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Joining of silicon nitride with Al–Cu alloys

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The sessile drop technique was used to evaluate the equilibrium contact angle and work of adhesion of molten Al–Cu alloys on Si_3N_4 at 1373 K under vacuum. The wettability of Al–Cu alloys on Si_3N_4 is improved by an addition of copper content up to 20 at %. The joining of Si_3N_4 to Si_3Ni_4 was also conducted using Al–Cu filler metal at a brazing condition of 1373 K for 3.6 ksec. The dependence of strength of the Si_3N_4 joint against the copper content in the filler corresponds to the copper content dependence of work of adhesion for molten Al–Cu alloy on Si_3N_4. The superior wettability and mechanical property of filler provide the superior strength of Si_3N_4 brazed with the filler. In particular, the Si_3N_4 joint brazed with Al–1.7 at % Cu filler exhibits the maximum fracture shear strength of 186.3 MPa at room temperature. This superior strength of Si_3N_4 brazed with Al–1.7 at % Cu filler is maintained at elevated temperatures up to 650 K.

1. Introduction

The joining of ceramics to metals has received considerable interest in recent years in connection with the practical application of ceramics. Aluminium possesses two superior properties; firstly aluminium wets well a variety of ceramics such as alumina [1], zirconia [2] and silicon nitride [3], and easily reacts with ceramics. For instance, aluminium forms AlN type sialon at the interface between aluminium and silicon nitride [4]. Secondly, aluminium is a soft metal which relaxes the stress that arises from the difference in the thermal expansion between the ceramics and metal in joints. Aluminium is often used as the brazing filler to join metals to ceramics [5–7]. These studies, however, are so far focused on the joining using pure aluminium filler.

In the present work the joining condition of Si_3N_4 brazed with the Al–Cu alloy fillers was investigated, and the strength of the joint is related to the wettability of the Al–Cu alloy on Si_3N_4 which is evaluated from the measured contact angle of the alloys. Furthermore, the joining strength of Si_3N_4 joints is also measured at elevated temperatures up to 773 K.

2. Experimental procedure

The pressureless sintered Si_3N_4 containing a few per cent Al_2O_3 and Y_2O_3 were used. Al–Cu alloys containing 0, 1.7, 5.0, 15.6, 38.9, 56.0 and 100 at % Cu were prepared by arc-melting the high purity aluminium and copper (99.99 mass %) in argon gas.

The wettability of the molten metal was evaluated by measuring the contact angle between the peripheral surface of a small sessile drop of molten metal and the horizontal surface of the ceramic substrate. Alloy samples of about 0.2 g in weight were placed on silicon nitride of 15 mm diameter and 3 mm thickness which had been polished mechanically with silicon carbide paper to No. 1000, and were heated at the rate of about 1.3 K sec^{-1} in a vacuum below 1.33 mPa. The molten drops on the ceramics were then photographed at regular time intervals through the glass-mounted window of the furnace. The contact angle, θ was measured in the printed photographs using a protractor for the angles above $\pi/2$ or using the relation of $2\tan^{-1}(d/l) = \theta$ for the angles below $\pi/2$ where d and l are the height and base radius of molten drop, respectively.

Si_3N_4 of 15 mm in diameter and 3 mm in thickness, and Si_3N_4 of 6 mm in diameter and 3 mm thickness were used for a lap joint. The joining was done using the lap joint of Si_3N_4 under a loading of 10 g with the Al–Cu fillers. The thickness of the filler metal after joining 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 lap joint was determined by shear fracture loading using a crosshead speed of 1.7×10^{-2} mm sec^{-1}. The microstructures and element distribution of joints were determined by means of a scanning electron microscope and an energy dispersive microanalyser, respectively.

3. Results and discussion

Fig. 1 shows the equilibrium contact angle of Al–Cu alloys as a function of copper content at 1373 K. The contact angles of the alloys at 3.6 ksec were taken as the equilibrium value since the angles reached some constant values. The equilibrium contact angle θ_∞ exhibits a minimum value of 0.23 radians at a copper content of 1.7 at %, and the angle increases with higher copper content. The melt at the contact angle between 0 and $\pi/2$ is said to be the wetting state, and the melt at the contact angle between $\pi/2$ and π begins to swell and is said to be the non-wetting state. The wetting of Al–Cu alloys on Si_3N_4 is seen to occur at the copper content below 50 at %. The wettability of

