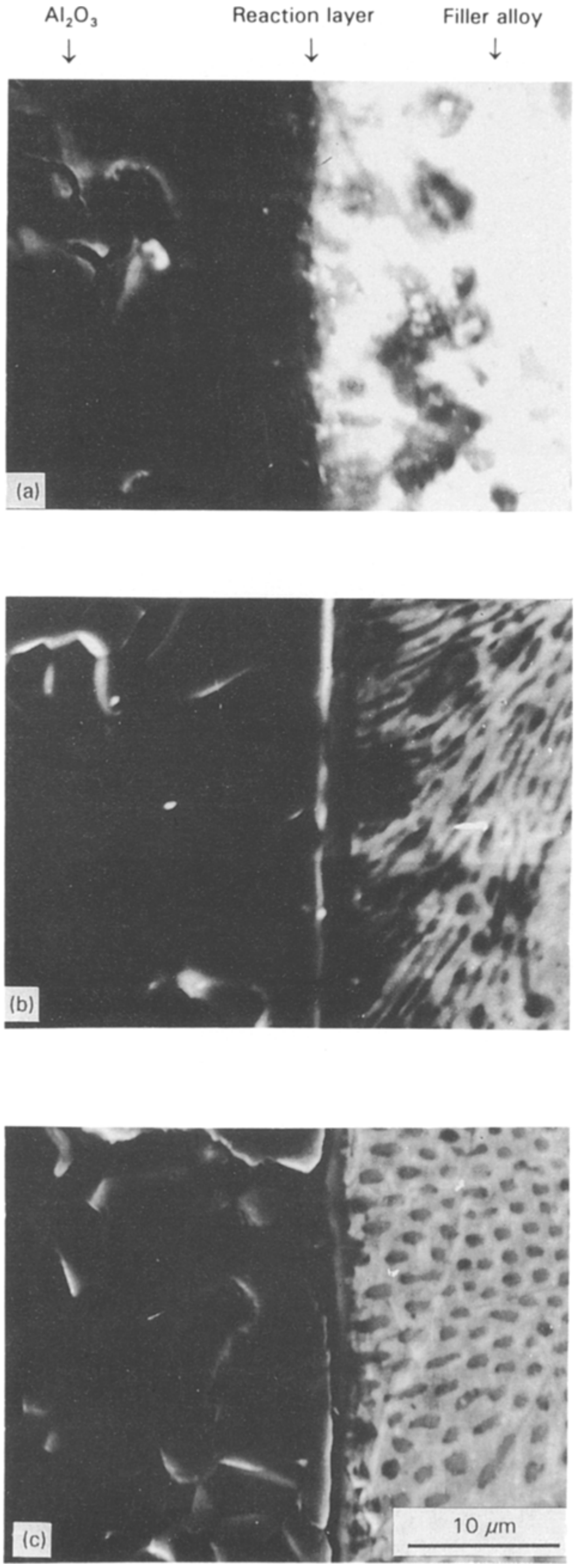


Figure 3. The microstructures of Al_2O_3/Ag–Cu–Ti interface at 1123 K for different time of (a) 0 ks, (b) 0.9 ks and (c) 2.7 ks.

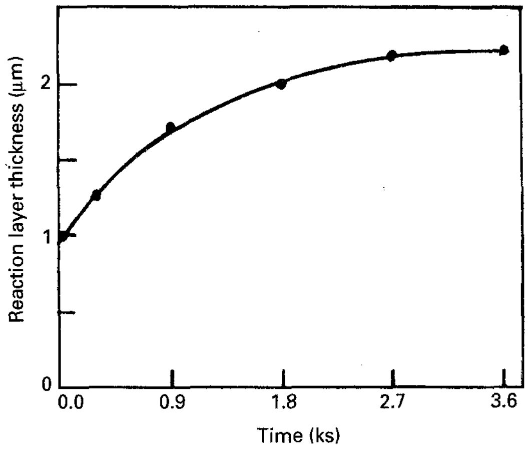


Figure 4. The effects of the holding time on the reaction layer thickness at the Al_2O_3/Ag–Cu–Ti interface heated at 1123 K.

layer is too thin, it is difficult to analyse the reaction products layer by layer as mentioned above.

