JOURNAL OF MATERIALS SCIENCE 27 (1992) 599–606

Diffusion bonding of alumina to steel using soft copper interlayer

A. UREÑA, J. M. GÓMEZ de SALAZAR, J. QUIÑONES
Departamento Ciencia de los Materiales e Ingenieria, Metalúrgica, Facultad Ciencias Químicas, Universidad Complutense de Madrid, Spain

The diffusion bonding of a low steel to alumina has been studied in the present work. Thin foils of a soft metal (copper) were used to reduce the effects of the residual stresses produced in the joint by thermal expansion mismatch. The strength of the joint was found to be influenced by the bonding parameters, but principally by the oxygen content both on the surface and in the copper matrix. The diffusion bonds have been mechanically tested using a three-point bending test. Maximum bending strengths of 100 MPa were achieved by using a 0.1 mm copper foil, and bonding in a oxidizing atmosphere ($P_{O_2} = 10^4$ Pa). SEM and EDS investigations have shown the presence of reaction products in the copper–alumina interface which controls the mechanical properties of the joint.

1. Introduction

During recent years, significant progress has been made in the development of engineering ceramic materials. The good combination of high mechanical strengths with low thermal and electric conductivities, and excellent resistance to corrosion and wear at high temperature, means that potential fields of applications have been opened for these materials. Some of these applications could be the replacement of metallic components in internal combustion engines, industrial heat exchangers, as wear-resistant material in metal processing or as impact-resistant material in the fabrication of armour-plates for tanks [1]. Most of these applications, however require the utilitation of conventional metallic materials. It involves the formation of ceramic–metal joints. Macroscopic metal–ceramic components can be joined using different methods [2–4] but the solid state diffusion bonding is being the most investigated one.

One of these dissimilar joints that are being investigated is the union between structural steels to tough ceramic materials such as alumina for the fabrication of armour plates [5].

The alumina–steel joint presents serious difficulties [6–8]; most important the high internal stresses generated within the bond interface during cooling. It is because of the great difference between the thermal expansion coefficients of the carbon steel (12.1 $\mu m\, m^{-1} K^{-1}$) and the alumina (7.6 $\mu m\, m^{-1} K^{-1}$). For this reason, although high strength joints could be obtained in the direct bond of both materials [8], they usually fail during the cooling process because of the thermal expansion mismatch effect. This effect has been proved to be more important when the bond area increases and the bond strength depends on this design parameter.

Most authors have proposed the use of metallic interlayers to reduce the residual stresses generated during the cooling process [10–12]. Composited interlayers made by powder metallurgical techniques are being employed to accommodate the chemical and physical incompatibility that exist between those dissimilar materials [13].

Suganuma *et al.* [10] have developed a laminated interlayer of Nb–Ni for diffusion bonding of alumina to stainless steel. Hatekayama [11] substituted the Nb by Ti despite the problem of formation of brittle intermetallic compounds. Both kinds of laminated interlayers are constituted by refractory metals which makes it necessary to bond at very high temperatures (1000 to 1400 °C).

Nicholas and Crispin [12] have succeeded in achieving a strong joint between alumina and an austenitic steel by using a soft metallic interlayer. They proposed the use of a thin film of aluminium inserted between the alumina and the steel which mitigates the expansion mismatch effects because of its ductility. The presence of aluminium in this type of joint, however, limits its application temperature.

The previous limitations mean that the present authors have selected copper as the interlayer for the steel–alumina joint. Copper does not form brittle intermetallic compounds with iron and strong joints can be obtained by diffusion bonding when copper with dissolved oxygen is used [14]. Copper also has other advantages like its intermediate melting point and its low prize in relation with other soft metals which could be employed with similar results (Ag, Au or Pt).

2. Experimental procedure

2.1. Materials and preparation

The ceramic material used in this study was a 99.9%

0022–2461/92 $03.00 + .12 © *1992 Chapman & Hall*

pure ALSINT alumina, with variable Na (< 0.005%) and Mg (< 0.1%) contents supplied by CERATEM. The other material was a low carbon steel (AISI-1015) with 0.15 wt % C and 0.50 wt % Mn. Two different types of copper were used as the interlayer: an electrolytic tough pitch copper (C 11000), with 0.04 wt % in oxygen and an oxygen-free low phosphorous copper (C 10800) with 0.005 wt % P. Both metals were supplied in the form of 1 mm thick sheets and laminated to 0.1 mm to be used as intermediate foils.

Alumina and steel cylinders of 10 mm diameter and two different lengths (10 and 30 mm) were bonded together to obtain specimens for metallographic and mechanical studies. The bond surfaces were ground to an average surface roughness of 0.2 μm. A 100 μm thick copper foil in the form of a 10 mm diameter disc was placed between both faying surfaces. All surfaces to be bonded were previously cleaned with acetone in an ultrasonic bath.

Some copper discs were pre-oxidized to obtain a superficial oxide film (Cu_2O). This test consisted of annealing the copper at 500 °C for 30 minutes, under different oxygen pressures in the range of 2×10^3 to 10^4 Pa. The thickness of the Cu_2O films obtained was measured by gravimetric techniques. Values from 0.1 to 1.2 μm thickness were obtained for the different oxidation conditions which appeared (Fig. 1). These discs were afterwards used to determine the influence of the oxide layer thickness on the mechanical strength of the joint.

