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Joining and wetting of CaO-stabilized ZrO_2 with Al–Cu alloys

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The contact angles of molten Al–Cu alloys on CaO-stabilized ZrO_2 have been measured using a sessile drop technique at 1373 K under a vacuum. The work of adhesion, W_{ad}, of an alloy against ZrO_2 was evaluated from the equilibrium contact angle of the alloy. The W_{ad} values Al–Cu alloys with copper contents up to 10 at % are the same or slightly higher than the value of 1.25 J m^{-2} for pure aluminium. On further increase in copper content, W_{ad} gradually decreases to 0.8 J m^{-2} for pure copper at 1373 K. The general trend in the work of adhesion against copper content of Al–Cu alloys is in accordance with the copper-content dependence of the joining strength of ZrO_2 joints brazed with the Al–Cu alloys. A ZrO_2 joint brazed with Al-1.7 at % Cu filler provides the maximum fracture strength of 105 MPa at room temperature, and this improved strength of ZrO_2 is maintained at elevated temperatures up to 773 K. The joining strength of a ZrO_2 joint brazed with an Al–Cu alloy is dominated by the mechanical properties of the alloy in addition to the wettability of the alloy against ZrO_2.

1. Introduction

In order to utilize the various properties of ceramics, the joining of ceramic to metal is needed and becomes an important technique. Generally, among techniques such as solid-state bonding, brazing and vaporized joining (vapour deposition), brazing is used extensively due to the easiness of the joining operation.

It is required to have a knowledge of the wetting behaviour of metals against ceramics for carrying out ceramic–metal joining by a brazing technique. The wetting behaviour of metals against ceramics and their joinability have been studied by Crispin and Nicholas [1] in some detail, and they showed that alloys containing an element that markedly affects the wetting behaviour have a higher ability of joining to alumina. Further, Naka *et al.* [2] have reported that factors such as the mechanical properties of the brazing filler metal as well as the wettability also operate in dominating the joinability of metals with ceramics.

Aluminium has a higher ability to join ceramics, with the property of relaxing the residual stress generated in the ceramics after the joining of ceramics such as alumina and silicon nitride to metal [2–4]. In this study, aluminium and aluminium–copper alloys were studied for their wettability to CaO-stabilized ZrO_2 and its relation to the joining ability was investigated.

2. Experimental procedure

CaO-stabilized cubic ZrO_2 containing 5.5 wt % CaO, 1.87 wt % SiO, 1.15 wt % MgO and 0.45 wt % Al_2O_3 was used. The flexural strength and specific gravity of the ZrO_2 are 196 MPa and 5.3, respectively. Al–Cu alloys containing 0, 1.7, 5.0, 15.4, 38.9 and 100 at % Cu were prepared by arc-melting high purity copper (99.99 wt %) in argon gas. The nominal composition and liquidus temperature of the Al–Cu alloys are shown in Table I.

The wettability of molten metals as shown in Fig. 1 was evaluated by measuring the contact angle between the peripheral surface of a small sessile drop of the molten metal and the horizontal surface of the ceramics substrate. Alloy samples of about 0.2 g were placed on ZrO_2 discs of 15 mm diameter and 3 mm thickness. The discs were polished mechanically with No. 1000 emery paper, and were heated at a rate of about 1.3 K sec^{-1} in a vacuum below 1.3 mPa. Fig. 2 shows a typical sessile drop of Al–15.4Cu alloy cooled after holding at 1373 K for 1.8 ksec. The molten drops on the ceramics were then photographed at regular time intervals through the glass window of the furnace. The contact angle θ was measured in the printed photographs using a protractor for angles above $\pi/2$ or using the relation $2\tan^{-1}(d/l)$ for angles below $\pi/2$ where d and l are the height and base radius of the molten drop, respectively.