The results of XRD analyses for samples heated at 1073 K and 1123 K were the same; Fig. 6 shows the XRD results for a sample heated at 1123 K for 1.8 ks. After mechanically removing the filler metal from the surface of Al_2O_3, a hard metal reaction layer appeared. XRD (Fig. 6a) showed that a thin layer of Ag and Cu still existed on the reaction layer. When chemically removing the Ag–Cu layer in 50% HNO_3 for about 60 s (in fact, it cannot be chemically removed further), a silver-grey colour layer appeared and XRD (Fig. 6b) showed that reaction products were Cu_2Ti_4O and AlTi. After mechanically removing this layer partially, XRD (Fig. 6c) showed that the remnant reaction layer was also composed of Cu_2Ti_4O and AlTi, but the peak height of AlTi increased while that of Cu_2Ti_4O decreased. Therefore, it can be suggested that the volume fraction of AlTi increased and that of Cu_2Ti_4O decreased when closer to the Al_2O_3.

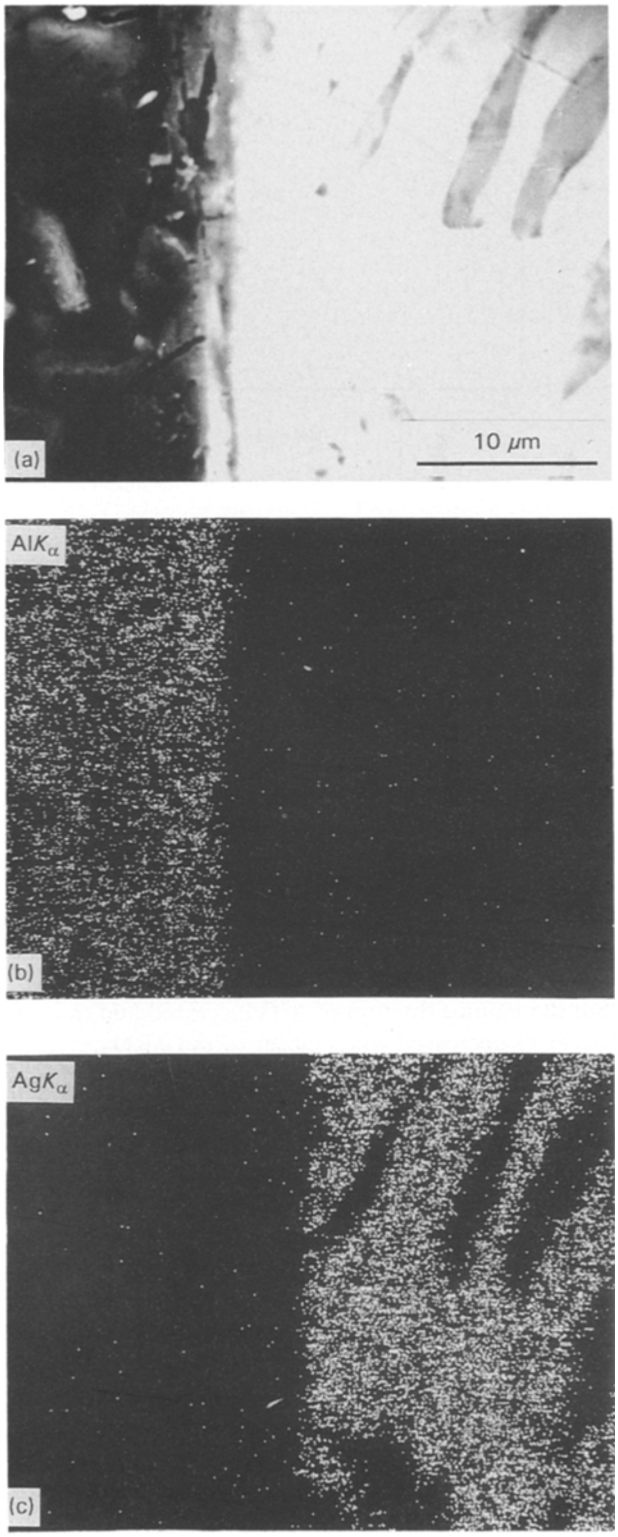
Using the same method, the reaction products at the interface of Al_2O_3/filler metal heated at 1173 K or above were analysed by XRD, and the reaction products were different from that at 1123 K or below. Fig. 7 shows the results of the sample heated at 1173 K for 1.8 ks. It can be seen that the reaction products were composed of Ti_2O, TiO and $CuTi_2$. It is also notable that the reaction products adjacent to the filler metal were $CuTi_2$ (Fig. 7a, b) and Ti_2O, TiO at the reaction layer near the ceramic (Fig. 7c, d). There were two distinct layers at the interface, which was consistent with the results of EDX elemental distribution and SEM interfacial microstructure.

