JOURNAL OF MATERIALS SCIENCE 27 (1992) 2061–2066

Interfacial reaction product and its effect on the strength of copper to alumina eutectic bonding

SUNG TAE KIM, CHONG HEE KIM
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Cheongryang, Seoul, Korea

Cu–Cu_2O eutectic bonding of copper to alumina has been studied at 1075 °C in nitrogen gas. In order to elucidate the reaction at the Cu/Al_2O_3 interface, the bonding time was prolonged up to 24 h at 1075 °C in nitrogen gas. $CuAlO_2$ was found at the Cu/Al_2O_3 interface, and it seems that $CuAlO_2$ was formed even with a short bonding time. $CuAlO_2$ enhanced the bonding strength. There seem to be two kinds of bonding mechanism working at the Cu/Al_2O_3 interface.

1. Introduction

With the development of new ceramic materials, there has been increasing demand for methods to join ceramic components to metal structures, and many bonding methods have been developed [1–3]. Cu–Cu_2O eutectic bonding is one of several ways of bonding copper to ceramics [4, 5]. It is used in electronic industries to manufacture copper-bonded alumina substrates for power semiconductor applications. The basic idea is to form a eutectic liquid around the copper that wets the alumina substrate. Generally, the bonding is carried out at a temperature slightly above the Cu–Cu_2O eutectic temperature, 1065 °C, in a slightly oxidizing atmosphere. Many workers have studied the bonding mechanism and the role of oxygen. O'Brien and Chaklader have [6] demonstrated that oxygen promotes wetting of copper to sapphire. Oxygen-rich liquid copper is known to form $CuAlO_2$ [7]. Yoshino [8] reported a critical concentration of oxygen far less than the eutectic concentration, above which bond strength shows no further increase. But it is not yet certain what is the reaction product at temperatures between 1065 and 1083 °C at the Cu/Al_2O_3 interface. The effect of interface layer formation on the mechanical properties of copper-to-alumina bonding is not known either. The purpose of the present study is to elucidate the interfacial reaction at temperatures between 1065 and 1083 °C, and to examine its effect on the mechanical properties of copper-to-alumina bonding. For these purposes, the bonding time was prolonged up to 24 h and microstructure and flexural strength were examined.

2. Experimental procedure

Alumina was prepared by sintering Al_2O_3 powder (AKP-20, Sumitomo Chemicals, Tokyo) without sintering aids. Sintering was done in a box furnace with a Kanthal Super heating element at 1600 °C for 2 h in air. Sintered alumina had 98% theoretical density and an average grain size of 5.8 μm.

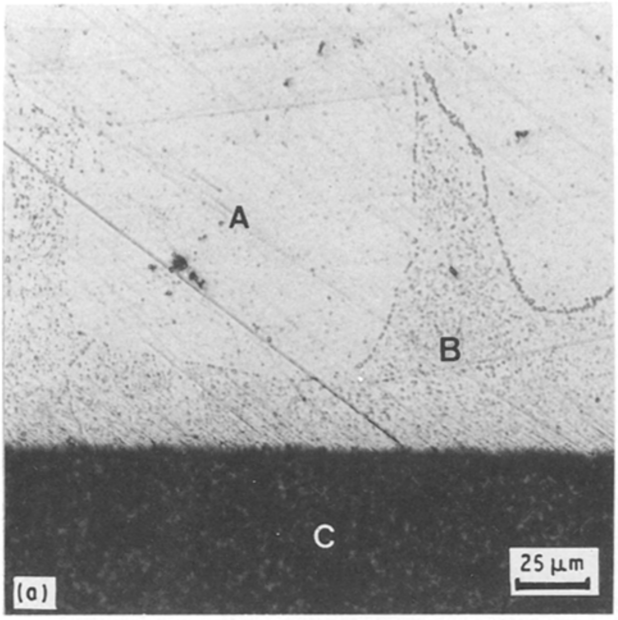
Two kinds of joining couple were prepared in this study. For microstructural examination, a sessile drop experiment was carried out using electrolytic copper machined into small cylinders, 5 mm in diameter and in length. The contact angle was not measured. For mechanical testing, sandwich-type joining couples were prepared using a commercial oxygen-free copper 0.03 mm thick. In all experiments, copper was cleaned in dilute nitric acid for 30 s, agitated in acetone and dried in hot air. Just after cleaning, the bonding experiment was performed.