2.2. Bonding conditions

During the present investigation several bonding parameters were controlled. Preliminary studies on diffusion bonding of copper to iron [14, 15] determined the optimum bonding condition for this kind of joint, which is quite similar to the copper–steel joint presented in the studied bonds. The bonding temperature and pressure were kept to 1000 °C and 3 MPa, respectively. The bonding times used were changed in the range proposed for copper–iron diffusion bonds (3 to 8 h) to obtain the optimum mechanical properties [15].

Another parameter whose influence was tested, was the presence of oxygen both dissolved in the copper interlayer and presented in the bonding atmosphere. Bonding environments with different oxygen pressures (from 2×10^{-4} to 10^4 Pa) were used during the heating process in an oxidation period to reach the bonding temperature. The oxygen was introduced to obtain the oxidizing atmosphere (10^4 Pa) during the heating stage from 700 °C and for oxidations times of 3 and 30 min without load application. When the bonding temperature was reached, the oxygen was pumped to reobtain a vacuum of 10^{-3} Pa maintained during the bonding time with pressure application. This bonding cycle is schematically shown in Fig. 2.

Some specimens bonded with low oxidizing atmosphere were heat treated at low temperature (250 °C) for 10 h, after bonding. This postbond heat treatment was applied for relieving the residual stresses which originated during cooling.

3. Results

3.1. Mechanical properties of the joints

The strength of the Al_2O_3–Cu–steel joints has been measured by a three-point bend test, using cylindrical bonded specimens of 60 mm high and 10 mm diameter. The load was applied on the bond interface, working with a span between the supports of 50 mm.

3.1.1. Influence of the oxygen contents in the copper interlayer and atmosphere

The effects of the oxygen concentration dissolved in the copper film used as interlayer and in the bonding environment were in some preliminary tests all made, with the same bonding parameters ($T_b = 1000$ °C; $P_b = 3$ MPa; $t_b = 5$ h). It was shown that the increase of oxygen content improves the mechanical strength

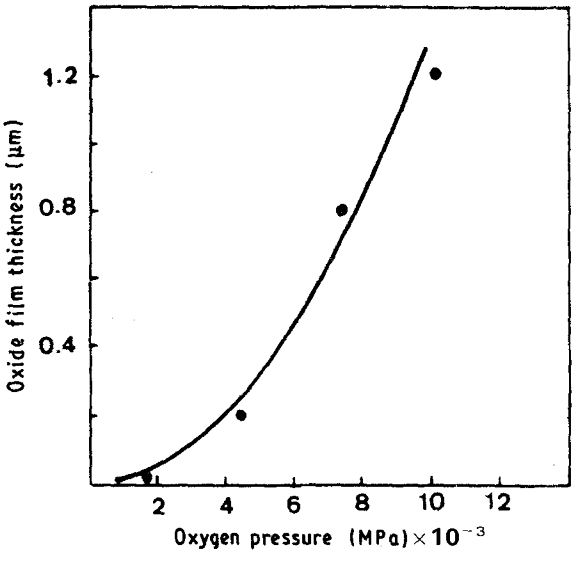

Figure 1 Thickness of the copper oxide film plotted versus oxygen pressure ($\times 10^{-3}$) in the oxidizing atmosphere.

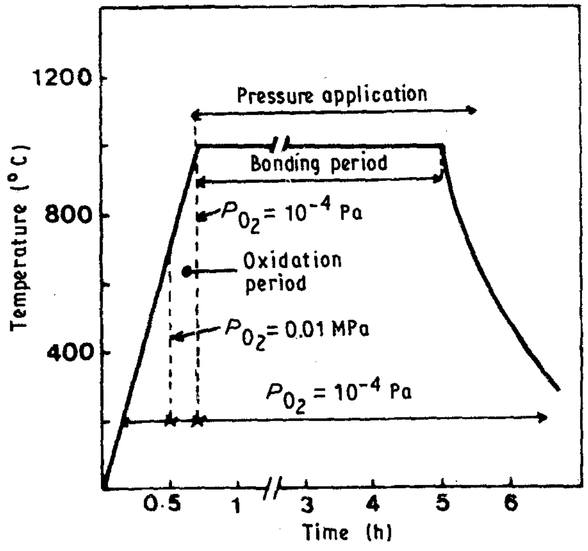

Figure 2 Scheme of the diffusion bonding cycles used.

TABLE I Bending strength of alumina-steel diffusion joints. Preliminary tests

Specimen[a]	Type of copper	Oxygen[b] pressure (Pa)	Bending strength	Post-bonding[c] heat treatment
FCA 1	C 10800	2×10^{-4}	< 5.0	No
FCA 2	C 10800	2×10^{-4}	12.5	Yes
FCA 3	C 10800	1×10^{4}	25.2	Yes
FCA 4	C 11000	2×10^{-4}	40.0	Yes
FCA 5	C 11000	1×10^{4}	52.5	Yes

[a] Bonding conditions: $T_b = 1000\,°C$, $t_b = 5$ h, $P_b = 3.0$ MPa.