Based on all of the above observations, it is concluded that a layer transition structure with $Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + CuTi_2/CuTi_2/$Ag–Cu is formed for samples heated at or above 1173 K. This is shown in Fig. 8.

4. Discussion

4.1. Interfacial reaction mechanism

There are some points of disagreement on the interfacial reaction between titanium-containing filler metal and alumina ceramics in the theoretical description and experimental results. On the basis of oxidation–reductions alone, titanium should not react with alumina ceramics even at higher temperatures [6], for example, the following reactions were applicable at



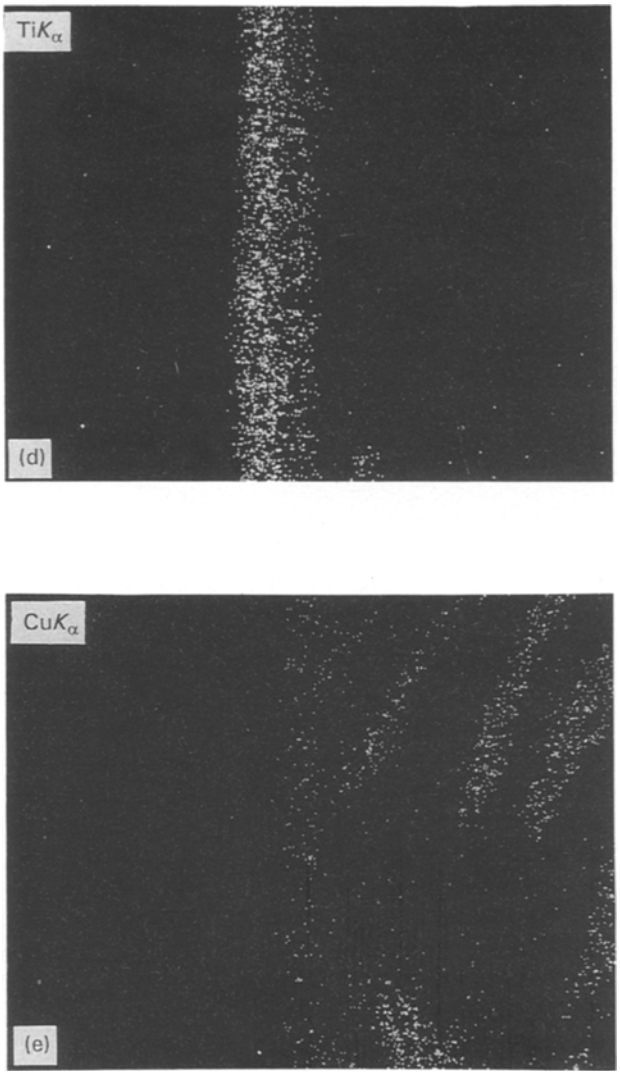


Figure 5. Images of (a) SEM and of (b–e) AlK_α, AgK_α, TiK_α and CuK_α X-rays at the same area heating at 1173 K for 1.8 ks.

