Joining of Alumina/Alumina Using Al-Cu Filler Metal and Its Application to Joining of Alumina/Aluminum†

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Abstract

The wettability of aluminum-copper alloys on alumina was investigated by a sessile drop technique in a vacuum, and the joining strength of alumina/alumina joint brazed with the aluminum-copper fillers was related to the wettability of the alloys. Further, alumina was metallized with aluminum or aluminum-4mass% copper alloy filler, and brazed to A1050 aluminum in a vacuum. The aluminum-4mass% copper filler provides the superior joining strength of 157 MPa for alumina/alumina joint, and 80 MPa for alumina/A1050 joint.

KEY WORDS: (Joining) (Brazing) (Ceramic-Metal Joining) (Alumina) (Aluminum) (Aluminum Filler) (Aluminum-Copper Alloy) (Aluminum)

1. Introduction

Ceramic materials have attracted recent interests in a variety of industrial fields because of their superior physical properties. The ceramics, however, represents the inerior workability resulted from the inherent embrittlement since the bonding of ceramics is composed of the ionic or covalent.

Several attempts were made to join the ceramics to metals from the actual application of ceramics[1-4]. The joining of alumina gasket was tried in the aluminum vacuum chamber which is recently used in the nuclear physics field[5]. In the conventional joining of alumina to aluminum, the nickel-plated alumina is brazed to aluminum using a aluminum brazing filler after the alumina is metallized with molybdenum-manganese method[5]. On the other hand, it has been reported that aluminum reacts with alumina[6], and alumina is brazed to alumina using pure aluminum[7]. Therefore, alumina could be brazed to aluminum after metallizing the alumina with aluminum. This direct brazing method of alumina to aluminum is more simpler than the molybdenum-manganese method.

In the present paper, the wettability of aluminum-copper alloys was investigated by a sessile drop technique in a vacuum, and the wettability was related to the joinability of the alloys against alumina. Further, the alumina metallized with the selected aluminum-copper filler was brazed to aluminum using BA4004, and the joining strength and the interface structure for the alumina/aluminum joint was investigated.

2. Experimental

The Al-Cu alloys in Table 1 were prepared by mixing Al and Cu in the purity of 99.99 mass%, where the Al-4 mass% Cu alloy for the example is represented as Al-4Cu alloy. Alumina (Al_2O_3) used in the purity of 99.62 mass%

Table 1 Nominal composition of Al-Cu alloys used.

Al-Cu	Cu (mass%)	Cu (at%)	Liquidus temperature (K)
Al	0	0	933
Al-4Cu	4	1.7	918
Al-10Cu	10	4.5	903
Al-30Cu	30	15.4	838
Al-60Cu	60	38.9	928
Al-75Cu	75	56.0	1178
Cu	100	100	1356

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contains 0.1 mass% MgO, 0.11 mass% CaO, 0.09 mass% SiO_2 as other impurity.

The wettability of Al-Cu alloys against Al_2O_3 was investigated by means of a sessile drop method. The Al-Cu alloys of about 40 mm^3 were placed on the alumina of 15 mm in diameter and 3 mm thickness which was mechanically polished with silicon carbide to No. 1000. The sessile dop was holded at 1373 K after melting with a heating rate of 1.42 K/s in 1.33 mPa. The contact angle between the peripheral surface of a small sessile drop of molten metal and the horizontal surface of the ceramic substrate was measured by photographically with a camera. In joining of Al_2O_3 to Al_2O_3, Al_2O_3 of 15 mm in diameter and 3 mm in thickness, and Al_2O_3 of 6 mm in diameter and 3 mm in thickness, which were polished with silicon carbide to No. 1000, were made a lap joint inserted with Al, Cu, or Al-Cu alloy foil under 6×10^{-3} kg (as stress of 2.1×10^{-3} Pa) with a heating rate of 1.42K/s to desired temperature in a vacuum. The thickness of Al-Cu alloy inserted was about 25 μm.

In joining of Al_2O_3 to Al (A1050 which is represented by 1050 later), Al_2O_3 of 15 mm in diameter and 3 mm thickness was metallized with Al or Al-4Cu filler at 1373 K for 3.6 ks in a vacuum, and the metallized layer was polished to the thickness of 0.1 mm. Further, the metallized Al_2O_3 was brazed to 1050 of 6 mm in diameter and 3 mm in thickness using 4004 alloy filler of 6 mm in diameter and 0.2 mm in thickness.

The joining strength of Al_2O_3/Al_2O_3 or $Al_2O_3/1050$ joint was evaluated by shear fracture testing using a cross head speed of 1.67×10^{-2} mm/s, and the joining strength of Al_2O_3/Al_2O_3 joint was also measured at elevated temperatures from room temperature to 773 K. The fracture surface of joints was analysed by means of scanning electron microscope, EDX microanalyser, and the microstructure in the joining interface was observed by photomicroscopy.