TABLE I Chemical composition and liquidus temperature of filler metals

Filler metal	Copper content (at %)	Liquidus temperature (K)
Al	0	933
Al–1.7Cu	1.7	918
Al–4.5Cu	4.5	903
Al–15.4Cu	15.4	838
Al–38.9Cu	38.9	928
Cu	100	1356

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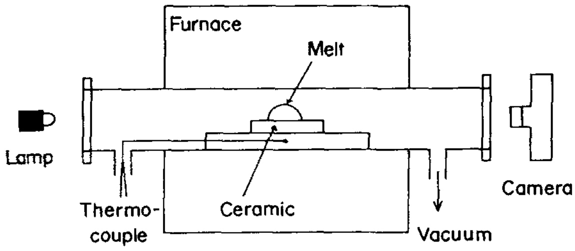

Figure 1 Schematic illustration of experimental system for sessile drop tests.

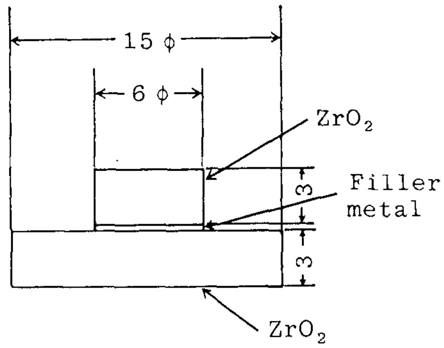

Figure 3 Lap joint of zicronia–zirconia (dimensions in millimetres).

ZrO_2 discs of 15 mm diameter and 3 mm thickness, and 6 mm diameter and 3 mm thickness (Fig. 3) were used for a lap joint. The joining was done by making the lap joint of ZrO_2 under a loading of 10 g with the filler under the same vacuum conditions as the sessile drop technique. The thickness of the filler metal was about 25 μm. The heating rate up to brazing temperature and the cooling rate to room temperature were 1.3 and 0.33 K sec^{-1}, respectively. The joining strength of the joint was determined by shear fracture loading with a crosshead speed of 1.7×10^{-2} mm sec^{-1}. The fracture surfaces of the joints were examined by scanning electron microscopy.

3. Results and discussion

3.1. Wetting behaviour

Fig. 4 shows the time-dependence of the contact angle at 1373 K for Al–Cu alloys. Although pure copper exhibited a gradual decrease in the contact angle, the time-dependence of the angle becomes significant with increasing aluminium content in Al–Cu alloys. In most cases the contact angle reached approximately its equilibrium value at 3.6 ksec. The composition (copper content) dependence of the equilibrium contact angle at 3.6 ksec is shown in Fig. 5. At 1373 K, the contact angle for Al–4.5 at % Cu alloy is almost the same as that for pure aluminium against ZrO_2 (1.05 rad), but the addition of 1.7 at % Cu slightly lowers the contact angle to 0.96 rad. For contents higher than 4.5 at % Cu the contact angle increases monotonically and reaches 2.01 rad for pure copper. At contact angles less than $\pi/2$ (1.57 rad) it is said that the melts wet ceramics, so it appears that Al–Cu alloys containing aluminium of more than 70 at % have wetted the ZrO_2.

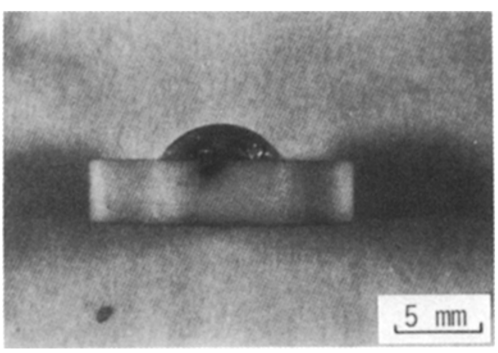

Figure 2 Example of sessile drop of Al–15.4 at % Cu alloy on zirconia surface cooled down from 1373 K.