[b] Oxygen pressure during heating process. Oxidizing condition ($P_{O_2} = 0.01$ MPa) applied during 3 min at 700 °C.

[c] Post-bonding heat treatment at 250 °C during 10 h.

of the joints (Table I). A maximum bending strength of 52 MPa was reached when an interlayer of C 11000 copper (0.04 wt % O_2) was used and the procedure was performed in an oxidizing environment ($P_{O_2} = 10^4$ Pa) introduced for only 3 min at 700 °C in the heating stage. Changing the C 11000 copper film by a free-oxygen copper interlayer (C 10800) and maintaining the previous bonding conditions, a decrease by more than a half in the bending strength was observed. This effect was more evident when high vacuum ($P_{O_2} = 2 \times 10^{-4}$ Pa) was used to bond. All these preliminary tests were made using bonded specimens with a low temperature heat treatment to produce stress relief. The failure in all these specimens, however, occurred preferentially through the copper–alumina interface.

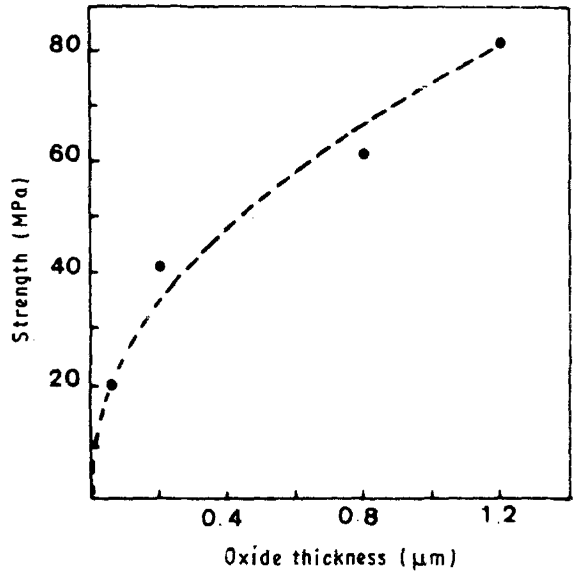

Figure 3 Dependence on the bonding strength of the oxide film thickness on copper surface.

3.1.2. Influence of the preoxidation of the copper interlayer

After the preliminary bonding test, the possibility of improving the bond strength when pre-oxidized C 11000 copper were used was studied. Fig. 3 shows the effects of the oxide film thickness on the bending strength for diffusion joints bonded at 1000 °C for 5 h, applying pressures of 5 MPa; the bonding procedures were carried out in a vacuum of 10^{-3} Pa, that means a P_{O_2} of 2×10^{-4} Pa during all the treatment. For these conditions a maximum strength of 80 MPa was obtained when an oxide film thickness of 1.2 μm was used. This thickness has been obtained by pre-oxidizing the copper at 500 °C per 30 min in an atmosphere with a P_{O_2} of 10^4 Pa.

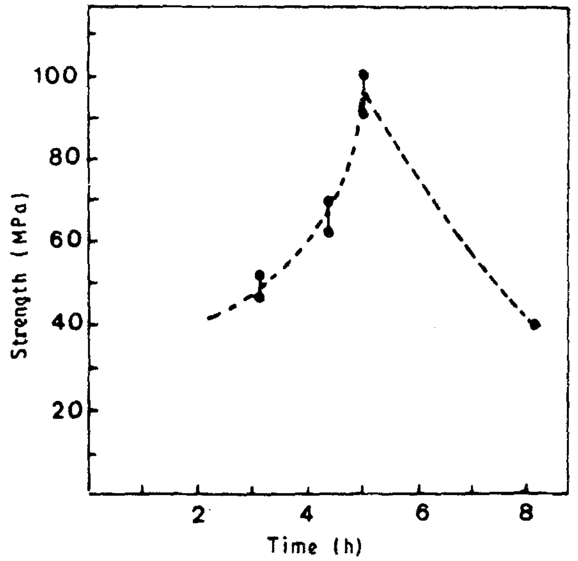

Figure 4 Bending strength plotted against bonding time for steel–copper–alumina joints bonded at 1000 °C, 5 h and 3 MPa with a P_{O_2} of 10^4 Pa in the oxidation period.

3.1.3. Influence of the bonding time for joints bonding in oxidizing atmosphere

The use of oxidizing atmospheres and preoxidized coppers improves the mechanical strength of the joints; in a third series of bonding tests, the possibility of producing the oxide film on the copper surface during the bonding procedure was investigated.

Fig. 4 shows the change of the bond strength with the bonding time for specimens, the pre-oxidizing treatment was substituted by the application of an oxidizing atmosphere ($P_{O_2} = 10^4$ Pa) during the heating up stage. For bonding times less than 5 h, to an increase in bonding time the mechanical strength of the joints is initially improved. Increasing the time up to that value, the bonding strength is, however, drastically reduced. The maximum bond strength obtained was 100 MPa for bonding times of 5 h. This value is higher than that obtained with similar bonding conditions but using pre-oxidized coppers. Under these conditions the failure was always located in the bulk ceramic except when bonding times of 8 h were used. To obtain these strengths, post-bonded heat treatment was not necessary.