Bonding was carried out in an alumina tube furnace at 1075 °C in flowing nitrogen gas. For the exact measurement of temperature and oxygen partial pressure, a CaO-stabilized ZrO_2 oxygen sensor was inserted through one end of the alumina tube. The other end of the tube was sealed with rubber stopper. The temperature was raised at 6 °C min^{-1} and the bonding time was varied from 10 min up to 24 h at 1075 °C. After bonding, specimens were furnace cooled.

For mechanical testing, sandwich-type joining couples were ground flat and diamond-polished on the tensile surface, and then cut into bend bars about $40 \times 2 \times 2$ mm, so that the interface was at the mid-plane of the bar, perpendicular to its long dimension. The surfaces of individual bend bars were ground flat and paralleled, and the edges were bevelled. Bars were tested at room temperature using Instron (Model No. 1127, Instron, USA) at a cross-head speed of 0.5 mm min^{-1}. The inner and outer spans of the four-point jig were 6 and 12 mm, respectively. Five or ten bars were tested for each condition.

The copper/alumina interface was analysed in several ways for the determination of reaction product and the microstructure of the interfacial region. Specimens from the sessile drop experiment were sectioned perpendicular to the interface, encapsulated in resin,

0022-2461 © *1992 Chapman & Hall*



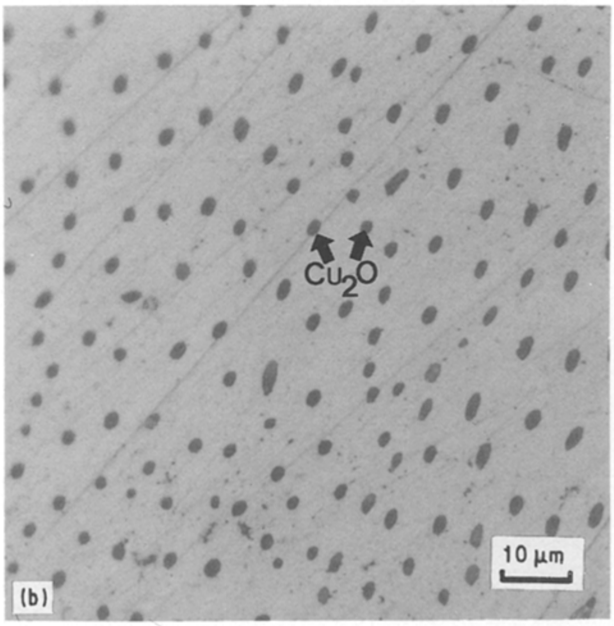


Figure 1 Optical micrographs showing (a) cross-section of the Cu/Al_2O_3 specimen bonded at 1075 °C for 10 min, and (b) magnified image of eutectic region of (a).

and then given a metallographic polish that was finished with 0.05 µm Al_2O_3 lapping. Polished cross-sections were examined with an optical microscope. Compositional analysis at the interface was carried out using an Auger electron beam microprobe (PHI 610, Perkin–Elmer, USA). The fracture surface of bend bars was examined with a scanning electron microscope (SEM).

The microstructure and phase analysis of the reaction product were examined in plan view after etching away unreacted copper with HNO_3 solution. The specimens obtained after etching were examined by SEM and X-ray diffractometor (XRD).

3. Results and discussion

3.1. Microstructure of interface

Cu/Al_2O_3 bonding was achieved by heating at 1075 °C for 10 min in nitrogen gas. Fig. 1 is the cross-sectional microstructure of Cu/Al_2O_3 bonding examined with the optical microscope. SEM was not suitable for examining the polished interfacial microstructure as only a vague image could be obtained. In Fig. 1a, A is the Cu matrix, C is Al_2O_3 and B is the Cu–Cu_2O eutectic region formed on Cu. Eutectic liquid was formed only around the Cu surface, and the shape of bulk Cu was remained unchanged after bonding. Fig. 1b is the magnified microstructure of the eutectic region, and presents a typical microstructure of Cu–Cu_2O eutectic liquid [5]. It consists of small particles in the Cu matrix, which are considered to be Cu_2O precipitates.

In Cu/Al_2O_3 eutectic bonding, exact temperature control is a critical factor. If the bonding temperature is below 1065 °C, Cu–Cu_2O eutectic liquid would not be formed and bonding could not be achieved. If the temperature is above 1083 °C, bonding might be achieved but the shape of the Cu would be deformed after bonding. Thus the temperature was kept successfully between 1065 and 1083 °C during the bonding experiment.

There are many contradicting reports on the reaction product of Cu/Al_2O_3 eutectic bonding. Sun and Driscoll [5] considered that $CuAlO_2$ would be formed at the Cu_2O/Al_2O_3 interface and its thickness would be about 10.0 nm. Lishi *et al.* [9] reported that $CuAl_2O_4$ was found at the interface. Recently, Yoshino [8] suggested that an unknown phase which is more unstable than $CuAlO_2$ would be formed.