3.2. Work of adhesion and joining strength

In order to evaluate the wettability of molten metals and alloys against ceramics, the work of adhesion W_{ad} is often used. W_{ad} is the work required to separate a unit area of solid–liquid interface into two surfaces, and is defined by the Young–Dupré equation

$$W_{ad} = \gamma_{LG}(1 + \cos\theta_\infty)$$

where γ_{LG} is the surface energy of the liquid and θ_∞ the equilibrium contact angle. Using the obtained values of θ_∞ and reported value of γ_{LG} [5], the W_{ad} of Al–Cu alloys is defined as shown in Fig. 6. The work of adhesion of Al–Cu alloys containing copper up to 10 at % is the same or slightly larger than for pure aluminium; in particular, at 1.7 at % Cu the value of W_{ad} is 1.3 J m^{-2} which is slightly larger than the value of 1.25 J m^{-2} for pure aluminium against ZrO_2. On further increase in copper content, W_{ad} gradually decreases to 0.8 J m^{-2} for pure copper. The composition dependence of W_{ad} in Al–Cu alloys deviates from the line exhibiting an ideal mixture of aluminium and copper at 1.7 and 40 at % Cu, which is represented by the broken line in the figure. This means that the alloys in these ranges of composition have some mutual interaction of aluminium and copper against ZrO_2. Such a mutual interaction on the wetting

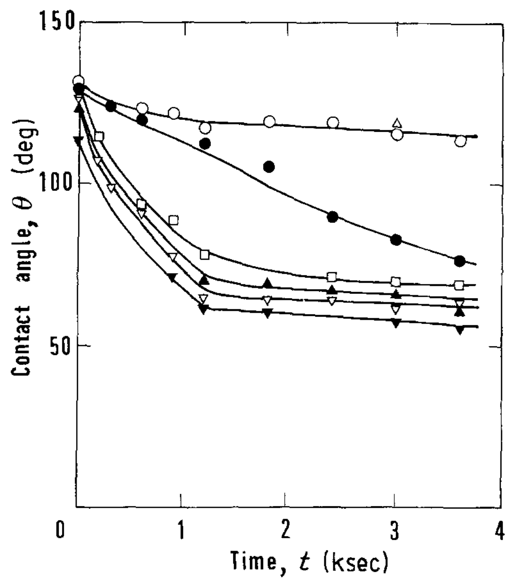

Figure 4 Time dependence of contact angle for Al–Cu alloys at temperature of 1373 K. (▽) Al, (▼) Al–1.7 at % Cu, (▲) Al–4.5 at % Cu, (□) Al–15.4 at % Cu, (●) Al–38.9 at % Cu, (○) Cu.

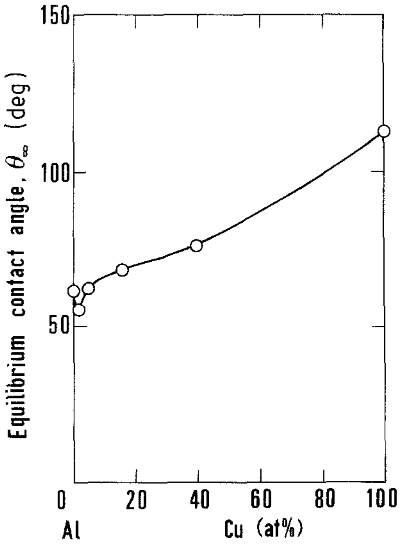

Figure 5 Effect of copper content on the equilibrium contact angle in wettability tests (1373 K, 3.6 ksec) of ZrO_2 by Al–Cu alloys.

appeared very markedly in the wetting of Al–Cu alloys against Al_2O_3 as reported by Naka *et al.* [6] in Fig. 6.

Next, in order to investigate the relevance of the wettability of Al–Cu alloys against ZrO_2 to the ability of joining, joining experiments were conducted. The Al–Cu alloys were placed between zirconia discs as shown in Fig. 3 and brazed at 1373 K for 3.6 ksec. Then the strength of the brazed joint was determined. In Fig. 7, the copper-content dependence of W_{ad} for the wettability of Al–Cu alloys against ZrO_2 at 1373 K and the joining strength are shown. The joining strength is markedly increased by the addition of copper up to 30 at % to aluminium; in particular, the addition of only 1.7 at % Cu approximately doubled (105 MPa) the joining strength of pure aluminium which is 53 MPa. For additions exceeding 30 at % Cu, the joining strength abruptly decreased and the joining strength of pure copper for ZrO_2 was only 5 MPa. The increased joining strength of 1.7 at % Cu alloy