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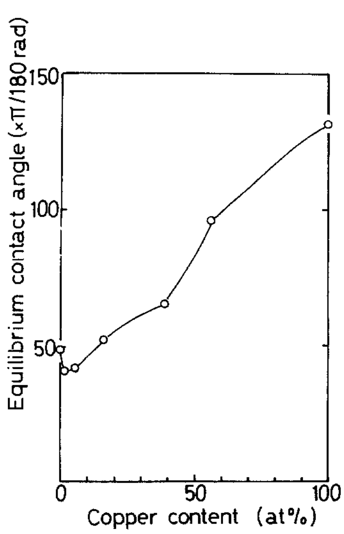

Figure 1 Copper content dependence of equilibrium contact angle for Al–Cu alloys on Si_3N_4 at 1373 K for 3.6 ksec.

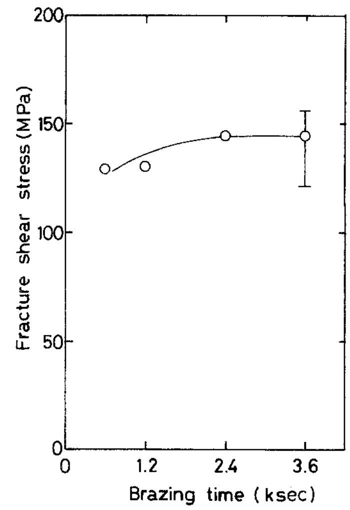

Figure 3 Change in fracture strength of Si_3N_4 using aluminium filler at a brazing temperature of 1373 K with brazing time.

ceramics with metals is often described by the work of adhesion, W_{ad} of the metal. W_{ad} is the work required to separate a unit area of the solid–liquid interface into two surfaces and is defined by the Young–Duprè equation as follows,

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

where γ_{LG} is the liquid surface energy. Using the present values of θ_{∞} and γ_{LG} for Al–Cu alloy at 1373 K [8], W_{ad} are calculated for Al–Cu alloys as shown in Fig. 2. The W_{ad} exhibits a maximum of $1.42\,J\,m^{-2}$ for 1.7 at % Cu alloy from $1.33\,J\,m^{-2}$ for aluminium and the addition of copper content up to 20 at % increases the W_{ad} of the alloys. This result shows that the wettability of alloys is improved by the addition of copper up to 20 at %. The alloys containing 40 at % copper content gives almost the same value as that of aluminium, and then the W_{ad} decreases markedly with increasing copper content to $0.45\,J\,m^{-2}$ for copper. The W_{ad} of Al–Cu alloys containing a copper content up to about 65 at % departs to the plus side from the ideal mixing, indicated by the dotted line in Fig. 2. Thus, the mutual wetting of aluminium and copper in the alloys on silicon nitride takes place, that is, the wetting of copper affects the wetting of aluminium in the alloys.

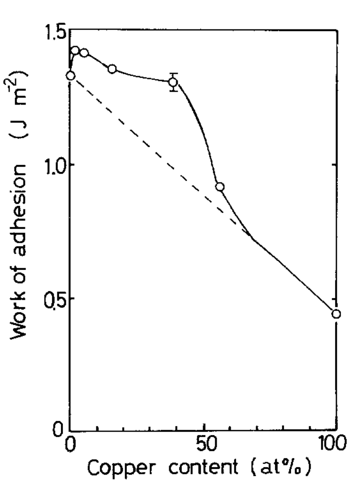

Figure 2 Copper content dependence of work of adhesion for Al–Cu alloys on Si_3N_4 at 1373 K.

The joining strength of Si_3N_4 to Si_3N_4 brazed with aluminium or Al–Cu fillers was investigated. Fig. 3 shows the change in shear strength of a Si_3N_4 joint brazed at 1373 K using an aluminium filler with brazing time. The strength increases with increasing brazing time and reaches the saturated value at a brazing time of 3.6 ksec. The strength of the joint brazed at the constant brazing time of 3.6 ksec is improved by an increase in brazing temperature as shown in Fig. 4. The results in Figs 3 and 4 suggest that the strength of the joint shows the same constant value when the molten alloy thoroughly wets the Si_3N_4.

Fig. 5 represents the change in shear strength of Si_3N_4 joints brazed at 1373 K for 3.6 ksec with copper content in the filler metals. The addition of copper content up to about 13 at % improves the strength of the joint, and in particular, the Si_3N_4 joint brazed with Al–1.7 at % Cu filler shows the maximum value of 186.3 MPa. Further, the strength of the joint is lowered remarkably with increasing copper content from 38.9 to 100 at % Cu in the filler.