In order to find the reaction product, the Cu/Al_2O_3 interface was observed using the optical microscope with high magnification (Fig. 2a). Microstructural observations provided no apparent evidence of a reaction between Cu and Al_2O_3. However, this result is not conclusive: a reaction product thinner than 0.1 µm would not be observable in cross section [10]. If the reaction rate is very slow, the amount of reaction product formed after a short reaction time will be very small and may be hard to detect at the interface. Thus the bonding time was prolonged upto 24 h with a view to making an observable amount of reaction product. If no reaction product is found even after a long reaction time, it can reasonably be concluded that there is no reaction at this temperature, and that bonding is achieved by Van der Waals force.

As expected, a reaction product was formed at the longer reaction time (Fig. 2b–d). At 6 h, its existence was hard to show clearly because of Cu_2O precipitates located at the interface. Over 12 h, it was formed as a continuous layer and its thickness increased continuously with time (Fig. 2c, d). When the surface of Al_2O_3 was examined with SEM after etching away the Cu, fine crystals about 1 µm were observed (Fig. 3). Considering the average grain size of Al_2O_3, these fine crystals should be the interfacial reaction product of Cu/Al_2O_3 eutectic bonding. XRD analysis revealed that $CuAlO_2$ was formed on the Al_2O_3 surface (Fig. 4b). Thus the fine crystals formed on the Al_2O_3 surface were concluded to be $CuAlO_2$. No new phase could be found by XRD in specimens reacted for 10 min.