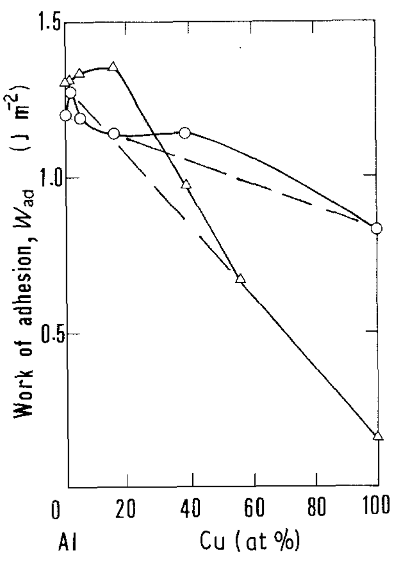

Figure 6 Variations of the work of adhesion (1373 K, 3.6 ksec) with copper content in Al–Cu alloys: solid material (○) ZrO_2 and (△) Al_2O_3 (from [6]).

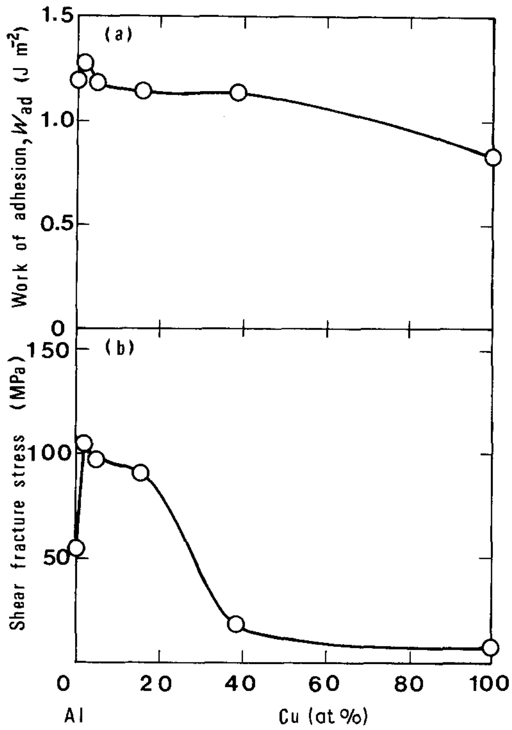

Figure 7 Dependence of (a) work of adhesion (1373 K, 3.6 ksec) and (b) room-temperature fracture shear stress (crosshead speed $1.67 \times 10^{-5}\,m\,sec^{-1}$) of zirconia joints on the copper content of Al–Cu alloys as filler.

corresponds to the increasing trend of the work of adhesion in the same alloy. In addition, the decreasing trend of the joining strength in alloys containing copper of more than 30 at % is also in accordance with the decreasing trend in the work of adhesion with increasing copper content in Al–Cu alloys against ZrO_2.

On further detailed examination of copper-content dependence of the joining strength of ZrO_2 with Al–Cu alloy fillers, although the work of adhesion of Al–38.9 at % Cu alloy against ZrO_2 is $1.15\,J\,m^{-2}$ which is approximately same as the W_{ad} of pure aluminium against ZrO_2 ($1.28\,J\,m^{-2}$), the joining strength of the brazed joint using the alloy as the filler metal is as low as 10 MPa. This indicates that the joining strength is determined not only by the work of adhesion but by other factors.