The dependence for the work of adhesion, W_{ad} in Fig. 2 corresponds to the dependence of the strength of joint against the copper content in Fig. 5. The strength of joint brazed with Al–38.9 at % Cu filler, however, represents the markedly low value of

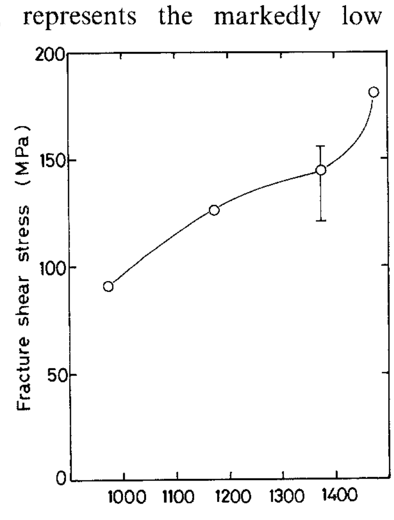

Figure 4 Change in fracture strength of Si_3N_4 using aluminium filler at a brazing time of 3.6 ksec with brazing temperature.

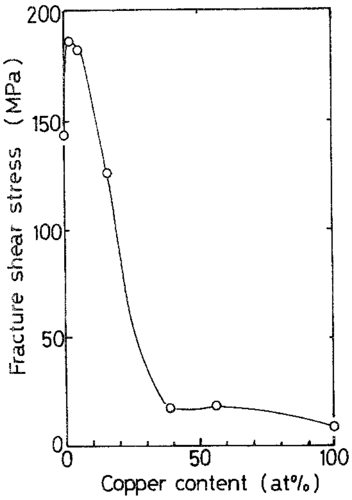

Figure 5 Change in shear strength of Si_3N_4 joint using Al–Cu alloy filler brazed at 1373 K for 3.6 ksec with copper content of the filler.

17.5 MPa. This suggests that another factor also dominates the strength of the Si_3N_4 joint. In the phase diagram of the Al–Cu system [9], the alloys containing copper content up to 32.8 at % Cu are composed of α solid solution + θ phase, and the alloys containing copper content of 32.8 to 50 at % are composed of (θ + η_2) phases. The inferior mechanical properties of Al–38.9 at % Cu filler is attributable to the low strength of the Si_3N_4 joint since the filler is composed of the brittle intermetallic compounds. These results indicate that the superior wettability and mechanical property of the filler metal provides the superior strength of the Si_3N_4 joint brazed with the filler metal.

Fig. 6 represents the structure of the fracture surface for Si_3N_4 joints brazed at 1373 K for 3.6 ksec with Al–Cu alloy fillers. The structures of the joints brazed with Al–Cu fillers containing a copper content up to 15.6 at % were composed of the fracture surfaces mixed with Si_3N_4 (shiny parts) and filler (dull parts) since the fracture of Si_3N_4 joint took place near the interface between Si_3N_4 and fillers. The fracture structure of the Si_3N_4 joint brazed with Al–38.9 at % Cu filler exhibits the brittle fracture structure of the filler and the original surface of Si_3N_4 since the fracture of the joint took place in the filler near the joining interface. The low wettability of copper against Si_3N_4 provides the fracture structure composed of a small amount of copper and the original surface of Si_3N_4.

These results indicate that the joints brazed with the fillers that possess the superior wettability and mechanical properties show the fracture surface to be mixed with both fracture surfaces of Si_3N_4 and filler.