3.2. Microstructural study of the bond interfaces

The Al_2O_3–Cu–steel joints have two different interfaces that could control their mechanical properties. Microstructural transformations that occurs in the copper–steel interface are completely similar to those studied by some of the present authors for the diffusion bonding of copper to iron [14, 15]. It has also been shown that it is the alumina–copper interface which really controls the mechanical properties of the studied joints. For this reason, the microstructural study was centred on that second one.

The SEM micrographs obtained for joints bonded with free-oxygen copper in a high vacuum ($P_{O_2} = 2 \times 10^{-4}$ Pa) shown that the obtained joint is only a mechanical union between both materials. Although the contact between both materials was excellent, because of the high plasticity of the copper and the great superficial porosity of the alumina, no evidence of chemical interaction between both parent materials was detected (Fig. 5). If, however, the bonding procedure is carried out in a slightly more oxidizing environment ($P_{O_2} = 2 \times 10^{-2}$ Pa) the first signs of chemical interaction appeared; isolated points of the copper surface that experience an oxidation forming Cu_2O. These oxide aggregates were generally located on the copper that penetrated into the alumina voids (Fig. 6). No reaction products between copper and alumina were, however, detected.

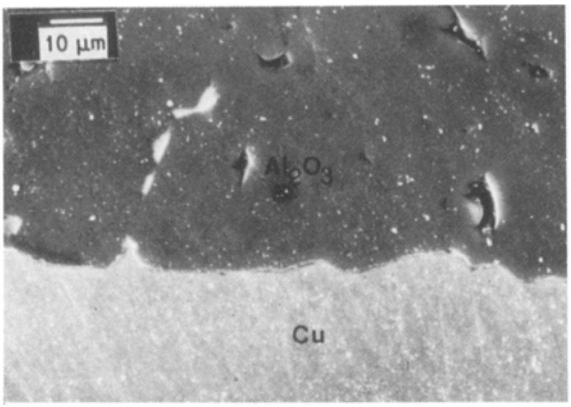

Figure 5 Microstructure of a Cu–Al_2O_3 interface bonded at high vacuum ($P_{O_2} = 2 \times 10^{-4}$ Pa).

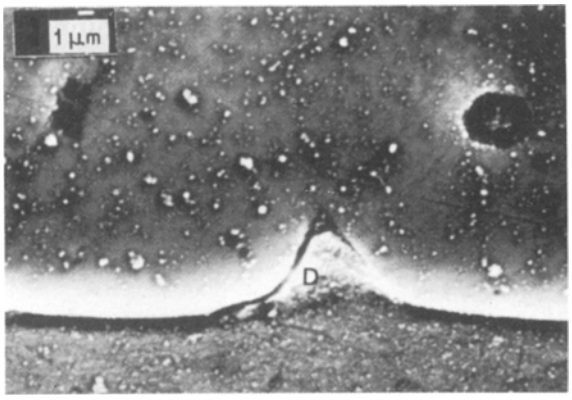

Figure 6 Cu_2O (D) formation in a superficial void of alumina ($P_{O_2} = 2 \times 10^{-2}$ Pa).

On the other hand, complex aluminium–copper oxides have been detected and indented by EDS microanalysis in the bond interface when copper interlayers with 0.04 wt % oxygen contents were used. These oxides are the hexagonal spinel $CuAlO_2$ and the cubic $CuAl_2O_4$ (Table II). The proportion of each one depends, however, on the oxygen content in the bonding atmosphere. For specimens bonded with P_{O_2} of 2×10^{-4} Pa and copper without preoxidizing treatment, the cubic spinel did not appear. Only the $CuAlO_2$ phase was present as isolated aggregates with variables sizes (3 to 10 µm), which appeared preferentially inside the alumina voids in contact with copper (Fig. 7a and b).

The increase of the oxygen content in the bonding atmosphere during the heating process produces an oxide film on the copper face which reacts with the alumina and produces an almost continuous layer of the binary oxide $CuAlO_2$ (Fig. 8). In these specimens some aggregates of the richer-oxygen spinel ($CuAl_2O_4$ have also been observed), although they are principally located in the zones close to the edge of the specimens, where the oxygen access is easier (Fig. 9).

3.3. Fracture surface study

The fractographic study carried out on specimens tested to bond provided additional information on the chemical interaction between the parent materials and its influence on the mechanical strength of the joint.

Failure in alumina–steel joints preferentially occurred through the alumina–copper interlayer interface, especially when high vacuum atmosphere or free-oxygen copper were used. On failure the surfaces of the joints bonded with free-oxygen copper in a high vacuum ($P_{O_2} = 2 \times 10^{-4}$ Pa) no evidence of formation of oxidized products was observed. The joint is produced by penetration of copper by creep deformation in the alumina voids producing a mechanical union.

