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Citation	Transactions of JWRI. 1989, 18(1), p. 81-86
Version Type	VoR
URL	https://doi.org/10.18910/10163
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Brazing of Si_3N_4 to Metals with Al Filler (Report I)†

– Si_3N_4/Si_3N_4 and Si_3N_4/Ti or Nb Joints –

Masaaki NAKA*, Masao KUBO** and Ikuo OKAMOTO***

Abstract

The wettability of molten aluminum on Si_3N_4 was investigated by a sessile drop technique in a vacuum. The joining of Si_3N_4 to Si_3N_4, and Si_3N_4 to Ti or Nb was performed using Al filler metal. The joining mechanism was investigated by transmission electron microscopy, scanning electron microscopy and EDX microanalysis.

The work of adhesion of aluminum on Si_3N_4 increases significantly with increasing temperature, and aluminum definitly wets Si_3N_4. The joining strength of Si_3N_4/Si_3N_4 joint with Al filler exhibits the maximum of 210MPa at elevated temperature of 373K, and decreases with further increasing testing temperature. The strength of Si_3N_4/Ti or Nb joint with Al filler is about half the strength of Si_3N_4/Si_3N_4 joint. The stress arisen from the thermal difference between Si_3N_4 and metal provides the detrimental effect on the strength of the Si_3N_4/metal joint. At the joining layer of Si_3N_4/Ti or Nb joint the intermediate phase of $TiAl_3$ or $NbAl_3$ was formed.

KEY WORDS: (Ceamic-Metal Joining) (Joining) (Brazing) (Ceramics) (Silicon Nitride) (Aluminum) (Filler Metal) (Titanium) (Niobium)

1. Introduction

Brazing is extensively used in the fabrication of ceramic/metal joints by using filler metals. Several filler metals for joining ceramics to metals have to contain the reactive elements such as titanium.

On the other hand, McDonald and Eberhart[1] have reported that the work of adhesion of molten metal on alumina is related to the free energy of oxide formation, and the high reactivity of molten aluminum against alumina. Naka *et al.*[2] have also indicated that aluminum among aluminum, copper and silver well wets silicon nitride, and the wettability of aluminum on Si_3N_4 increases markedly with increasing temperature. These results suggest the utility of aluminum as the brazing filler metal for silicon nitride.

Aluminum possesses other superior property ; aluminum is a soft metal which relaxes the stress arisen from the difference of thermal expansion between ceramic and metal during joining.

In this paper the wettability of aluminum was evaluated by measuring the contact angle on Si_3N_4 in a vacuum, and the brazing of Si_3N_4 to metals such as Nb and Ti was performed using Al filler metal. Furthermore, the joining mechanism was investigated by measuring the joining strength of Si_3N_4/Si_3N_4 and Si_3N_4/metal joints, and observing the microstructure of the joint.

2. Experimental

The pressureless sintered Si_3N_4 containing a few percent of Al_2O_3 and Y_2O_3 was used. The purity of aluminum was 99.99 mass%. The metals were Ti, Nb, Cu and Ag in a high purity. The wettability of molten aluminum, copper and silver to Si_3N_4 was evaluated by measuring the contact angle between the peripherral surface of sessile drop and horizontal surface of Si_3N_4 in a vacuum below 1.33mPa as shown in **Fig. 1**. The heating rate up to desired temperature was 1.7K/s, and the sessile drop apparatus is shown in **Fig. 2**.

Si_3N_4 of 15 mm in diameter and 3 mm in thickness, and Nb (or Ti) of 6 mm in diameter and 3 mm in thickness was used for a lap joint. First, the metallizing of

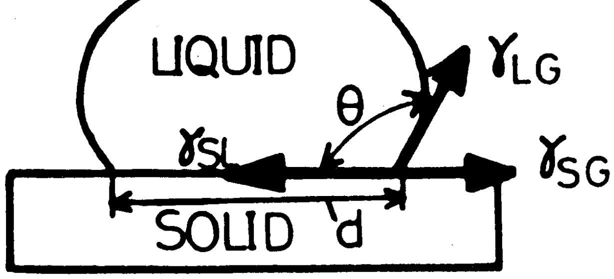

Fig. 1 Schematic of contact angle of liquid drop on Si_3N_4.

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

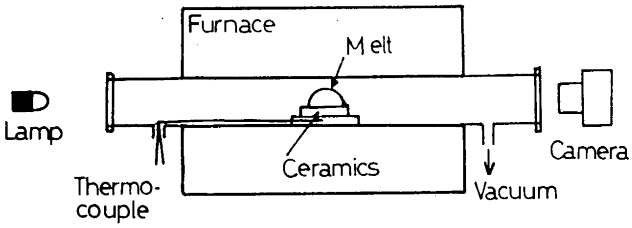

Fig. 2 Sessile drop apparatus.