The testing temperature dependences of the strength

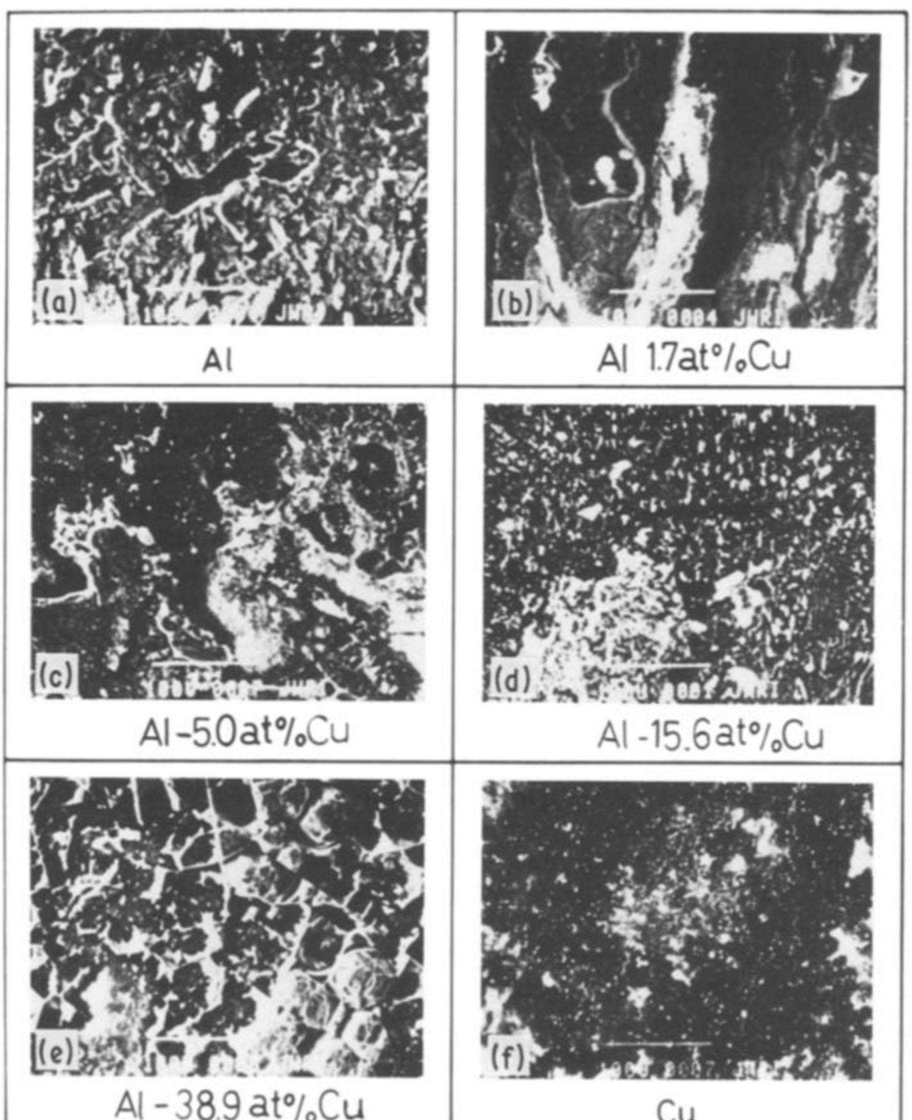

Figure 6 Fracture shear structure of Si_3N_4 joint brazed at 1373 K for 3.6 ksec with Al–Cu alloy filler. (a) Al, (b) Al–1.7 at % Cu, (c) Al–5.0 at % Cu, (d) Al–15.6 at % Cu, (e) Al–38.9 at % Cu, (f) Cu.

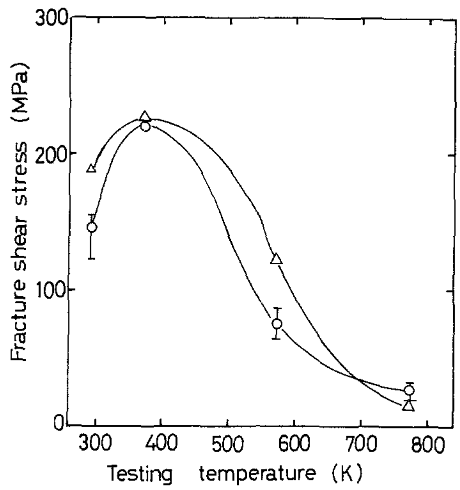

Figure 7 Effect of testing temperature on fracture shear strength of Si_3N_4 joints brazed at 1373 K for 3.6 ksec using (○) aluminium and (△) Al–1.7 at % Cu alloy fillers.

of Si_3N_4 joints brazed at 1373 K for 3.6 ksec with aluminium and Al–1.7 at % Cu fillers in Fig. 7 exhibit the maximum values of 210 and 238 MPa for Al and Al–1.7 at % Cu filler, respectively. The release of stress arising from the difference between the thermal expansion of Si_3N_4 and fillers in the joint accounts for the increase in strength of the Si_3N_4 joint at the testing temperature of 373 K. Furthermore, the strength of the Si_3N_4 joint falls with increasing testing temperature as shown in Fig. 7. The superior strength of the Si_3N_4 joint with Al–1.7 at % Cu filler is maintained at testing temperatures up to 650 K.