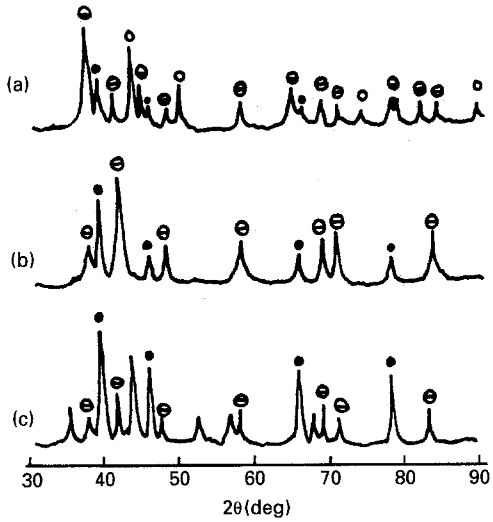


Figure 6. XRD patterns of interface reaction layer between Al_2O_3 and Ag–Cu–Ti filler metal heated at 1123 K for 1.8 ks. Unmarked peaks belong to alumina. (a) Apparent reaction layer after mechanically removing Ag–Cu brazing filler, (b) true reaction layer after chemically removing thin Ag–Cu layer in 50% HNO_3 for 1 min, (c) the remnant reaction layer after mechanically removing the true reaction layer partially, ◒, Ag; ○, Cu; ●, AlTi; ⊖, Cu_2Ti_4O.

2073 K

$$\mathrm{Ti\,(l)} + 1/2\mathrm{O_2\,(g)} \rightarrow \mathrm{TiO\,(S)} \qquad (1)$$

$$\Delta G^\circ_{(\mathrm{TiO})} = -284.519\ \mathrm{kJ\,mol^{-1}}$$

$$2/3\mathrm{Al\,(l)} + 1/2\mathrm{O_2\,(g)} \rightarrow 1/3\mathrm{Al_2O_3\,(s)} \qquad (2)$$

$$\Delta G^\circ_{(\mathrm{Al_2O_3})} = -343.096\ \mathrm{kJ\,mol^{-1}}$$

$$\mathrm{Ti\,(l)} + 1/3\mathrm{Al_2O_3\,(s)} \rightarrow \mathrm{TiO\,(s)} + 2/3\mathrm{Al\,(l)} \qquad (3)$$

$$\Delta G^\circ = +58.577\ \mathrm{kJ\,mol^{-1}}$$

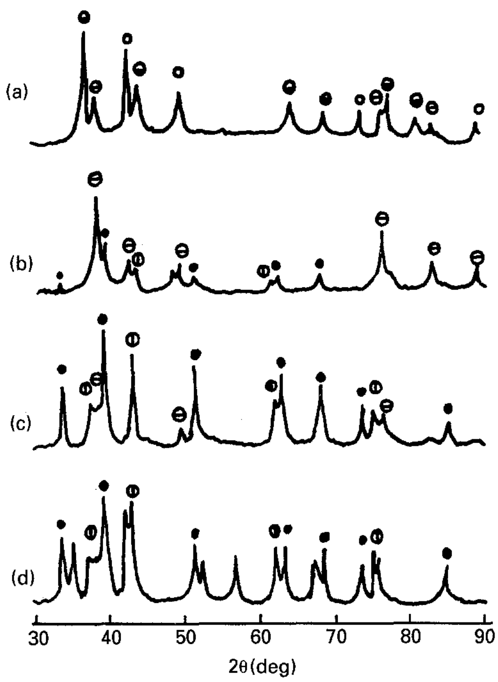


Figure 7. XRD patterns of interface layer between Al_2O_3 and Ag–Cu–Ti heated at 1173 K for 1.8 ks. Unmarked peaks belong to alumina. (a) Apparent reaction layer after mechanically removing Ag–Cu brazing filler, (b) true reaction layer after chemically removing thin Ag–Cu layer in 50% HNO_3 for 1 min, (c) and (d) the remnant reaction layer after mechanically removing the reaction layer partially, ◒, Ag; O, Cu; ●, Ti_2O; ⦶ TiO; ⊖, $CuTi_2$.