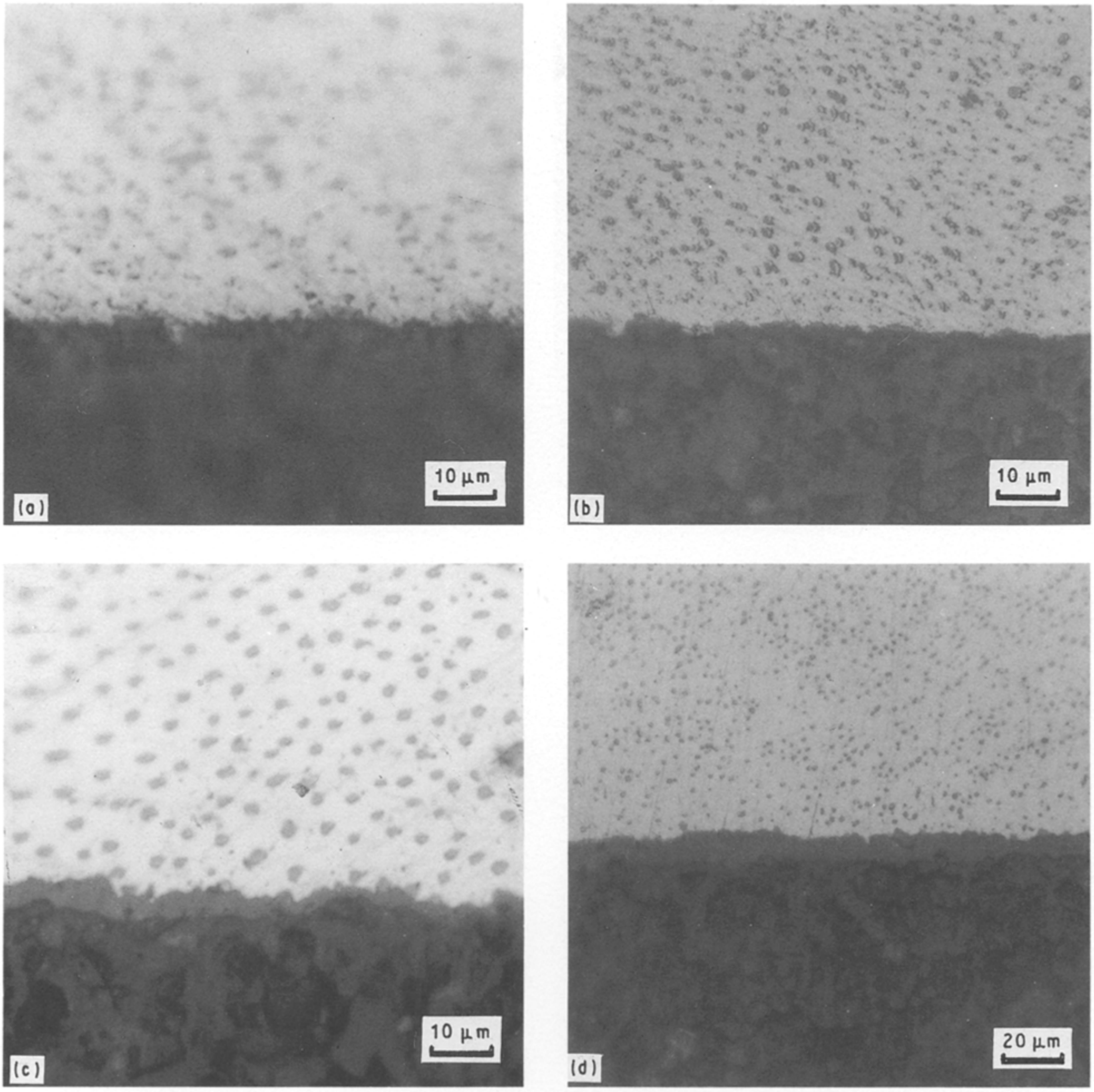


Figure 2 Optical micrographs showing the microstructural change of Cu/Al_2O_3 interface with time: (a) 10 min; (b) 6 h; (c) 12 h; (d) 24 h.

The thickness variation of $CuAlO_2$ with time was measured (Fig. 5), and showed a linear dependence on time. This means that growth of the $CuAlO_2$ layer is a reaction-controlled process: if it was a diffusion controlled process, it would show a parabolic dependence on time. The linear growth rate of the $CuAlO_2$ layer was calculated from the slope of Fig. 5 to be $\sim 8 \times 10^{-5}$ μm s^{-1}. Thus the $CuAlO_2$ formation is a very slow reaction. By assuming a linear dependence, its thickness at 10 min was extrapolated, and the calculated value was about 0.05 μm. This value is beyond the resolution of optical microscope or XRD. Thus it may be hard to show whether $CuAlO_2$ was formed at Cu/Al_2O_3 interface in cases of short bonding time, either by optical microscope or by XRD.

3.2. Bonding strength

Fig. 6 shows the average flexural strength variation of joined bars with time. Average flexural strength was 35 MPa for 10 min bonding, and increased with time up to 250 MPa for 20 h bonding. Over 20 h, it showed a slight decrease with time. Fig. 7 shows the fracture surface of an Al_2O_3 bar joined with Cu by heating for 10 min (a), 12 h (b) and 35 h (c), respectively. In specimens heated for short time (Fig. 7a), fracture progressed through the Cu/Al_2O_3 or Cu/Cu_2O interface. In the 12-h-bonding specimen, the fracture surface consisted of Al_2O_3 and $CuAlO_2$ (Fig. 7b). In specimens heated for more than 20 h, fracture was originated in the Al_2O_3 matrix (Fig. 7c).

It has been reported that in Cu/Al_2O_3 eutectic bonding, the Cu_2O/Al_2O_3 interface is stronger than the Cu/Cu_2O, and the Cu/Cu_2O interface is much weaker than the Cu/Al_2O_3 [8]. In the present work, the fracture surface consisted of Al_2O_3 and Cu_2O particles in 10-min specimens. The increase of flexural strength with time was attributed to the formation of the $CuAlO_2$ layer. At short bonding times, the $CuAlO_2$ was trivial and flexural strength was low. As

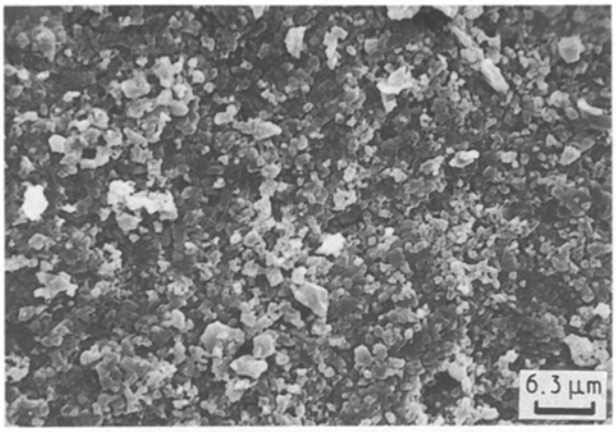


Figure 3 Scanning electron micrograph showing $CuAlO_2$ crystals formed on the Al_2O_3 surface. Cu was etched away from Al_2O_3 with HNO_3 solution.