TABLE II EDS microanalysis of the spinel oxides formed during diffusion bonding of copper to alumina

Phase composition	$CuAlO_2$ Calculated (wt %)	$CuAlO_2$ Theoretical (wt %)	$CuAl_2O_4$ Calculated (wt %)	$CuAl_2O_4$ Theoretical (wt %)
Al	21.90	22.04	29.70	29.75
Cu	49.30	51.83	35.10	34.98
O	28.80	26.13	35.20	35.26

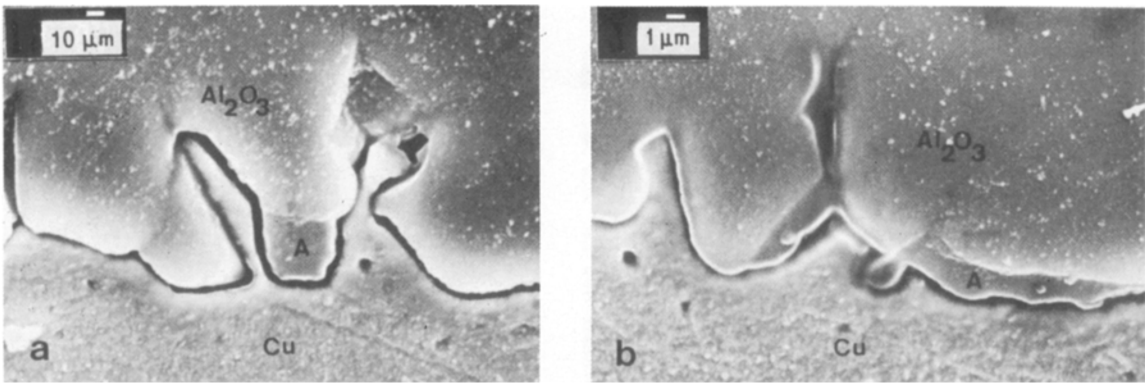

Figure 7 $CuAlO_2$ aggregated (A) formed in the C 11000 copper–alumina interface.

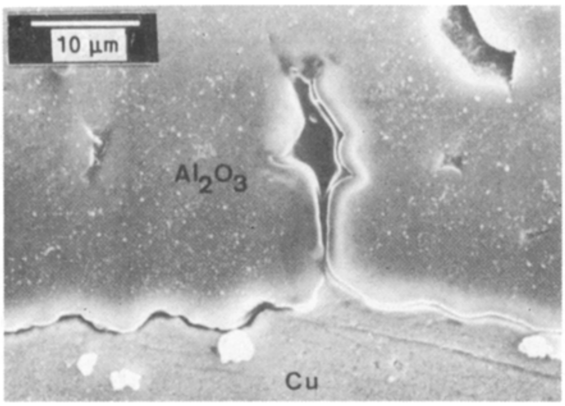

Figure 8 Continuous layer of $CuAlO_2$ spinel formed in a diffusion joint bonded with an oxidation pressure of 10^4 Pa.

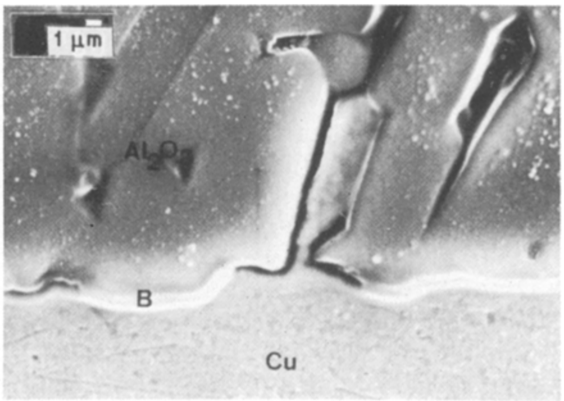

Figure 9 Detail of $CuAl_2O_4$ aggregates ($P_{O_2} = 10^4$ Pa).

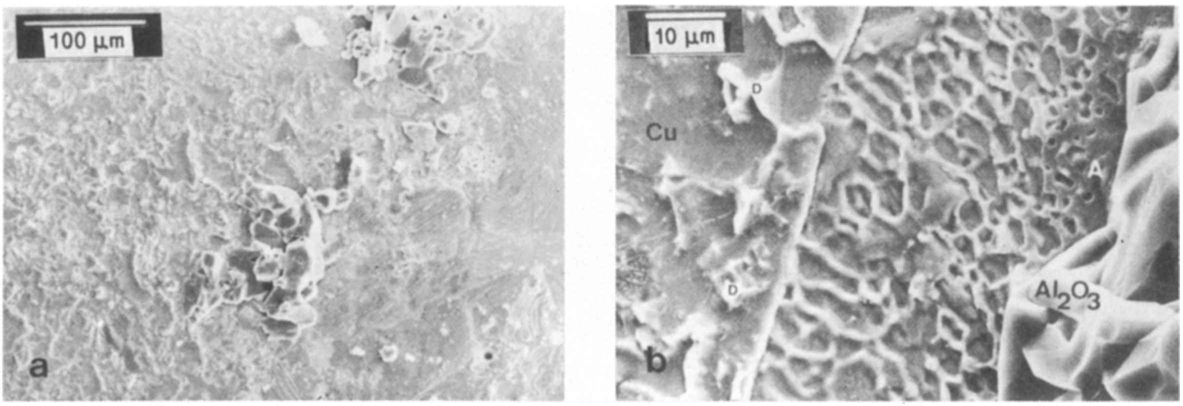

Figure 10 (Left) Fracture surface through the C 11000–alumina interface. (right) Detail of different failure zones: (A) $CuAlO_2$ spinel and (D) Copper oxide.