As measures of the strength of the Al–Cu alloys, their hardness, the aluminium side section of the Al–Cu binary equilibrium phase diagram, and their solidified microstructures are shown in Fig. 8. In the figure, alloys with copper contents up to 32.8 at % are composed of α and θ phases and the microstructures (Figs 8a to c) are composed of large amounts of α solid solution (Al–Cu). It is considered that, as shown in Fig. 7, the joining strengths against ZrO_2 of Al–Cu alloys with copper contents up to 32.8 at % are also the same as or higher than the joining strength of pure aluminium against ZrO_2. On the other hand, alloys with copper contents of 32.8 to 50 at% in the phase diagram are composed of $(\theta + \eta_2)$; in the microstructure of Fig. 6, these phases are shown as a dark matrix. These dark phases are composed of intermetallic compounds which have a higher hardness than pure aluminium but have considerable brittleness. Such a brittleness of

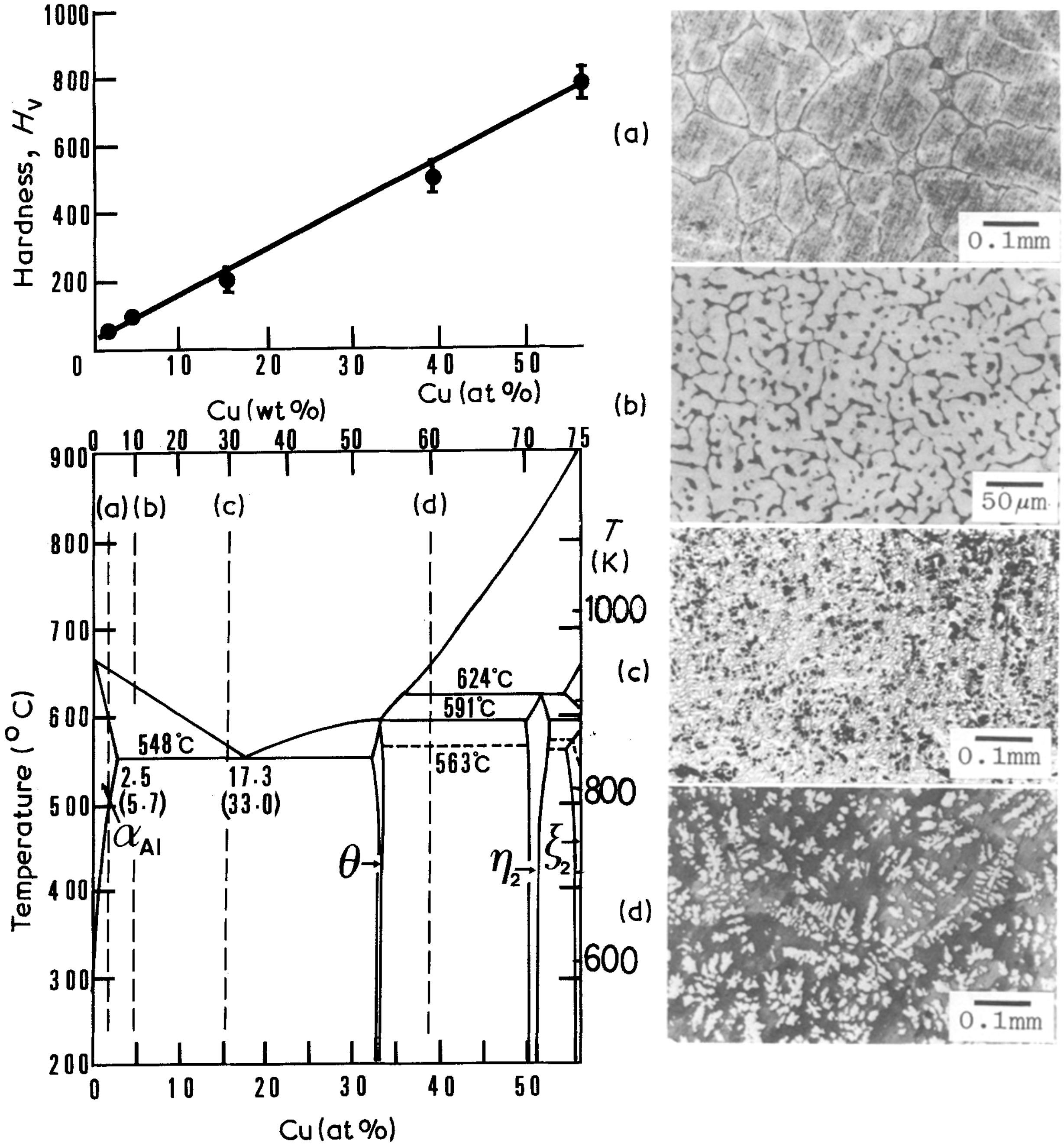

Figure 8 Indication of filler metal compositions in the Al–Cu phase diagram, and their measured hardness values (kg mm^{-2}) and microstructures.