3. Results and Discussion

3.1 Wettability of Al-Cu Alloys

Fig. 1 shows the copper content dependence of equilibrium contact angle for Al-Cu alloys on Al_2O_3 at 1373 K. Although the contact angle of the alloys decreases with time, the angle reachs the equilibrium value at 3.6 ks. The equilibrium contact angle of the alloys decreases a little from 0.907 rad of Al to 0.872 ras of Al-10 mass% Cu alloy, and increases to 2.65 rad of pure copper with the further increase in copper content.

The work of adhesion for molten alloy is given by Young-Duprè equation as Wad = γ_{LG} $(1 + \cos\theta_\infty)$, where γ_{LG} is the surface energy of molten alloy, and θ_∞ is the

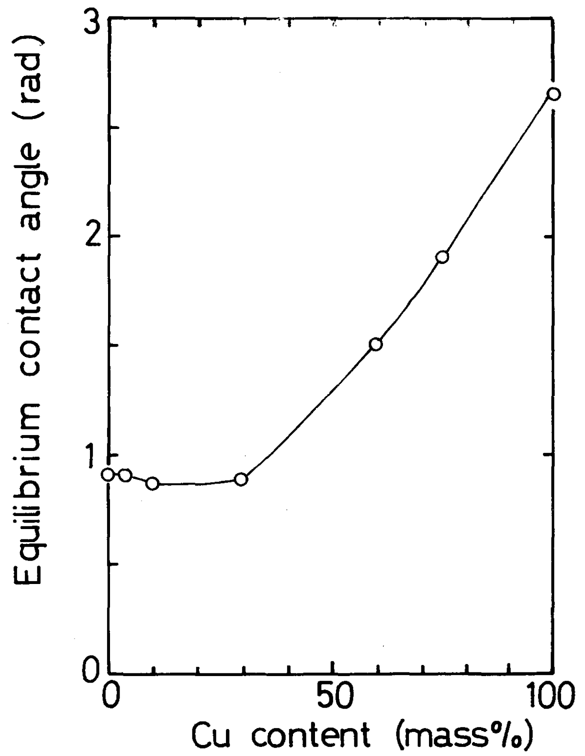

Fig. 1 Equilibrium contact angle of Al-Cu alloys on Al_2O_3 at 1373 K.

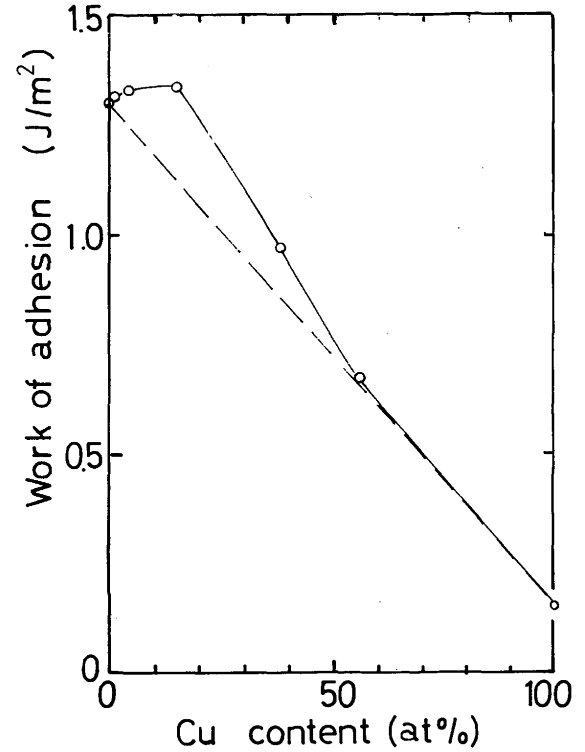

Fig. 2 Work of adhesion of Al-Cu alloys against Al_2O_3 at 1373 K.

equilibrium contact angle. The work of adhesion, Wad, for Al-Cu alloys on Al_2O_3 is represented in Fig. 2 using γ_{LG} for Al-Cu alloys by Elemenko's data[8] and the equilibrium contact angle in the present work. The Wad in Fig. 2

is plotted against copper content expressed in terms of at%. The Wad of Al-Cu alloys increases from 1.31 J/m^2 of Al to 1.35 J/m^2 of Al-15.4 at%Cu alloy and definitely decreases to 0.157 J/m^2 of Cu with increasing copper content. According to McDonald[9], the larger the standard free energy of oxide formation for metallic atom is, the larger the Wad of molten metal on Al_2O_3 is. Since the free energy of Al_2O_3 is larger than that of copper oxide, the result in Fig. 2 is interpreted by McDonald's model. Aluminum shows the better wettability against alumina than copper. The Wad of Al-Cu alloys at the copper content of 0 to 60 at% departs from the value represented by the broken line which represents the linear additivity of Wad against copper content. This result implies that the wettability of aluminum on Al_2O_3 affects the wettability of copper on Al_2O_3 with each other.