Increasing the oxygen content dissolved in the copper film and using an oxidizing atmosphere for a few minutes in the heating process gives a light superficial oxidation of copper. The formation of a narrow layer of the binary spinel $CuAlO_2$ is favoured. Although the failure in these joints occurred again through the Al_2O_3–Cu interface, a local rupture zone could be observed in the bulk alumina (Fig. 10a and b). The proportion of these zones decreases towards the edges of the specimen, where the joints are only produced by a mechanical effect and no spinel formation was detected.

The failure in diffusion joints bonded with C 11000 copper in an oxidizing atmosphere during the heating process ($P_{O_2} = 10^4$ Pa), always occurred through the parent alumina. In those zones, however, where the rupture was located close to the bond interface, the penetration of copper inside the interconnected void of the alumina could be observed (Fig. 11a). Inside this void, chemical interaction regions between the copper and the alumina grains were detected. They presented the formation of intermediate composition zones, similar to the "necks" formed between solid particles in sinterizing processes (Fig. 11b). The EDS

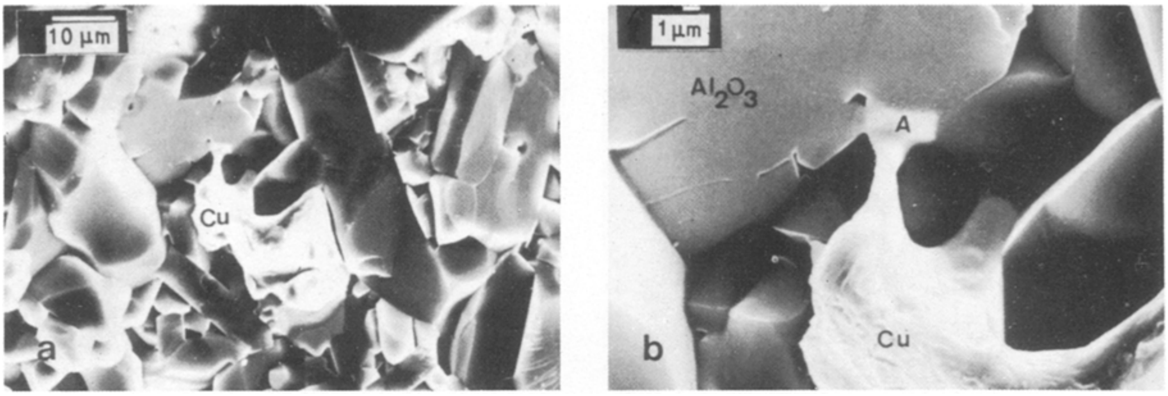

Figure 11 (a) Failure surface through the bulk alumina. (b) Detail of copper–alumina contact with spinel formation of the $CuAlO_2$ spinel (A).

microanalysis showed that there was a copper concentration gradient in the neck, with the formation of $CuAlO_2$ at the contact point with alumina.

The increase of the P_{O_2} in the bonding atmosphere also favours the formation of the spinel oxide $CuAl_2O_4$ which appears as poliedric aggregates with size close to 1 µm (Fig. 12).

4. Discussion

The microstructural study, both on polished and fracture surfaces provided enough information to propose a model to explain the formation of the copper–alumina joint. This model consists of three stages where the dominant mechanisms are different.

4.1. Physic contact stage

The high refractivity of the ceramic material and its high elastic limit turn the alumina into a passive element at this first stage. The superficial microdeformation of the copper, both by elastic deformation and creep mechanisms, is responsible for both surfaces which are in contact, stabilizing a physical connection between them.

The type of copper interlayer or the bonding environment do not influence the physical contact stage being the bonding pressure and the temperature which controls the previous mechanisms.

4.2. Superficial oxidation stage

The previous microstructural studies have shown that the formation of a strong steel–copper–alumina joint, with a chemical interaction between the ceramic and the copper requires the formation of an oxide film on the copper surface. This fact has been also observed by other authors in work on pre-oxidized copper [16, 17]. Mechanical tests, however, proved that this oxide can be formed during the heating-up process of the bonding procedure, resulting in a stronger joint than when pre-oxidizing copper was used.

The oxidation of copper to form Cu_2O at 1000 °C is only possible when the partial oxygen pressure is greater than 10^{-3} Pa [18]. For this reason, specimens bonded with lower P_{O_2} did not present any evidence of chemical interaction. The formation of Cu_2O was limited to isolated points in contact with the alumina void, in which the oxygen content could be higher.

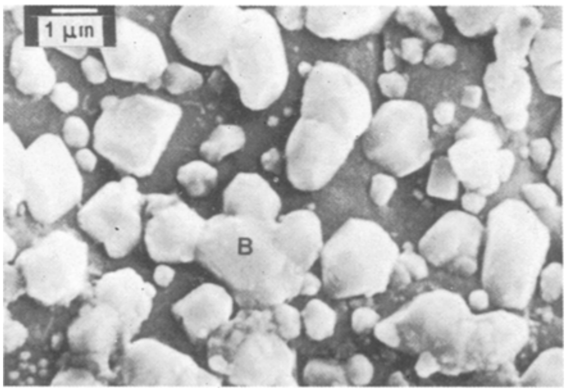

Figure 12 $CuAl_2O_4$ aggregates (B) formed on copper side fracture.