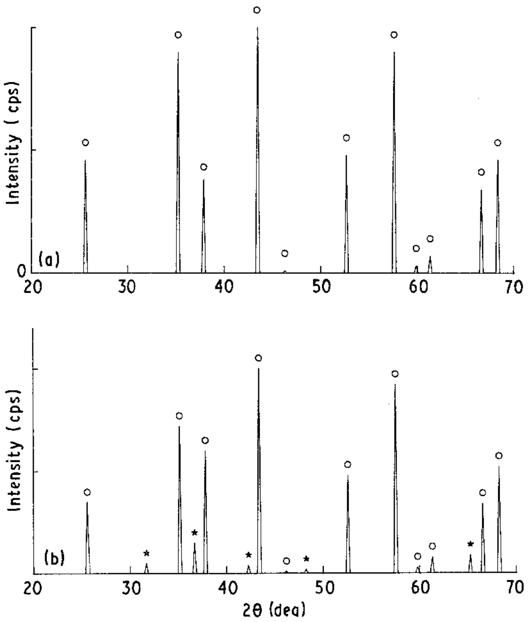


Figure 4 XRD patterns of Al_2O_3 surface after etching away Cu. Reacted for (a) 10 min and (b) 13 h. ∗, $CuAlO_2$; ○, Al_2O_3.

the bonding time was increased, the $CuAlO_2$ layer formed a continuous layer and its thickness increased. With the formation of $CuAlO_2$, the Cu/Al_2O_3 and Cu_2O/Al_2O_3 interfaces are replaced by $Cu/CuAlO_2$, $Cu_2O/CuAlO_2$, and $Al_2O_3/CuAlO_2$ interfaces. These new interfaces are considered to be stronger than the Cu/Al_2O_3 and Cu_2O/Al_2O_3 interfaces, and seem to contribute to the increase of flexural strength.

It is not yet certain whether the formation of $CuAlO_2$ reduces the thermal mismatch stress between Cu and Al_2O_3. $CuAlO_2$ has the rhombohedral space group R 3 m with $a = 0.28584$ nm, $c = 1.6958$ nm at room temperature, and is reported to have a great directionality in coefficient of thermal expansion (CTE). The CTE for the a axis is $11.0 \times 10^{-6}\,°C^{-1}$, about three times larger than $4.1 \times 10^{-6}\,°C^{-1}$ for the c axis [11]. The reported CTEs of Al_2O_3 and Cu are $8 \times 10^{-6}\,°C^{-1}$ and $20 \times 10^{-6}\,°C^{-1}$, respectively [12, 13]. If random orientation of $CuAlO_2$ is assumed, the formation of $CuAlO_2$ seems to be detrimental to

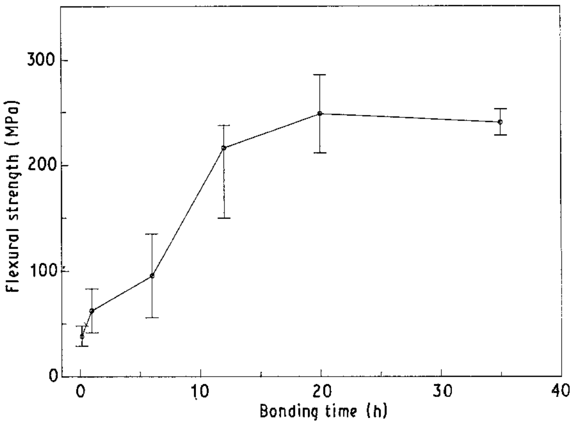


Figure 5 Thickness variation of $CuAlO_2$ with time.

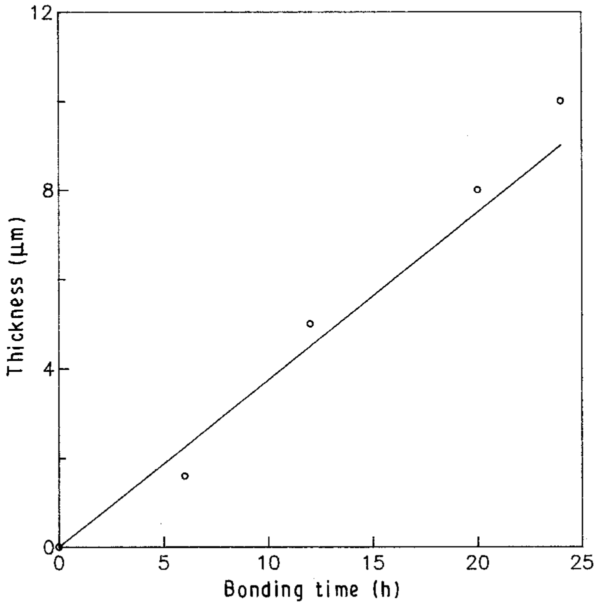


Figure 6 Variation of flexural strength with bonding time.

mechanical properties. Thus, the decrease of flexural strength over 20 h was attributed to the weakening effect of Al_2O_3 by $CuAlO_2$.