3.2 Fracture Shear Strength of Alumina Joint

In this section, the joining strength of Al_2O_3/Al_2O_3 joint brazed with Al, Cu and Al-Cu fillers is described and related to the wettability of metals. Figs. 3 and 4 show the brazing temperature dependence, and the brazing time dependence of joining strength for Al_2O_3/Al_2O_3 joint using Al filler, respectively. The joining strength of the joint exhibits the maximum value of 80 MPa at the brazing temperature of 1373 K, where the brazing time at 1473 K is 600 s to prevent the vaporization of Al. The joining strength increases a littel with increasing the brazing time at the brazing temperature of 1373 K, and provides 80 MPa or more.

The variation of joining strength of Al_2O_3/Al_2O_3 joint with copper content in the Al-Cu filler is shown in the brazing condition of 1373 K and 1.8 ks. The joining strength of Al_2O_3 joint rises from 80 MPa for the joint with Al filler with an increase in copper content up to 30 mass%, and exhibits the maximum value of 157 MPa for the joint with Al-4Cu filler. With copper content of 30 mass% or more the joining strength of Al_2O_3 joint definitely lowers to 2.5 MPa or lower.

The trend of Wad of Al-Cu alloys in Fig. 2 corresponds to the trend of joining strength of Al_2O_3 joint brazed with the Al-Cu alloys against copper content in the alloys in Fig. 5. However, the joining strength of Al_2O_3 joint with the Al-Cu alloys containing Cu content up to 30 mass% is higher than that of Al_2O_3 joint brazed with Al though the work of adhesion for Al-Cu alloys is the almost same as that of Al.

Moreover, the joining strength of Al_2O_3 joint with Al-60 Cu alloy is the same low value of 2.5 MPa as that Al_2O_3 joint with Cu which possesses the smallest Wad though the Wad of Al-60 Cu alloy is the half of pure Al. These facts indicate that the factors other than the work of adhesion of alloy also dominates the joining strength of Al_2O_3 joint brazed with Al-Cu alloys.

The stress in the ceramic/metal joint is, in general, arisen from the difference of the thermal expansion coefficient between ceramic and metal. The partial relaxation of stress in ceramic/metal joint at elevated temperatures would lead to improve the joining strength of the joint.

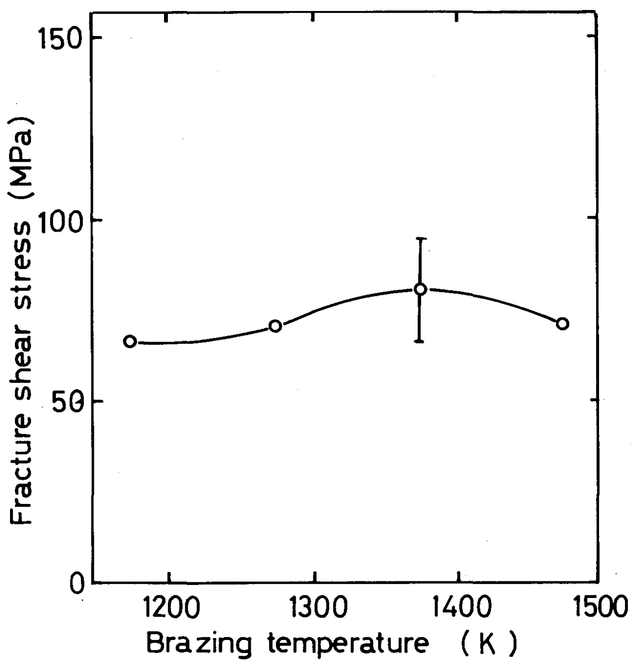

Fig. 3 Change in fracture shear stress of $Al_2O3/Al/Al_2O_3$ joint with brazing temperature at brazing time of 1.8 ks.