The change in the fracture structures of Si_3N_4 joints brazed at 1373 K for 3.6 ksec using aluminium and Al–1.7 at % Cu fillers with testing temperature are shown in Figs 8 and 9, respectively. The fracture structure mixed with the brittle fracture structure of Si_3N_4 and ductile fracture structure of the filler for both joints at testing temperatures below 373 K, and the general ductile fracture structures of the fillers at temperatures above 573 K are shown for both joints. The decrease in strength of aluminium and Al–1.7 at % Cu alloy fillers accounts for the decrease in strength of the Si_3N_4 joint brazed with the fillers.

4. Conclusions

The sessile drop technique has been used to measure the contact angle of Al–Cu alloys on Si_3N_4, and to evaluate the work of adhesion of the alloys as a measure of adhesive intensity. The equilibrium contact angle of the alloys at 1373 K exhibits a minimum value of 0.23 radians for a 1.7 at % Cu content, and furthermore, the equilibrium contact angle rises with increasing copper content in the alloys. The work of adhesion for Al–Cu alloys on Si_3N_4 at 1373 K from 1.33 J m^{-2} for aluminium through the maximum of 1.42 J m^{-2} for Al–1.7 at % Cu alloy to 0.45 J m^{-2} for copper. The wettability of aluminium on Si_3N_4 is improved by increasing the copper content up to 20 at % Cu.

The dependence of the strength of the Si_3N_4 joint brazed with Al–Cu fillers at 1373 K for 3.6 ksec against the copper content in the fillers shows a similar dependence to work of adhesion for the fillers on

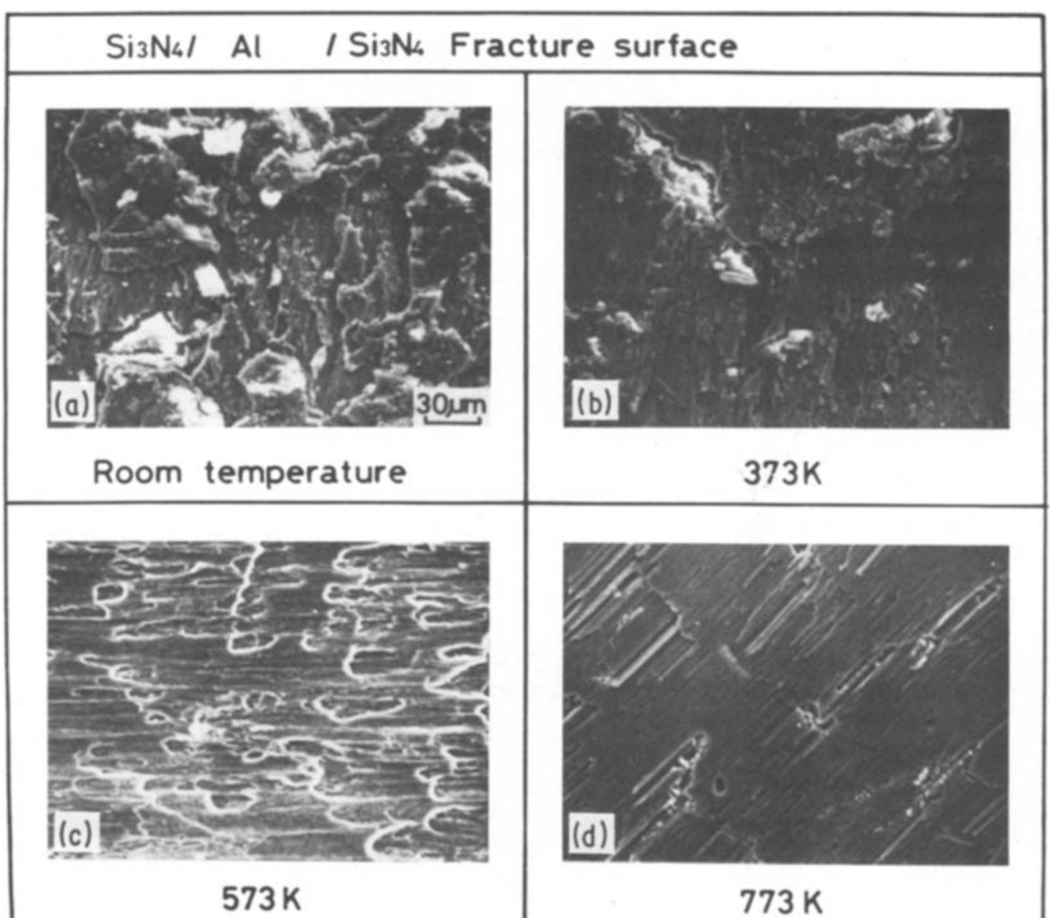

Figure 8 Change in fracture structure of Si_3N_4 joints brazed at 1373 K for 3.6 ksec using aluminium filler with shear testing temperature. (a) Room temperature, (b) 373 K, (c) 573 K, (d) 773 K.