Using a copper interlayer with oxygen content of 0.04% favours the superficial oxidation of copper during the bonding procedure. At 1000 °C, the Cu_2O particles presented in the C 11000 copper, dissolved in the matrix which has an oxygen solubility of 0.0044% at this temperature (Fig. 13) [19]. The oxygen diffusion toward the copper free surface provides the formation of Cu_2O on them, and also accelerates the dissolution of the Cu_2O particles dispersed in the copper matrix.

For this reason, the superficial oxidation stage is controlled by the bonding temperature, the partial oxygen pressure in the bonding environment and the concentration of oxygen dissolved in the copper interlayer.

4.3. Chemical interaction stage

During the first and second stages, no type of chemical interaction is produced between copper and alumina. The formation of a binary oxidizing phase (spinels) occurs during a third stage because of different chemical reactions between the oxide copper and alumina.

The microstructural study shows that the $CuAlO_2$ phase is the first one to be formed. Jacob and Alcock [20], have studied the Cu_2O–CuO–Al_2O_3 systems, established that $CuAlO_2$ spinel can be formed by

$$2Cu + \tfrac{1}{2}O_2 + Al_2O_3 \rightarrow 2CuAlO_2 \qquad (1)$$

$$Cu_2O + Al_2O_3 \rightarrow 2CuAlO_2 \qquad (2)$$

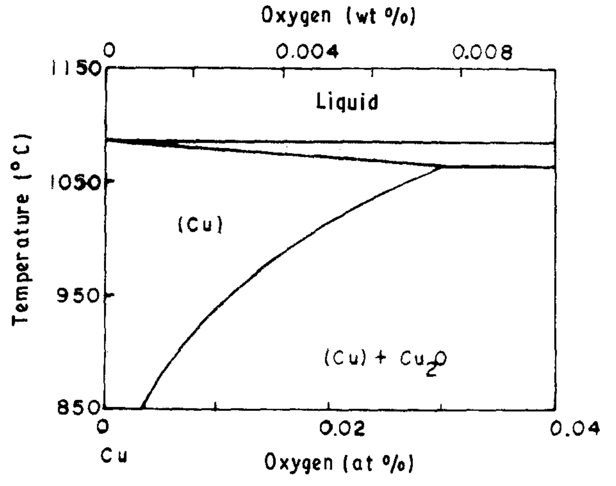

Figure 13 Detail of copper-rich side of the Cu–O phase diagram.

At the bonding temperature used (1000 °C), only Reaction 2 is thermomechanically possible.

Formation of $CuAl_2O_4$ spinel requires more oxidizing conditions as shown in the microstructural study. For this compound, Jacob and Alcock proposed the following reactions [20]

$$CuAlO_2 + \tfrac{1}{2}Al_2O_3 + \tfrac{1}{4}O_2 \rightarrow CuAl_2O_4 \quad (3)$$

$$2CuAlO_2 + \tfrac{1}{4}O_2 \rightarrow CuAl_2O_4 + \tfrac{1}{2}Cu_2O \quad (4)$$

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4 \quad (5)$$

Although at 1000 °C all three reactions are thermodynamically viable. Reaction 5 needs the formation of CuO on a copper surface. The bonding conditions used are not, however, so oxidant as to form it. The formation of the $CuAl_2O_4$ spinel is thus produced from the $CuAlO_2$ phase, either by chemical interaction with alumina in a oxidizing atmosphere or by direct oxidation. For bonding with low oxygen concentration, Reaction 4 will be the most probable. It is shown that because of the presence of $CuAlO_2$, particles close to the Cu_2O ones have been observed in the fracture surface (Fig. 12).

The spinel growth will be controlled by the mobility of the metallic cations in the matrix (Cu^+ and Al^{3+}). They will move in opposite directions while the O^{2-} anions will stay practically stationary. The increase in the bonding time favours the growth of the spinel layer. This fact explains why a reduction of the joint strength was observed when a long bonding period was used.

The third stage will be controlled by the bonding temperature, and especially oxygen concentrations in the copper and bonding atmosphere.

The proposed model is schematically represented in Fig. 14, and can be also appeared in the solid state bonding of the alumina to other metals (e.g. Mg, Co, Fe and Ni), which form spinel phases similar to those studied.

5. Conclusions

Copper foil can be used as a soft interlayer for the diffusion bonding of alumina and carbon steel. Diffusion bond strength is controlled by the alumina–copper interface and its mechanical properties depend strongly on the oxygen concentration both in the bonding environment and in the copper foil.

In order to obtain strong joints it is necessary to produce a chemical union by topotactic reaction between copper and alumina. It involves the presence of Cu_2O on the copper surface that reacts with Al_2O_3 to form the spinel oxides $CuAlO_2$ and $CuAl_2O_4$.

The diffusion bonding method developed produces the *in situ* formation of the copper oxide during the bonding process, without the necessity of using pre-oxidized copper interlayers.