the filler metal resulted in the lower strength of ZrO_2 joints brazed with 38.9 at % Cu alloy. Thus, the strength of a ZrO_2 joint brazed by using an Al–Cu alloy as the filler metal depends also on the mechanical properties of the filler metal in addition to the work of adhesion of the filler metal against zirconia.

3.3. Temperature dependence of the joining strength

Brazing with pure aluminium and Al–1.7 at % Cu alloy exhibited higher joining strengths of a ZrO_2 joint, so the temperature dependences of the joining strength of both joints were studied from room temperature to 773 K. As shown in Fig. 9, both the joining strengths reached a maximum at 373 K and gradually decreased with increasing temperature. It can be considered that the maximum arose from relaxation of the residual stress in the joint, induced after joining by the difference in the thermal expansion coefficients of ZrO_2 and the Al–Cu alloy. In addition, the improved joining strength achieved by the addition of 1.7 at % Cu to aluminium is retained at higher temperatures as shown in Fig. 9.

Fracture surfaces of the ZrO_2 joints brazed with aluminium and Al–1.7 at % Cu alloy are shown in Figs 10 and 11, respectively, as a function of temperature. In Fig. 10, the fracture surface of the zirconia joint brazed with aluminium is composed of the brittle fracture surface of ZrO_2 near the joining interface and the ductile sheared fracture surface of aluminium, for test temperatures below 573 K. At higher temperatures, for example at 673 K, the fracture occurred just at the interface and only the ductile shear fracture surface of aluminium is observed. In Fig. 11, the

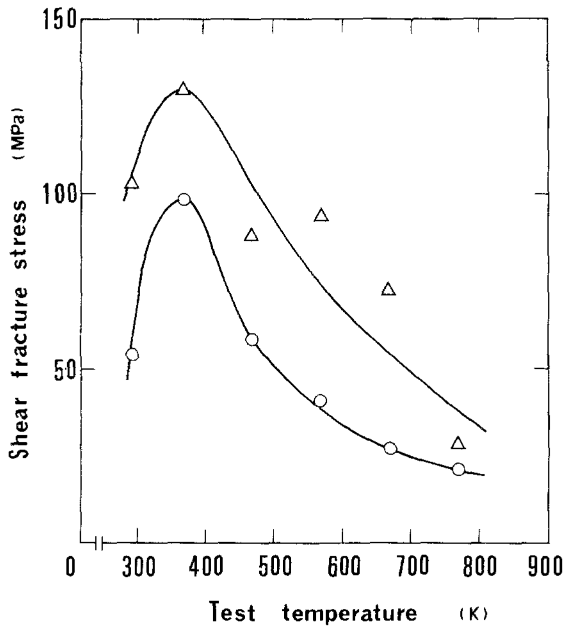

Figure 9 Temperature dependence of shear fracture stress in zirconia joints brazed at 1373 K for 3.6 ksec with (○) aluminium and (△) Al–1.7 at % Cu alloy.

fracture surface is composed of the brittle fracture surface of ZrO_2 and the ductile sheared fracture surface of Al–1.7 at % Cu alloy below 673 K. At higher temperatures than 673 K, only the shear fracture surface of the alloy was observed. According to these fracture surface observations, the higher strength of joints brazed with Al–1.7 at % Cu alloy is reflected in the improved wettability of the alloy against ZrO_2 and the retained strengthening effect up to a higher temperature of the filler metal itself due to the addition of copper.