3.3. Bonding mechanism

In this study, the oxygen partial pressure measured by a ZrO_2 oxygen sensor was about 10^{-4} atm. The concentration of dissolved oxygen in the Cu could be calculated by Sievert's law [6]. From the data of Wilder [14], the Sievert's law coefficient was found to be 485

$$[O^{2-}] = 485 P_{O_2}^{1/2} \qquad (1)$$

with $[O^{2-}]$ in at % and P_{O_2} in atm.

The equilibrium concentration of oxygen is about 1.6 at % at 1075 °C [5]. The calculated oxygen concentration in Cu was about 5 at %, and this value was greater than the exact eutectic concentration. So it seems that some Cu_2O remained undissolved in the

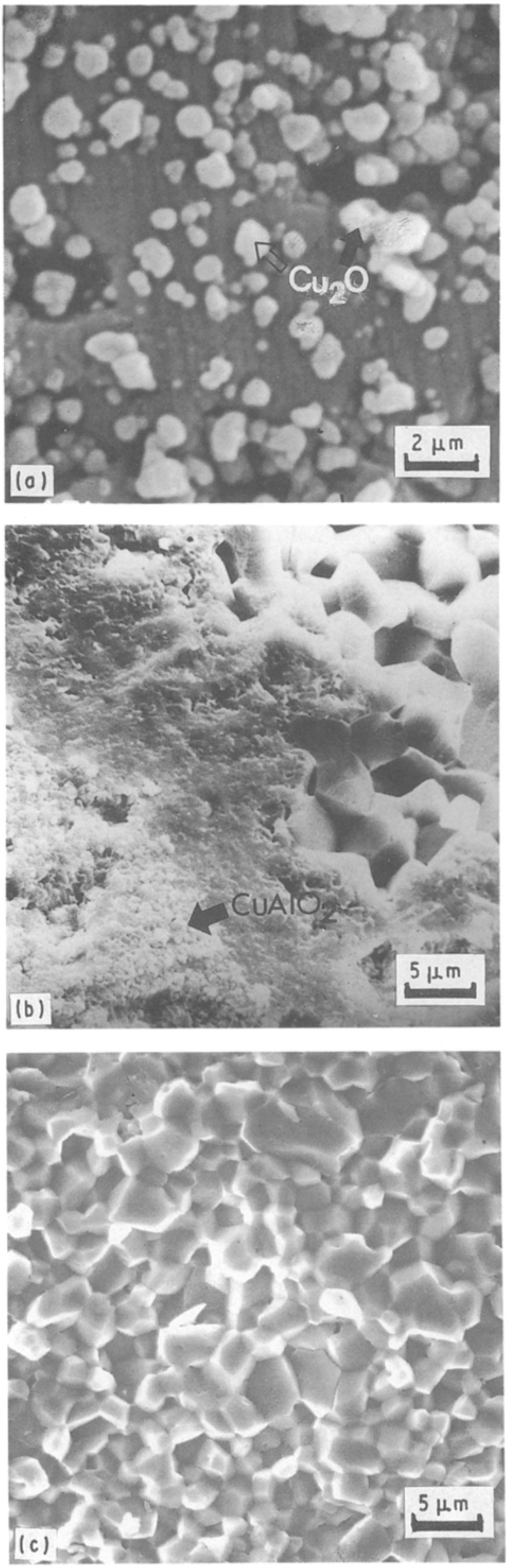


Figure 7 Scanning electron micrographs showing the ceramic part of the fractured surface of joined bars reacted for (a) 10 min; (b) 12 h; (c) 20 h.