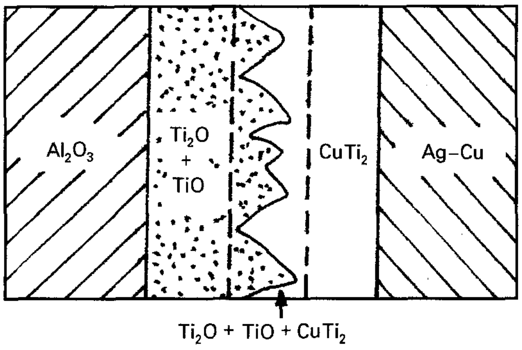


Figure 8. Schematic microstructure at the interface of Al_2O_3/Ag–Cu–Ti heated at or above 1173 K.

Thus, on the basis of these reactions, Al_2O_3 would be more stable because of its lower free energy of formation and higher free energies of the reaction products formation. However, titanium has been found to react with alumina ceramics [10–14]. Moorhead *et al.* [8] thought that this apparent anomaly could be explained on the basis of the free energies of solution of oxygen in the titanium and, to a lesser degree, on the solubility of aluminium in titanium. Oxygen is soluble in titanium up to 34 at % (independent of temperature), and aluminium is soluble up to 15 at % (at 1273 K), the reaction may proceed with the reaction products soluble to a considerable extent in the molten filler metal.

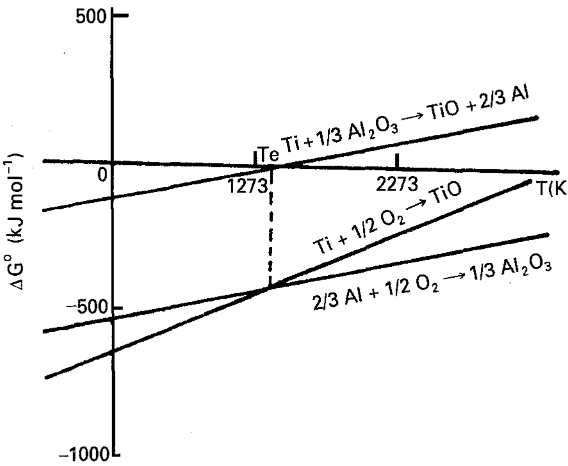


Figure 9. Variation with temperature of ΔG° for reactions 1–3.

We think it is not sufficient to explain that Equation 3 cannot occur at other temperatures simply with the thermodynamic calculation at 2073 K. As is known, the standard free energy change ΔG° varies with temperature and whether the reaction given by Equation 3 will occur or not is mainly dependent on the value of $\Delta G^\circ_{(TiO)} - \Delta G^\circ_{(Al_2O_3)}$. According to the van't Hoff equation

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H^\circ}{T^2} \qquad (4)$$

when the reaction is under constant pressure and without phase transformation for reactants and products, the enthalpy is independent of temperature. Integration of Equation 4 gives

$$\Delta G^\circ = \Delta H^\circ + cT \qquad (5)$$

where, c is a constant of integration. Equation 5 indicates that a plot of ΔG° versus T is a straight line of slope equal to c.

The free energies of formation of TiO (Equation 1) and Al_2O_3 (Equation 2) are $-412.216\,\mathrm{kJ\,mol^{-1}}$ and $-410.264\,\mathrm{kJ\,mol^{-1}}$ at 1373K [15], -284.519 kJ mol^{-1} and -343.096 kJ mol^{-1} at 2073 K [6], respectively. Therefore, the free energy changes of formation of TiO and Al_2O_3 can be represented by the equations

$$\Delta G^\circ_{(TiO)} = -662.102 + 0.182\ T \qquad (6)$$

$$\Delta G^\circ_{(Al_2O_3)} = -542.072 + 0.096\ T \qquad (7)$$

then, the free energy change ΔG° for Equation 3 is

$$\Delta G^\circ = \Delta G^\circ_{(TiO)} - \Delta G^\circ_{(Al_2O_3)} = -120.030 + 0.086\ T \qquad (8)$$

when $\Delta G^\circ = 0$, the equilibrium is established. So we can obtain an equilibrium temperature $T_e = 1396$ K for Equation 3. If $T > T_e$, Equation 3 cannot occur in a positive direction, and if $T < T_e$, it can occur not only due to the decrease of the free energy of the system but also due to the increase of entropy. The relationship between the free energy changes and temperature is shown in Fig. 9. Although the calculations are made approximately, it can predict the tendency of the reactions.