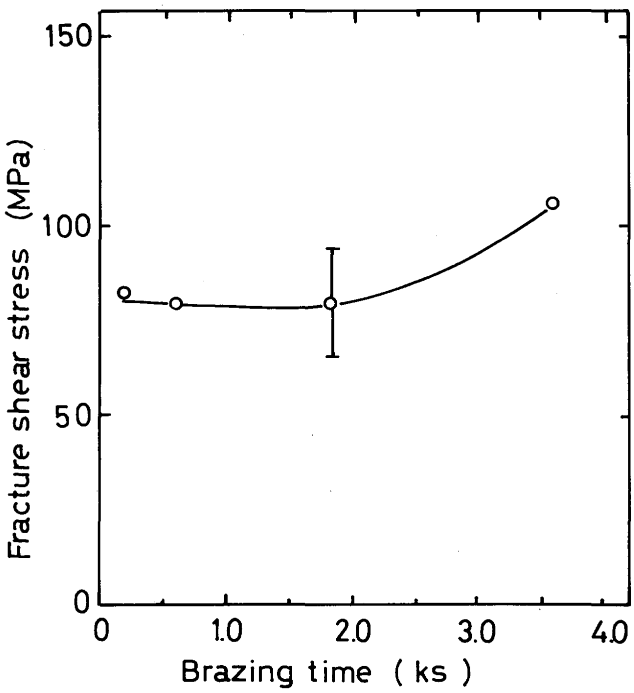

Fig. 4 Change in fracture shear stress of $Al_2O_3/Al/Al_2O_3$ joint with brazing time at brazing temperature of 1373 K.

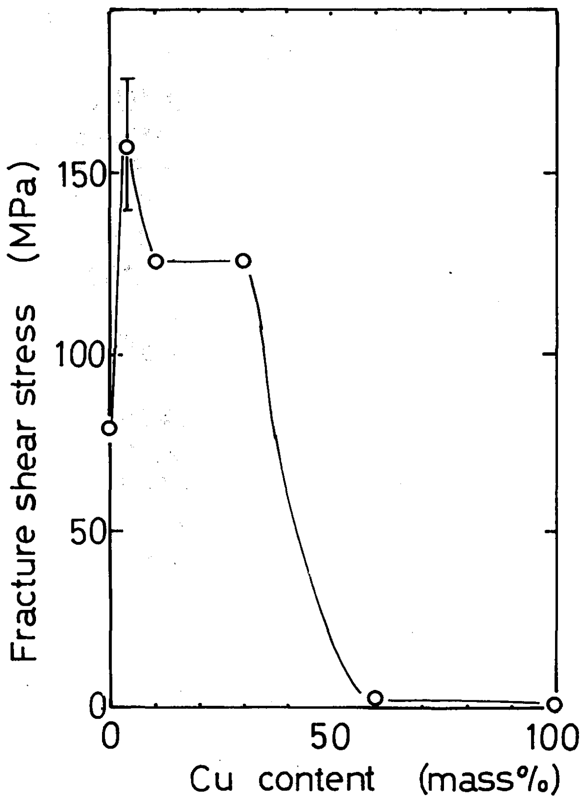

Fig. 5 Change in fracture shear stress of Al_2O_3/Al-Cu/Al_2O_3 joint brazed at 1373 K for 1.8 ks with Cu content of Al-Cu alloys.

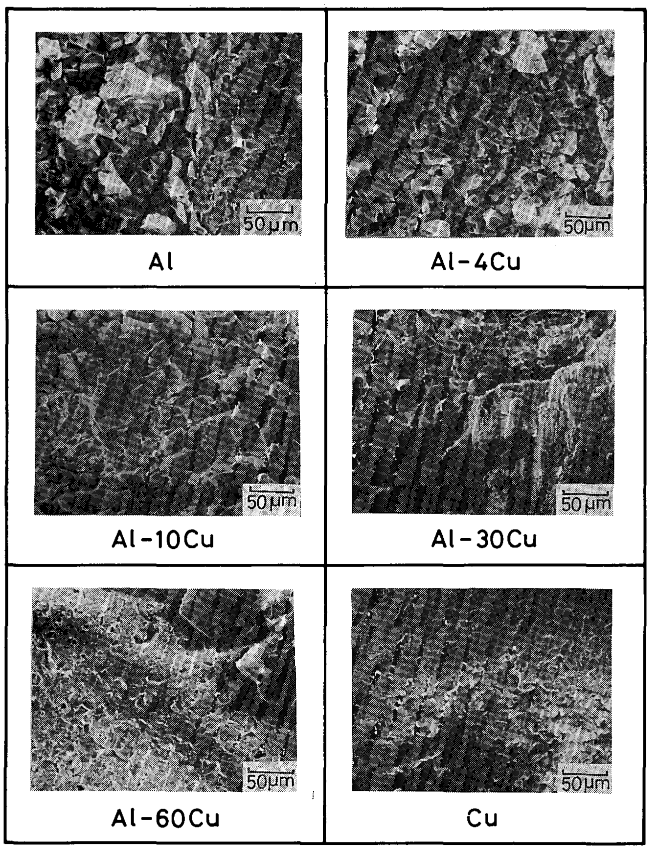

Fig. 6 Fracture surface of Al_2O_3/Al-Cu/Al_2O_3 joint after shear testing.