Si_3N_4 with aluminum was conducted at 1373K for 3.6ks in 1.33mPa, and then the lap joint with Al thinned down to 0.1 mm thickness was made in the joining condition of joining temperatures of 1273K (for Nb) and 1073K (for Ti) and brazing time of 300s under a load of 10 g.

The joining strength of the lap joint was determined under shear fracture loading at a cross head speed of 1.7 X 10^{-2} mms^{-1}. The microstructure of Si_3N_4/metal was investigated by means of scanning electron microscope and EDX microanalyser.

3. Results and Discussion

3.1 Wettability of molten aluminum on Si_3N_4

Figure 3 shows the temperature dependence of the equilibrium contact angle of molten aluminum, copper and silver on Si_3N_4. The contact angle of molten metal was taken at 3.6ks as equilibrium value since the angle reached the final contact value. The angle was the lowest for aluminum with the highest temperature dependence, indicating the best wettability among the three metals.

In general, at a contact angle between 0 and $\pi/2$, the shape of the melt is convex and is said to be wetting at contact angles between $\pi/2$ and π the melt begins to swell and is said to be in the non-wetting state[3]. The wetting of aluminum on Si_3N_4 begins at temperatures above 1240K. The angles of silver are slightly higher than that of copper in Fig. 3.

The work of adhesion, Wad, often becomes a measure of adhesion intensity, Wad is the work required to separate a unit area of solid-liquid interface into two faces and is defined by Young-Duprè equation,

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

where γ_{LG} is the liquid energy. Using the data and their temperature coefficient $\alpha = d\gamma_{LG}/dT$ available from the literature[5] and the measured θ_∞ for three metals, the work of adhesion, W_{ad}, of the three metals against Si_3N_4 calculated at various temperatures are shown in **Fig. 4.** Compared with copper and silver, aluminum greatly increases the work of adhesion, Silver shows a lower value than that of copper.

The work of adhesion, W_{ad} of metals against Al_2O_3[1] or cubic ZrO_2[4] is related to the formation energy of

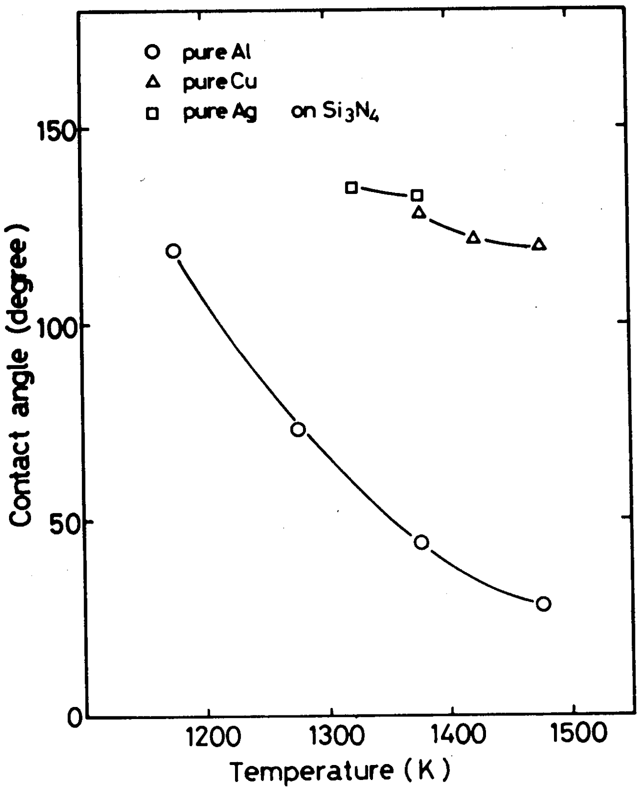

Fig. 3 Temperature dependence of equilibrium contact angle of Al, Cu and Ag on Si_3N_4.