4. Conclusions

Using the sessile drop technique, the wettabilities of aluminium and Al–Cu alloys at 1373 K under a vacuum were evaluated. From measured values of the equilibrium contact angle, values of the work of adhesion of Al–Cu alloys against ZrO_2 were determined. At 1373 K, the work of adhesion of Al–Cu alloys containing copper up to 30 at % were almost the same as the work of adhesion of pure aluminium; the value was 1.2 J m^{-2} for pure aluminium and was increased (improved) to 1.25 J m^{-2} for Al–1.7 at % Cu alloy. The trend in the dependence of copper content on the work of adhesion was almost in accordance with the trend in the copper-content dependence of the joining strength of zirconia joints brazed with various Al–Cu alloys as the filler. The addition of copper up to 30 at % to aluminium improved the joining strength of ZrO_2 joints brazed with pure aluminium. The joining strength of a joint brazed with Al–1.7 at % Cu alloy was as high as 105 MPa compared to 52 MPa for that brazed with pure aluminium. The significant decrease in the joining strength of a ZrO_2 joint brazed with Al–30 at % Cu alloy was due to the strength decrement of the alloy itself. Thus the joining strength of the brazed joint is controlled by the mechanical properties of the filler metal in addition to the work of adhesion of the alloy against ZrO_2.

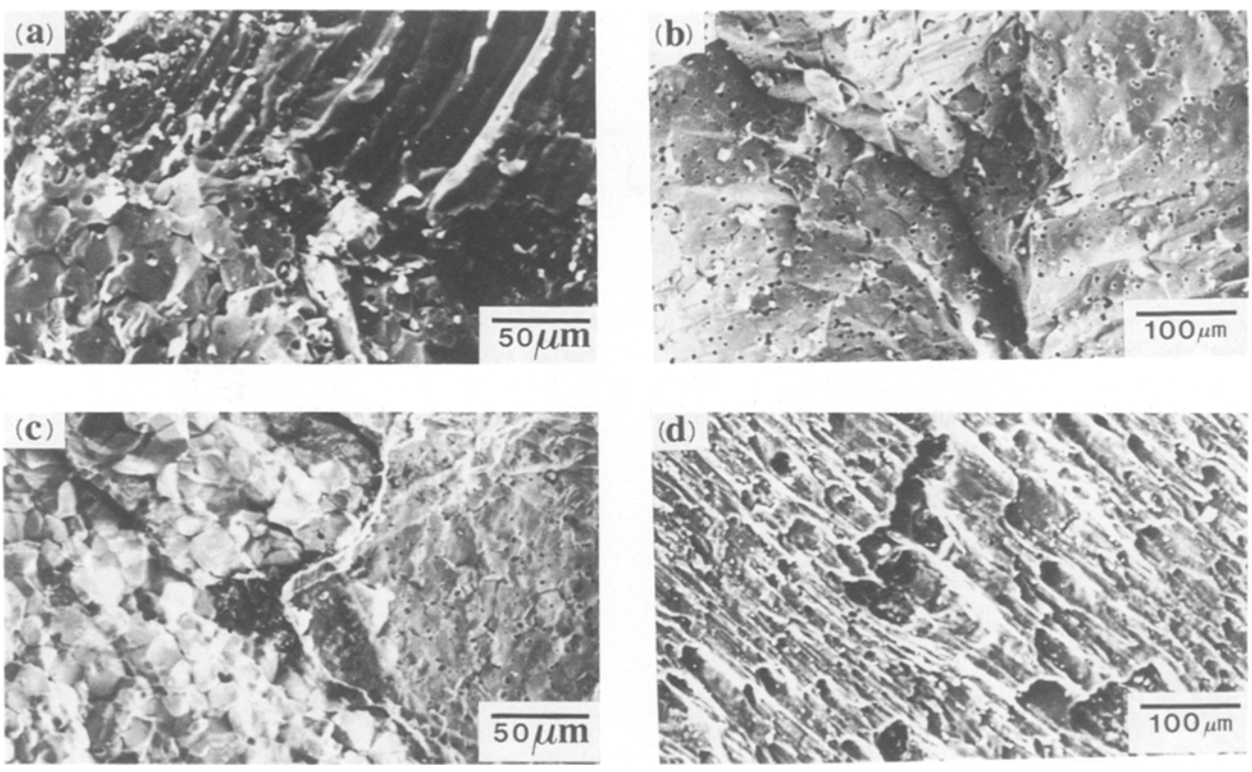

Figure 10 Scanning electron micrographs of shear fracture surfaces of ZrO_2 joints brazed by aluminium: temperature of fracture (a) 373 K, (b) 473 K, (c) 573 K and (d) 673 K.