Since the of Al_2O_3 joint does not show clearly this improvement of the strength at elevated temperatures as described later, the role of the stress does not operate in the Al_2O_3 joint brazed with Al-Cu alloys.

According to Al-Cu phase diagram[10], Al-Cu alloys containing Cu content up to 53.5 mass% are composed of $(\alpha_{Al} + \theta)$ phases, and the alloys containing Cu content from 53.5 to 70 mass% are composed of $(\theta + \eta_2)$ phases. The Al-60Cu alloy which is composed of the hard and brittle intermetallic compounds provides the low joining strength of Al_2O_3 joint.

In conclusion, the superior wettability and mechanical properties of the filler provide the superior joining strength of ceramic/metal joint.

Fig. 6 shows the fracture surface of Al_2O_3/Al_2O_3 joint using Al-Cu alloy fillers. Al_2O_3/Al_2O_3 joint using Al-Cu alloy fillers with Cu content up to 30 mass% shows the fracture surface mixed with Al_2O_3 and fillers fractured near the joining interface. Al_2O_3/Al_2O_3 joint using Al-60Cu alloy filler shows the original surface of Al_2O_3 which does not fracture itself. The fracture crack propagates to the interface between Al_2O_3 and the filler since the work of adhesion for Al-60 Cu alloy is low as shown in Fig. 2.

3.3 The Joining Strength of Al_2O_3/Al_2O_3 joint at Elevated Temperatures

Fig. 7 shows the joining strength of Al_2O_3/Al_2O_3 joints brazed with Al and Al-4Cu fillers which are selected from the above-described results in the joining condition of 1373 K and 1.8 ks. The Al_2O_3 joint brazed with Al-4Cu filler provides the higher strength than that of Al_2O_3 joint brazed with Al filler at testing temperatures up to 700 K. Although the both joints shows the small variation in the strength with testing temperatures up to 500 K, the drastic decrease in the strength takes place with a further increase in testing temperature.

The fracture surfaces of Al_2O_3 joints with Al and Al-4Cu fillers in Figs. 8 and 9 reveal that the transition of the fracture surface from the mixed surfaces of Al_2O_3 and fillers in low testing temperature to the general ductile shear fractures of fillers in higher testing temperature takes place at testing temperature above 573 K for Al_2O_3 joint with Al filler, and at temperature above 673 K for Al_2O_3 joint with Al-4Cu filler.

These experiments demonstrate that the decrease in the joining strength with increasing the testing temperature results from the softening of Al or Al-4Cu filler. It is

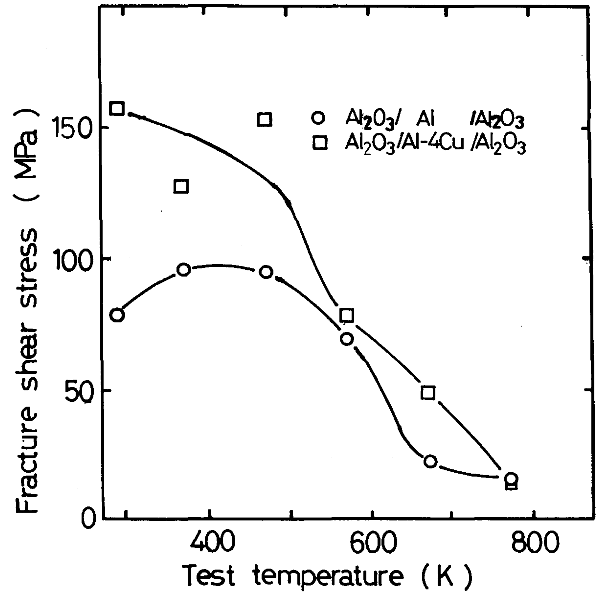

Fig. 7 Testing temperature dependence of fracture shear stress of $Al_2O_3/Al/Al_2O_3$ and Al_2O_3/Al-4mass%Cu/Al_2O_3 joints brazed at 1373 K for 1.8 ks.