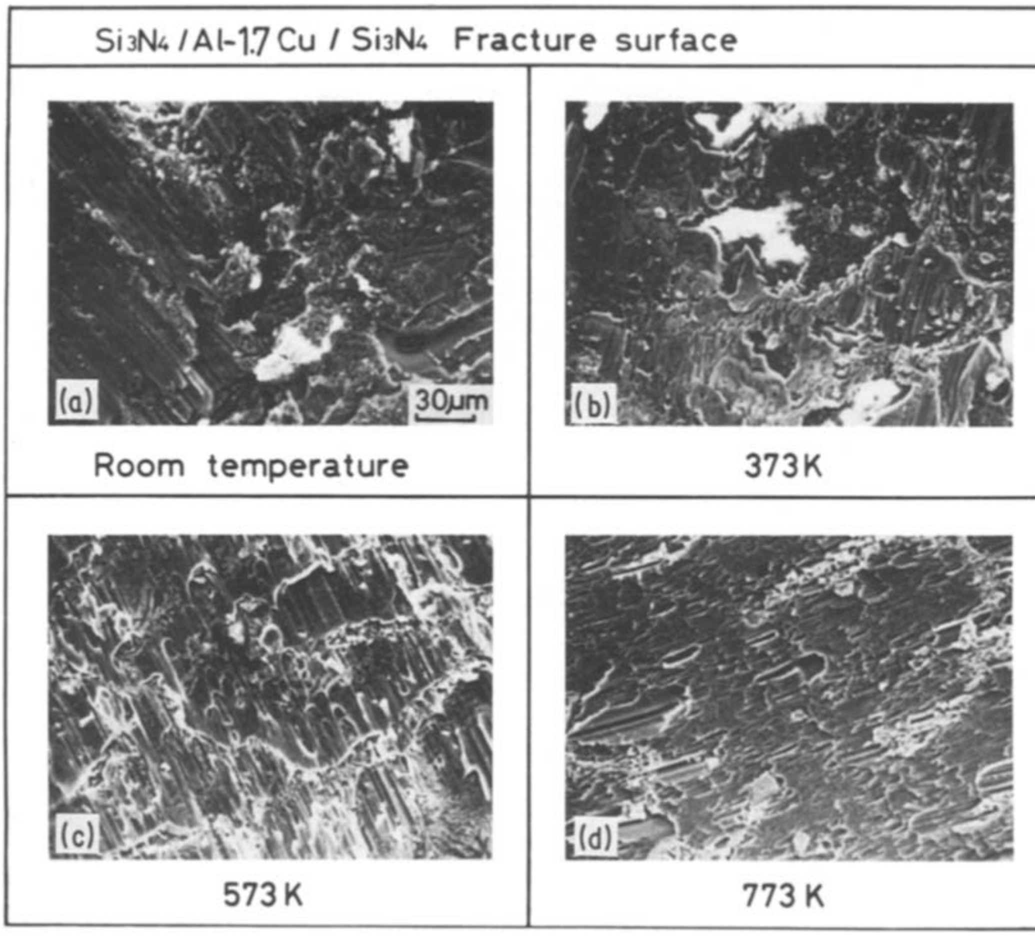

Figure 9 Change in fracture structure of Si_3N_4 joints brazed at 1373 K for 3.6 ksec using Al–1.7 at % Cu alloy filler with shear testing temperature. (a) Room temperature, (b) 373 K, (c) 573 K, (d) 773 K.

Si_3N_4 against the copper content. The addition of copper content up to 13 at % to the filler improves the strength. In particular, the strength of the Si_3N_4 joint reaches the maximum of 186.3 MPa for the Al–1.7 at % Cu filler. The improved strength of Si_3N_4 with Al–1.7 at % Cu filler is maintained at temperatures below 650 K. The superior wettability and mechanical properties of Al–Cu fillers containing a copper content up to 13 at % provides the superior strength of the Si_3N_4 joint brazed with the fillers.

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