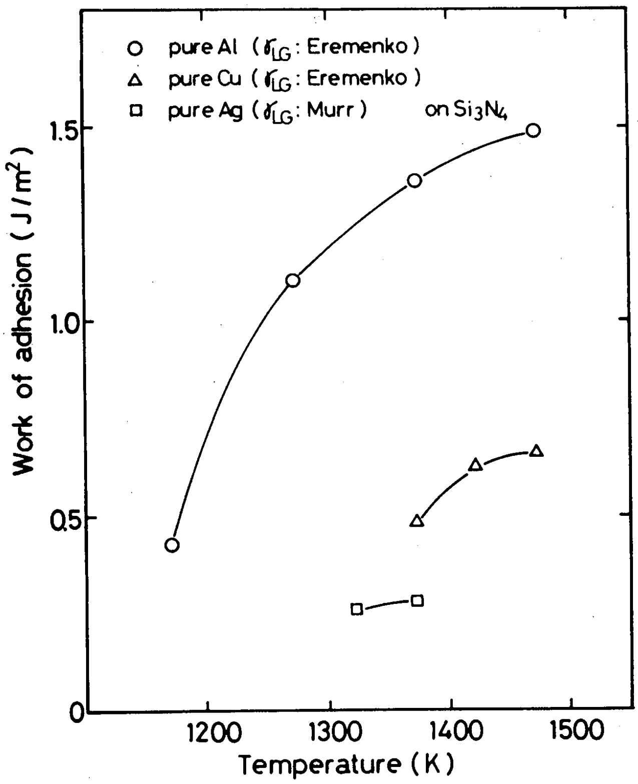

Fig. 4 Temperature dependence of work of adhesion, Wad, of Al, Cu and Ag on Si_3N_4.

oxide, and the wetting of oxide ceramics with metals is controlled by the ease with which oxidation of the metals occurs. On the other hand, the wetting of silicon nitride ceramics may be related to the ease of nitride formation of the metals.

In order to identify the intermediate phase at the interface of Al/Si_3N_4 joint, the microstructure of the sessile drop made at 1473K for 3.6ks was observed using a scanning electron microscope and a transmission electron microscope. **Figure 5** shows the interface of Al/Si_3N_4 sessile drop, and the intermediate phase between aluminum and Si_3N_4 is not clear and very thin. **Figure 6** shows the microstructure of the interface using a transmission electron microscope. The intermediate phase is formed at the interface of aluminum and Si_3N_4. The intermediate phase is composed of fine grains in diameter of 10nm and grows preferentially in the grain boundaries of Si_3N_4. The electron and X-ray diffraction patterns of the intermediate phase are identified as R15-AlN type sialon. In a part of the interface the amorphous phase of Al_2O_3 was also observed. The results of Figs. 5 to 6 indicate that aluminum definitely wets Si_3N_4 and is applicable to the brazing filler for Si_3N_4.

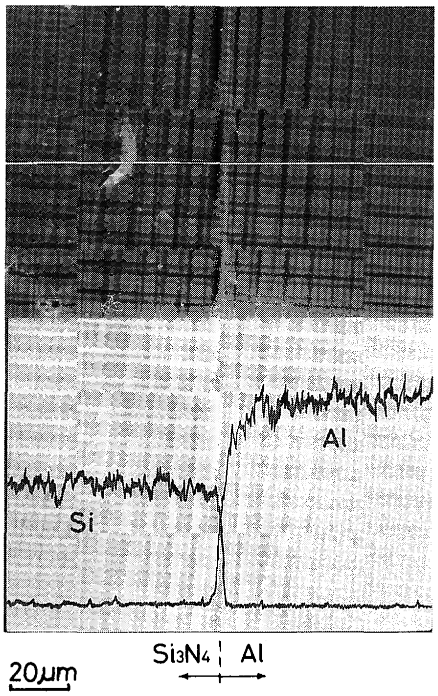

Fig. 5 Microstructure and line analyses of Al and Si in Al/Si_3N_4 sessile drop cooled down from 1473K.

3.2 Joining strength of Si_3N_4/Si_3N_4 and Si_3N_4/Ti or Nb joints

Figure 7 represents the testing temperature dependence of the strength of Si_3N_4/Si_3N_4 joints brazed at 1373K for 3.6ks using Al filler. The strength of Si_3N_4/Si_3N_4 joint shows the maximum value of 210MPa at 373K. 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. Furthermore, the strength of the Si_3N_4/Si_3N_4 joint falls with increasing testing temperature.

The change in the fracture structures of Si_3N_4/Si_3N_4 joints brazed at 1373K for 3.6ks using aluminum with testing temperature is shown in **Fig. 8**. The fracture mixed with the brittle fracture structure of Si_3N_4 and ductile fracture structure of the filler below 373K, and the general ductile fracture structure of the filler above 573K are shown in Fig. 8. The decrease in strength of aluminum filler accounts for the decrease in strength of the Si_3N_4 joint.