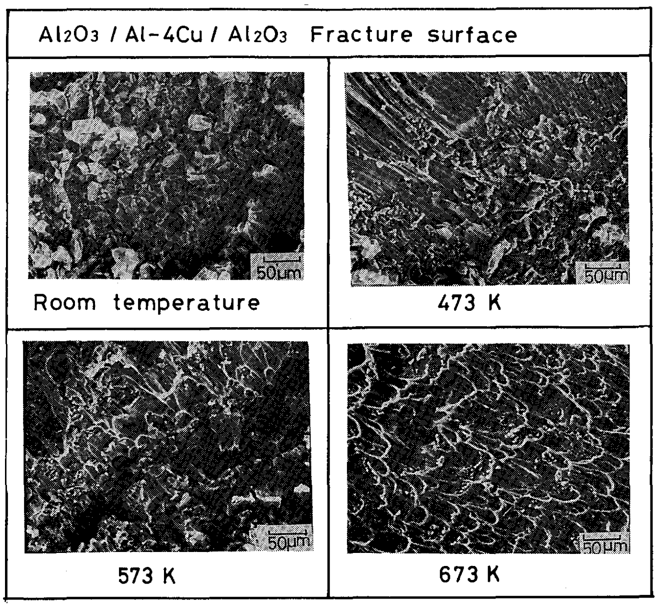

Fig. 8 Fracture surface of $Al_2O_3/Al/Al_2O_3$ joint after shear testing at temperatures from room temperature to 673 K.

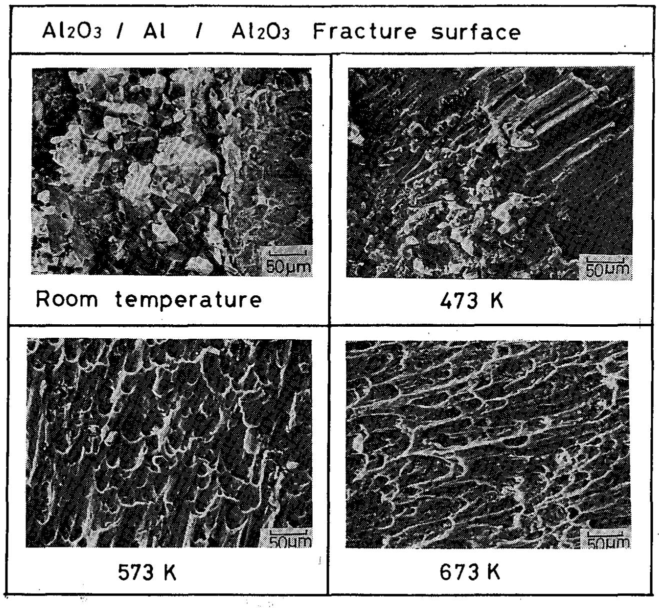

Fig. 9 Fracture surface of Al_2O_3/Al-4mass%Cu/Al_2O_3 joint after shear testing at temperatures from room temperature to 673 K.

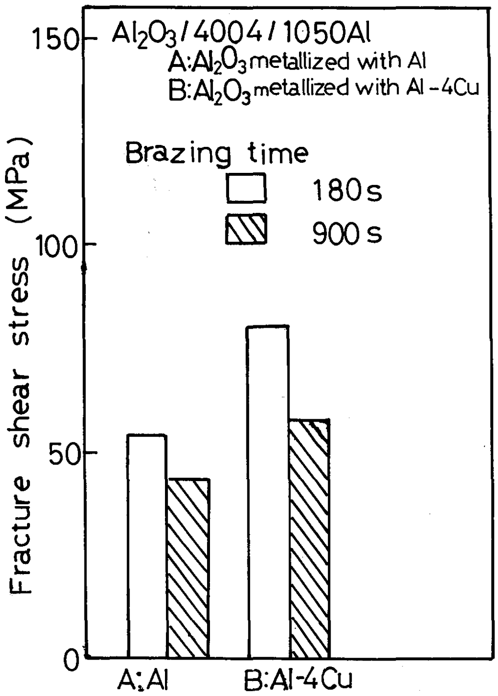

Fig. 10 Fracture shear stress of Al_2O_3/4004/1050Al joints brazed at 883 K for 180 s and 900 s, where Al_2O_3 is metallized with Al or Al-4mass%Cu filler.

also known that the elevated temperature strength of Al alloy decreases at temperature from 423 to 475 K, and the same decrease in the joining strength of Si_3N_4/metal joint[11].

3.4 Joining Strength of Al_2O_3/A1050 joint.

Fig. 10 shows the joining strength of Al_2O_3/1050 joint. The joint metallized with Al-4Cu filler provides the higher value than that of the joint metallized with Al filler at the both brazing times of 180 s and 900 s. For instance, the values of the joints with Al and Al-4Cu fillers at the brazing time of 180 s are 55 MPa and 80 MPa, respectivelly. The strength of the joints at the brazing time of 180 s is higher than that of the joints at the brazing time of 900 s. This reason will be discussed later by the structure observation.