From above thermodynamic calculations Ti can react with Al_2O_3 to form TiO in the temperature range 1173–1323 K. Because of the lack of the thermochemical data it is difficult to explain the formation of other reaction products from the viewpoint of thermodynamics.

The chemical interaction in the system studied can be described by the reduction reaction of the alumina with titanium in the alloy and dissolved into the filler alloy, followed by precipitation of AlTi, Ti_2O or TiO at the interface at different heating temperatures. With the increase in temperature and time, titanium diffuses from the filler metal into the interface near the Al_2O_3, the above reactions may proceed and the reaction layer thickness be increased. When a continuous thin layer of AlTi, Ti_2O and TiO formed, it was difficult for titanium to diffuse further through the interface, therefore, further reaction was restricted, and because of the excessive titanium in the vicinity of Ti_2O, TiO or AlTi layer, Cu_2Ti_4O or $CuTi_2$ nucleated and grew at the interface.

Kritsalis *et al.* [10] 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 alloy according to the micrographic observations and the microprobe line scans of composition. One layer near the Al_2O_3 was titanium monoxide, $TiO_{1 \pm x}$, with $x \leqslant 0.05$ and another layer near the alloy corresponded to the compound Cu_2Ti_2O. Naidich *et al.* [11] reported the formation of the metallic-type oxide TiO continuous layer at the Cu/Al_2O_3 interface. Cho *et al.* [12] found δ-TiO and γ-TiO present at the interface of Al_2O_3/Ag–Cu–0.5Ti joints. Santella *et al.* [13], reported the Cu_3Ti_3O phase presented in the Ag–Cu–Sn–2Ti/Al_2O_3 system. Naka *et al.* [14] found $(Al, Ti)_2O_3$ and TiO_x were formed at the interface of Al_2O_3/CuTi joints. We have not found all of the reaction products mentioned above in the present analyses but the reaction conditions may have been different.

It was also notable that when the alumina was reduced and dissolved in liquid at or above 1173 K, oxygen in solution reacted with titanium and formed Ti_2O or TiO, while the remaining alloy became richer in Al. In fact, the analyses revealed that the Al concentration in the alloy was still low compared with the expected value at equilibrium. This was probably due to the fact that, after a transition period, the reaction continued very slowly by diffusion through the continuous layer of titanium oxide formed at the interface.

Figs 2 and 4 show that the reaction layer thickness increased with the increment of temperature and time, but the rate of increment reduced as the temperature became higher and the time became longer. The growth rate of the reaction layer in this process can be represented approximately by Fick's law as

$$X = k\,(\mathrm{D}t)^{\frac{1}{2}} \tag{9}$$

where X is the reaction layer thickness, and k is a material coefficient. The relationship of Equation 9 was confirmed from the results of Fig. 10. Therefore, the growth rate of the reaction layer obeys the parabolic rate law, and it is governed by the diffusion of participating elements. Generally, the thermal variation of k follows the Arrhenius law,

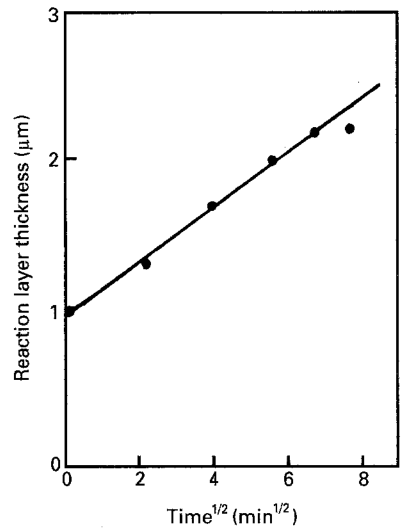


Figure 10. The relation of the reaction layer thickness and holding time at Al_2O_3/Ag–Cu–Ti interface heating at 1123 K.