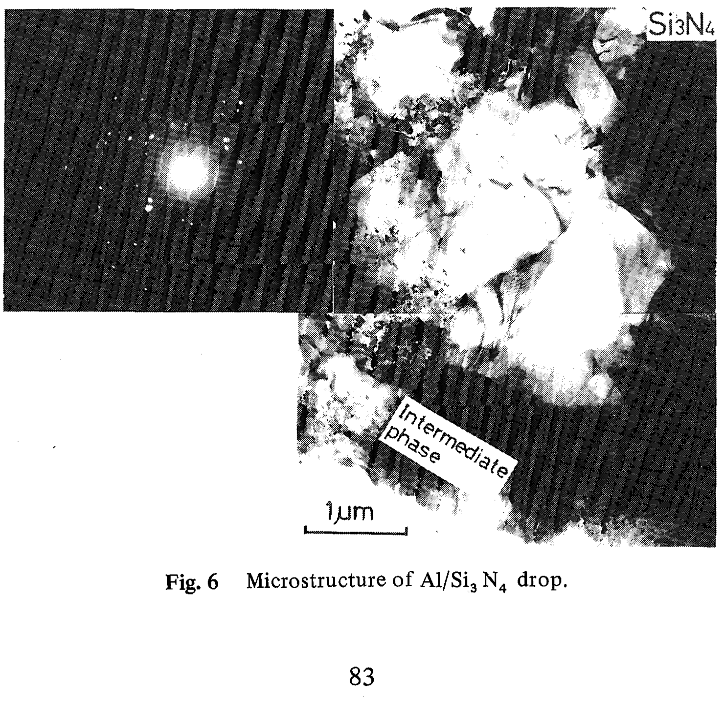

Fig. 6 Microstructure of Al/Si_3N_4 drop.

The Si_3N_4/Nb or Ti joint is made using Al filler. Si_3N_4 was metallized with Al filler at 1373K for 3.6ks. The metallized Al was thinned down to 0.1 mm in thickness, and then the Si_3N_4 brazed with Nb or Ti by the metallized Al filler.

Figure 7 also shows the change in fracture strength of Si_3N_4/Nb or Ti joint with testing temperature. The strength, 100 MPa, of Si_3N_4/Ti or Nb joint is half the strength of Si_3N_4/Si_3N_4 joint at room temperature. The stress arisen from the difference of thermal expansion coefficient between Si_3N_4 and metal is attributable to the decrease in the strength of the Si_3N_4 joint. The strength of Si_3N_4/Nb joint is a little higher than that of Si_3N_4/Ti joint, and the strength of both joints decreases with increasing testing temperature. As shown in the change in fracture structures of Si_3N_4/Nb or Ti joints with testing temperature in **Figs.** 9 and 10, the joints represent the ductile fracture surfaces of Al fillers at all testing temperatures. Teh decrease in the strength of Al filler is attributable to the decrease in the strength of Si_3N_4/metal joint.

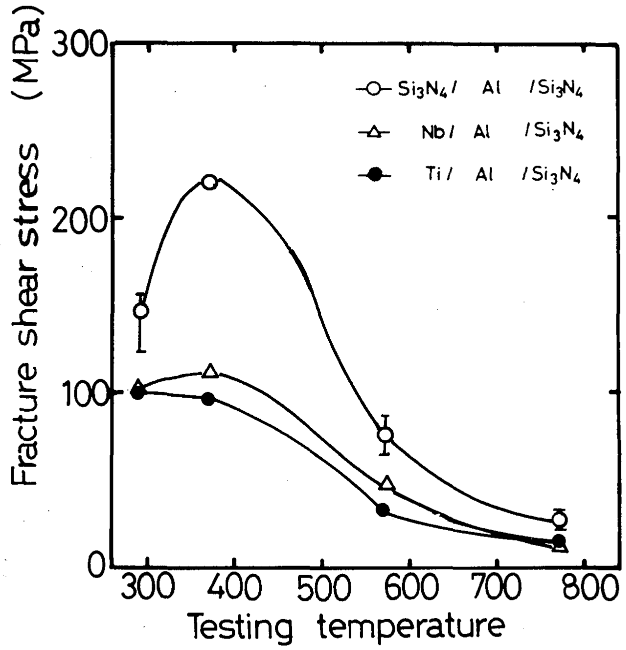

Fig. 7 Testing temperature dependence of fracture shear strength of Si_3N_4/Si_3N_4 joint brazed at 1373K for 3.6ks using Al filler.