Fig. 11 represents the fracture surface of Al_2O_3/1050

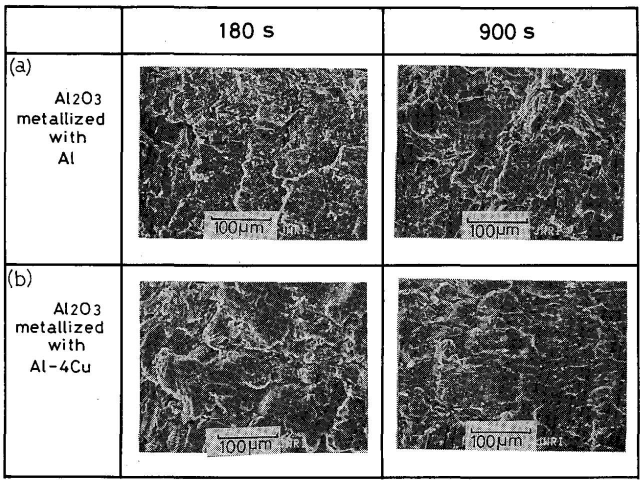

Fig. 11 Fracture surface of Al_2O_3/4004/A1050 joint after shear testing, where Al_2O_3 is metallized with Al(a) or Al-4mass%Cu (b) filler.

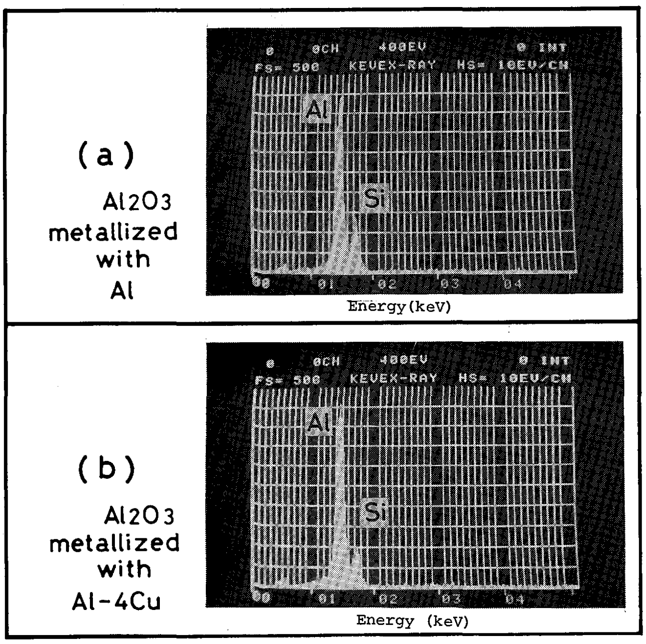

Fig. 12 EDX analyses of fracture surface of Al_2O_3/4004/A1050 joints brazed at 883 K for 180 s, where Al_2O_3 is metallized with Al (a) or Al-4mass%Cu (b) filler.

joint brazed with the same condition as that in Fig. 10. The element analyses in the joints using Al and Al-4Cu fillers brazed at the brazing time of 180 s are shown in Fig. 12. The fracture takes place near the BA4004 filler which joins the metallized layer with 1050.

Fig. 13 shows the microstructures of Al_2O_3/1050 joints which are metallized with Al(a) and Al-4Cu(b) fillers. The figure presents the total view of microstructure for the interface with low magnification, and also the magnified microstructure with high magnification. The layer of Al-Si alloy in the BA4004 filler is observed for the both joints brazed with Al and Al-4Cu fillers, and the string-