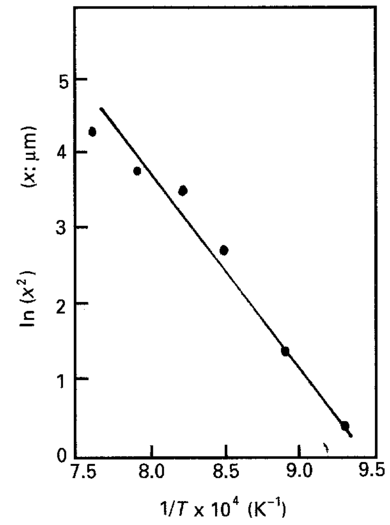


Figure 11. The relation of the reaction layer thickness and heating temperature at Al_2O_3/Ag–Cu–Ti filler metal interface.

$$k = k_0 \exp\,(-Q/RT) \tag{10}$$

where k_0 is a material constant and Q the activation energy for diffusion. As the holding time was constant (1.8 ks), the following equation is obtained using Equations 9 and 10

$$\ln(X^2) = -Q/RT + \ln K \tag{11}$$

The relationship of Equation 11 is confirmed from the result of Fig. 11. The activation energy can be calculated from the slope of the $\ln(X^2) - 1/T$ straight line. Because of the lack of activation energies of the diffusion of participating elements in the reaction layer, it is difficult to analyse the controlled process from the thermodynamic. However, according to the fact that the interfacial reaction products were compounds of titanium and the reaction layer thickness was related to with the titanium content concentrated at the interface, it can be suggested that the reaction layer growth was controlled mainly by the diffusion of titanium in the reaction layer.

4.2. Stability of joined Al_2O_3

Generally, the bonding strength at room temperature with a growing reaction layer is thought to be influenced by two factors: the reaction layer strength and interfacial bonding strength between the reaction layer and the ceramic. Interfacial bonding strength was presumed to be sum of chemical bonding strength at the interface and mechanical interlocking strength of the interface. In the system, the reaction between the ceramic and the alloy occurred strongly, such as Al_2O_3/Ag–Cu–Ti joints, and the contribution of chemical bonding to the joint strength was greater than that of mechanical interlocking, while the strength of the reaction layer itself was mainly dependent on the interfacial morphologies. When the heating temperature was low and the holding time was short, the interfacial reaction was insufficient and both strength of the interfacial bonding and the reaction layer were low. when the heating temperature was higher and the holding time was longer, the strength of the reaction layer may have been decreased because the amount of brittle reaction products increased. On the other hand, the true contact area between the reaction layer and the ceramic decreased (Fig. 1c) due to the thermal expansion mismatch and the larger difference of temperature from joining temperature to room temperature, and this may result in a decrease in joint strength. Therefore, a stable and highly reliable joined interface of Al_2O_3 may be obtained under a suitable joining temperature and holding time from a point of view of the interfacial microstructures and morphologies.

5. Conclusion

The interfacial reaction of Al_2O_3 and Ag–Cu–Ti alloy was investigated by scanning electron microscope and X-ray diffraction, respectively. The effects of joining temperature and holding time on the interfacial reaction were also evaluated. Results of testing have shown that the alumina can strongly react with Ag–Cu–Ti alloy and the joining conditions have a large influence on the interfacial reaction. With an increase in temperature and holding time, the reaction layer thickness was increased but the rate of increment decreased when the temperature and time increased further and its growth was mainly controlled by the diffusion of titanium through the reaction layer. The reaction products were Cu_2Ti_4O and AlTi at or below 1123 K. However, there were two distinct layers at the interface at or above 1173 K, 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 layer transition structure with $Al_2O_3/Ti_2O + TiO/Ti_2O + TiO + CuTi_2/CuTi_2$/Ag–Cu formed at the interface.

According to the analyses of interfacial microstructures and morphologies, a lower or a higher joining temperature and a shorter or a longer holding time were disadvantageous for a stable and highly reliable joined interface.

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Received 31 January
and accepted 22 July 1994