The maximum bonding strengths of 100 MPa have been obtained by bonding under the following conditions: $T_b = 1000$ °C, $t_b = 5$ h, $P_b = 3$ MPa. These bonds were carried out using an interlayer of copper with 0.04 wt % oxygen and introducing a partial oxygen pressure of 10^4 Pa during the heating stage without load application. The rest of the process was carried out in a vacuum of 10^{-3} Pa ($P_{O_2} = 2 \times 10^{-4}$ Pa). This mechanical strength was higher than that obtained using pre-oxidizing copper interlayers and failure always occurred in the bulk alumina.

The highest bending strength obtained is related to the formation of an almost continuous reaction layer between copper and alumina. This layer was identified as $CuAlO_2$. The increase of this layer over certain thickness with the increase of bonding time produces a decrease of the bond strength.

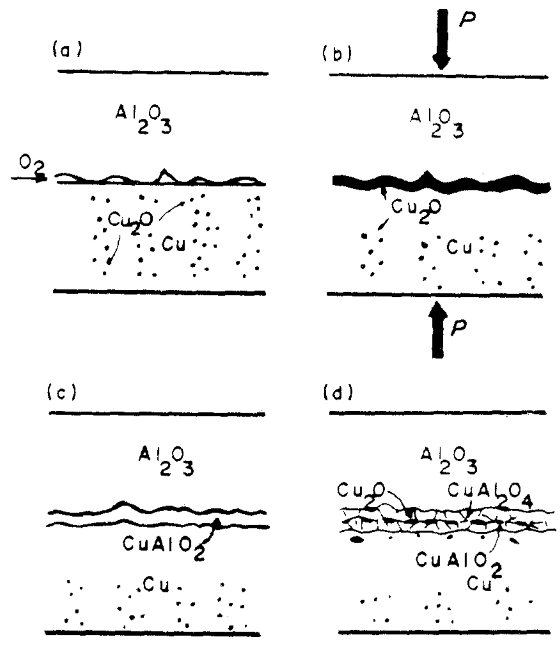

Figure 14 Schematic model of alumina–C 11000 diffusion bonds (a) Physical contact, (b) Formation of Cu_2O on copper surface, (c) Formation of $CuAlO_2$ spinel, (d) Formation of $CuAl_2O_4$ spinel by decomposition of $CuAlO_2$ one.

References

1. E. M. LEONE, R. N. KATZ and J. J. BURKE (eds), "Ceramics of High-Performance Applications". Vol III (Plenum, New York, 1979).
2. M. G. NICHOLAS and D. A. MORTIMER, *Mater. Sci. Technol.* 1 (1985) 657.

3. ASM, "Metal Handbook" Vol 2, 9th Edn (American Society of Metals, Metals Park, OH, 1983).
4. J. F. LUNCH, P. G. RUDERER and W. H. DUCHKORTH, *J. Amer. Ceram. Soc.* (1966).
5. W. E. BORDIGE, R. V. ALLEN and P. T. WHELAN, *J. Phys. C* **47** (1986) 131.
6. J. T. KLOMP, **5** (1970) 501.
7. *Idem., Amer. Ceram. Soc. Bull.* **49** (1970) 204.
8. *Idem., Ceram. Bull.* **51** (1972) 683.
9. K. SUGANUMA, T. OKAMOTO and K. KAMACHI, *J. Mater. Sci.* **22** (1987) 2702.
10. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI and M. SHIMIDA, *J. Mater. Sci. Lett.* **4** (1985) 648.
11. F. HATEKAYAMA, K. SUGANUMA and T. OKAMOTO, *J. Mater. Sci.* **21** (1986) 2455.
12. M. G. NICHOLAS and R. M. CRISPIN, *ibid.* **17** (1982) 3347.
13. G. YIASEMIDES, Proceedings 2nd International Conference "Diffusion Bonding Applications" Cranfield, 28–24 March, 1990.
14. F. CALVO, A. UREÑA, J. M. GOMEZ DE SALAZAR, F. MOLLEDA and A. J. CRIADO, *J. Mater. Sci.* **23** (1988) 1231.
15. F. CALVO, A. UREÑA, J. M. GOMEZ DE SALAZAR and F. MOLLEDA, *J. Mater. Sci. Lett.* **8** (1989) 137.
16. M. COURBIERE, G. TRABELSI, D. TREHEUX, C. BERAUD, C. ESNOUF and G. FANTOZZI, "High Tech Ceramics", edited by P. Vinconzini (Elsevier, Amsterdam, 1987) p. 2599.
17. C. BERAUD, M. COURBIERE, C. ESNOUF, D. JUVE and D. TREHEUX, *J. Mater. Sci.* **24** (1989) 4545.
18. F. D. RICHARDSON and J. H. E. JEFFES, *Proc. R. Soc.* **281** (1957) 1023.
19. J. P. NEWMAN, T. ZHONG and Y. A. CHANG, *Bull. Alloys Phase Diagrams* **5** (1984) 2.
20. K. T. JAKOB and C. B. ALCOCK, *J. Amer. Ceram. Soc.* **58** (1975) 192.

Received 21 June 1990
and accepted 31 January 1991