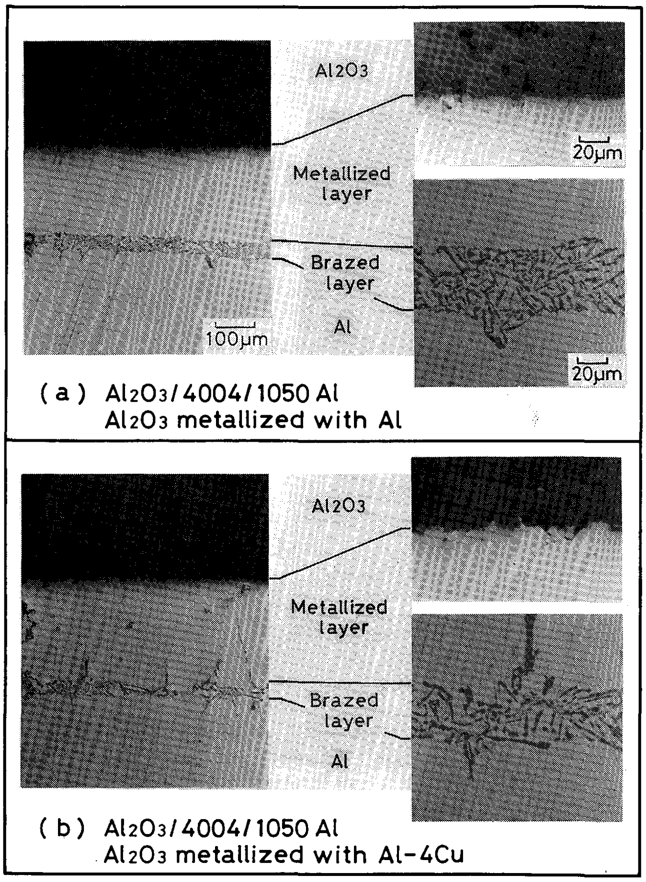

Fig. 13 Microstructure of Al_2O_3/4004/1050 joint brazed 883K for 180 s, where Al_2O_3 is metallized with Al (a) or Al-4mass%Cu (b) filler.

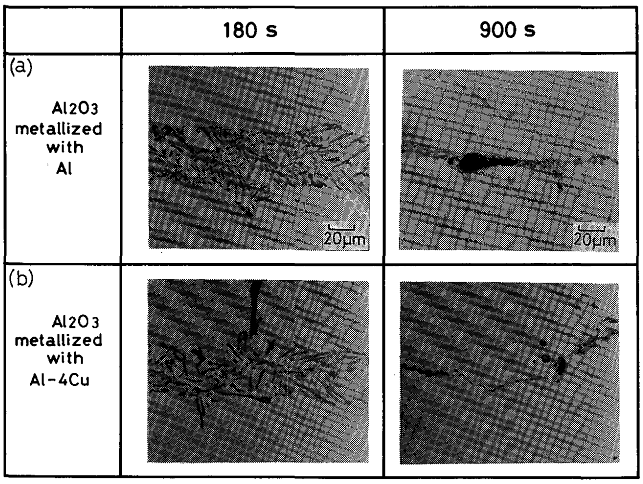

Fig. 14 Microstructure of interface between metallizing layer with Al (a) or Al-4mass%Cu (b) and A1050 brazed at 883K for 180 s or 900 s.

like silicon is formed by the eutectic reaction in the Al-Si layer.

Since the intermediate phase between Al_2O_3 and Al in the metallized layer is not observed, the intermediate phase is very thin.

Fig. 14 reveals the change in the microstructure including bandlike silicon with the joining time. At the brazing time of 900 s, the split-phenomena of the BA4004 filler took place by the diffusion of bandlike silicon into 1050 and the metallized layer. The composition of BA4004 filler is enriched with aluminum, and the remained liquid parts flow out from the joint surface. The formation of void in the joining layer which is resulted from the flow-out of BA4004 is attributable to the degradation of joining strength of Al_2O_3 joint in Fig. 10.

4. Conclusion

The sessile drop technique was conducted to measure the contact angle of molten aluminum-copper (0 – 100 mass% Cu) alloys against alumina under vacuum, and the joining strength of alumina to alumina joint using aluminum- copper filler metals was measured by fracture shear loading. Further, alumina was metallized with aluminum or 4 mass% copper-aluminum alloy filler, and brazed to A1050 under vacuum. The results obtained are summarized as follows.

(1) The work of adhesion of Al-Cu alloys to alumina at 1373 K increases from 1.31 J/m^2 for pure Al to 1.35 J/m^2 for 30 mass% Cu containing alloy, and decreases to 0.157 J/m^2 for pure copper. This results suggest that on aluminum rich side the interaction of aluminum and copper in the alloys affects the wetting of aluminum and copper against alumina.

(2) The shear strength of alumina/alumina joint with Al-Cu fillers depends on the work of adhesion of the Al-Cu fillers, and also on the strength of the fillers. The fillers composed of $(\alpha + \theta)$ phases are applicable to joining of alumina. In particular, alumina/alumina joint with 4 mass%Cu -aluminum filler exhibits the high strength of 157 MPa.

(3) The change in strength of Al_2O_3/Al_2O_3 joint with Al-4 mass% Cu filler with testing temperature is small up to 500 K. At further higher temperature the strength of the joint decreases with softening of the alloy.

(4) After metallizing alumina with Al or Al-4 mass% Cu filler at 1373 K for 3.6 ks, the alumina is brazed to A1050 with BA4004 at 883 K for 180 s or 900 s. The joining strength of Al_2O_3/Al joint whose Al_2O_3 is metallized with Al-4 mass% Cu filler exhibits the higher value than that of Al_2O_3/Al joint where Al_2O_3 is metallized with Al.

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