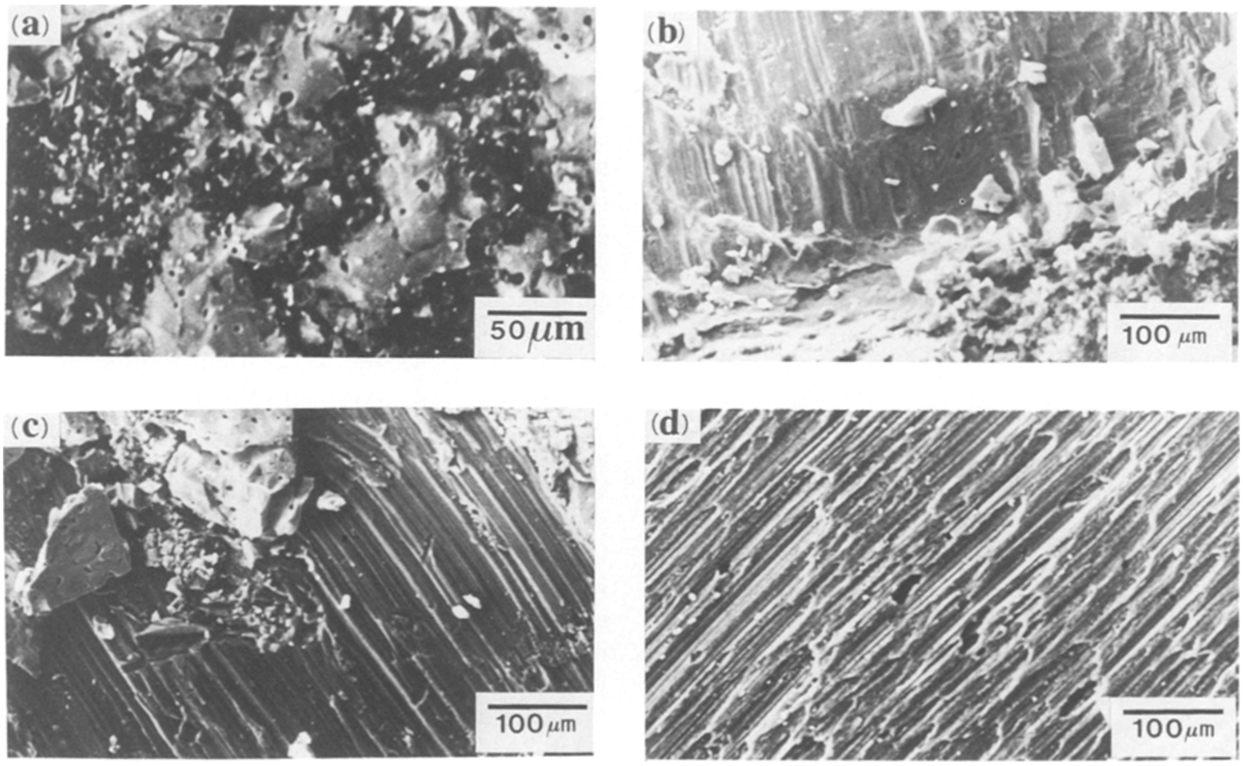

Figure 11 Scanning electron micrographs of shear fracture surfaces of ZrO_2 joints brazed with Al–1.7 at % Cu alloy: temperature of fracture (a) 373 K, (b) 473 K, (c) 573 K and (d) 773 K.

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