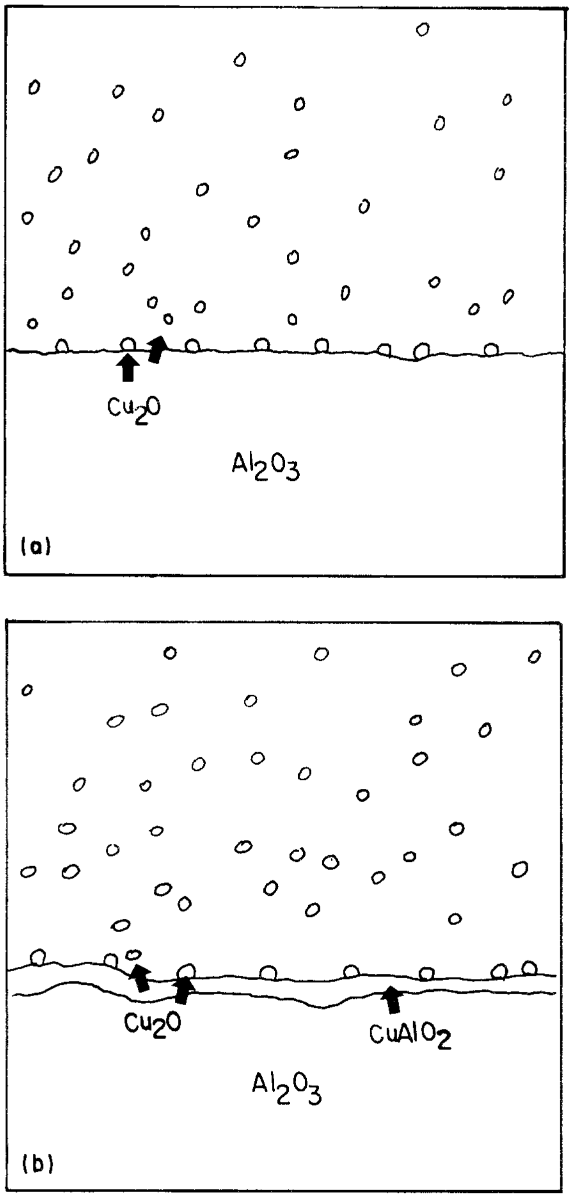


Figure 8 Schematic diagrams of Cu/Al_2O_3 interface at (a) 10 min and (b) 24 h.

Cu–Cu_2O eutectic melt. Thus, the interfacial microstructure of the 10-min specimen at bonding temperature could be drawn schematically, as in Fig. 8a. As the bonding time was prolonged, continuous $CuAlO_2$ was formed and its thickness was increased. Thus the interfacial microstructure of the 12-h specimen can be drawn as in Fig. 8b. There are two kinds of interface in Fig. 8a: Cu[O]/Al_2O_3, and Cu_2O/Al_2O_3. Here, Cu[O] represents the Cu melt with an equilibrium concentration of oxygen. At the Cu_2O/Al_2O_3 interface, a solid state reaction may occur [7], such as

$$Cu_2O(s) + Al_2O_3(s) = 2CuAlO_2(s) \qquad (2)$$

If $CuAlO_2$ is formed only by this reaction, in order to make a continuous layer Cu_2O should cover all the surface of Al_2O_3, or its number should increase with time at the interface. According to microstructural observations of the interface, the number of Cu_2O at Al_2O_3 surface does not show a great change with time (Fig. 2). This means that there are not enough Cu_2O precipitates to form a continuous $CuAlO_2$ layer at the interface, which suggests that the $CuAlO_2$ formation

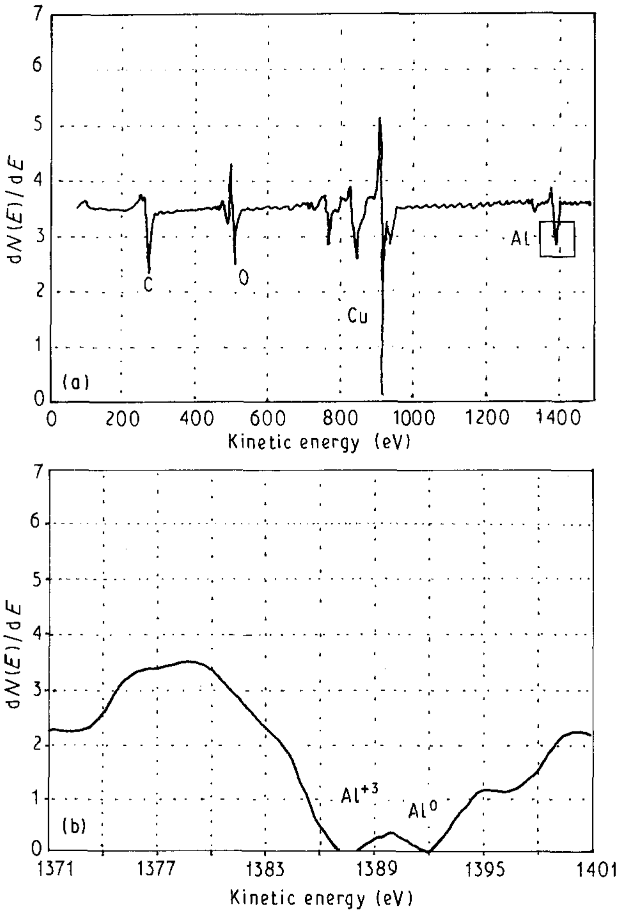


Figure 9 Auger electron spectrum of (a) Cu/Al_2O_3 interfacial region and (b) magnification of Al peak of (a).

reaction is not confined within the Cu_2O/Al_2O_3 interface as Sun and Driscoll [5] suppose, but rather occurs through the interface. Therefore, it is likely that there is another mechanism to form $CuAlO_2$ at the Cu[O]/Al_2O_3 interface.

Fig. 9a shows an Auger spectrum of the interfacial region for a 12-h bonded specimen: Al, Cu and O were detected. When the Al peak is examined with higher resolution (Fig. 9b), it can be seen that the Al peak was split in two. This demonstrates that there are two kinds of Al atom at the Cu/Al_2O_3 interface, having different valence states: one is the +3 state, and the other the 0 state of Al. The Al^{3+} peak seems to originate from Al_2O_3 and/or $CuAlO_2$. The Al^0 peak means the elementary state. As Al was not detected in used Cu, the origin of Al^0 is considered as Al_2O_3. Provided that Al_2O_3 has some solubility to Cu[O], aluminum and oxygen will go into Cu[O]. $CuAlO_2$ will be precipitated when Cu[O] is saturated with Al and O. At room temperature, Al^0 will be detected at the Cu side of the interfacial region. Thus it is proposed that the dissolution of Al_2O_3, and the precipitation of $CuAlO_2$ take place at the Cu[O]/Al_2O_3 interface. This solution and precipitation of Al_2O_3 is thought to be a very slow reaction which controls the slow growth rate of $CuAlO_2$. Once the $CuAlO_2$ layer covers all the interface, the growth of this layer will continue by diffusion of Cu, Al and O through the $CuAlO_2$ layer.

4. Conclusions

Cu–Al_2O_3 eutectic bonding was studied at 1075 °C in nitrogen gas. $CuAlO_2$ was found at the interface as a continuous layer after a prolonged bonding time. The thickness variation of $CuAlO_2$ showed a linear dependence on time within a 24 h range, which means that the formation of $CuAlO_2$ may be a reaction-controlled process. When bonding time is short, it seems that the $CuAlO_2$ thickness is too thin to be found by microscope or XRD, because the formation rate is so slow. The average flexural strength showed a monotonic increase, from 35 MPa at 10 min to 250 MPa at 20 h. Above 20 h, flexural strength decreased slightly. Fracture surface examination showed that the fracture mode changed with time. It is concluded that the Cu/$CuAlO_2$, $Cu_2O/CuAlO_2$, and $Al_2O_3/CuAlO_2$ interfaces are stronger than the Cu/Al_2O_3 and Cu_2O/Al_2O_3 interfaces. There seem to be two kinds of bonding mechanism working at the interface.

Reference

1. R. E. LOEHMAN and A. P. TOMSIA, *Amer. Ceram. Soc. Bull.* **67** (1988) 375.
2. H. MIZUHARA, E. HUEBEL and T. OYAMA, *ibid.* **68** (1985) 468.
3. J. A. PASK, *ibid.* **66** (1987) 1587.
4. F. BURGESS, U.S. Patent No. 3 766 637 (1973).
5. Y. S. SUN and J. C. DRISCOLL, *IEEE Trans.* **23** (1976) 961.
6. T. E. O'BRIEN and A. C. D. CHAKLADER, *J. Amer. Ceram. Soc.* **57** (1974) 329.
7. A. C. D. CHAKLADER, A. M. ARMSTRONG and S. K. MISRA, *ibid.* **51** (1968) 630.
8. Y. YOSHINO, *J. Amer. Ceram. Soc.* **72** (1989) 1322.
9. W. LISHI, J. HAAG and G. PETZOW, in "Microstructure and Properties of Ceramic Materials", edited by T. S. Yen and J. A. Pask (Science Press, Beijing, China, 1984) p. 125.
10. R. E. LOEHMAN, A. P. TOMSIA, J. A. PASK and S. M. JOHNSON, *ibid.* **73** (1990) 552.
11. T. ISHIGURO, N. ISHIZAWA, N. MIZUTANI and M. KATO, *J. Solid State Chem.* **41** (1982) 132.
12. "Engineering Properties of Selected Ceramic Materials" (American Ceramic Society, Ohio, 1966) p. 21.
13. E. A. BRANDES (ed) "Smithells Metals Reference Book", 6th edn (Butterworths, London 1983) p. 14–1.
14. T. C. WILDER, *Trans. AIME* **236** (1966) 1035.

Received 14 November 1990
and accepted 25 March 1991