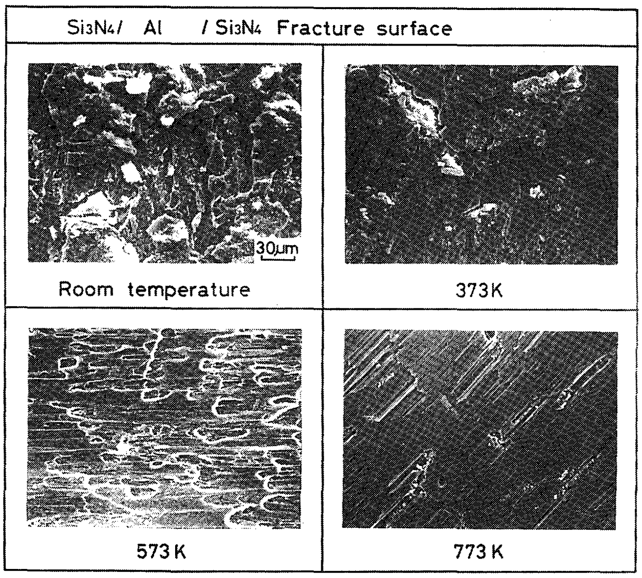

Fig. 8 Change in fracture structure of Si_3N_4/Si_3N_4 joint brazed at 1373K for 3.6ks using Al filler with testing temperature.

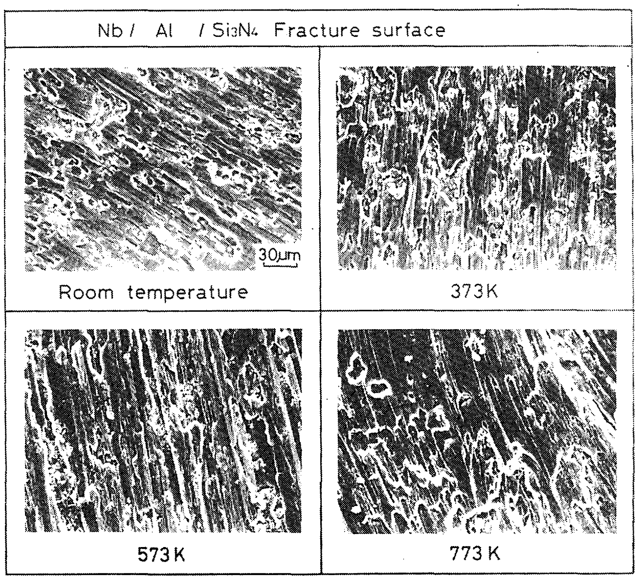

Fig. 9 Change in fracture structure of Si_3N_4/Ti joint using Al filler with testing temperature.

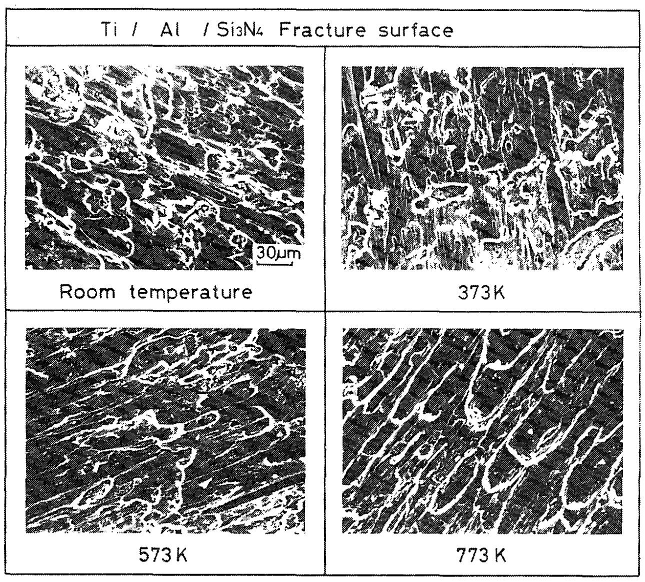

Fig. 10 Change in fracture structure of Si_3N_4/Nb joint using Al filler with testing temperature.

3.3 Joining microstructure of Si_3N_4/Ti or Nb joint

The microstructural analyses were performed using energy dispersive X-ray (EDX) microanalysis and scanning electron microscopy.

The microstructure and line analyese for Ti, Al and Si in Si_3N_4/Al/Ti joint brazed with Al filler at 1073K for 300s are shown in **Fig. 11**. In the joining layer, the granular intermediate phase $TiAl_3$ is formed as shown in **Fig. 12** using EDX microanarises, and further the titanium matrix is melted down to the interface of Si_3N_4 by the dissolution action of aluminum.

Figure 13 shows the microstructure and line analyses

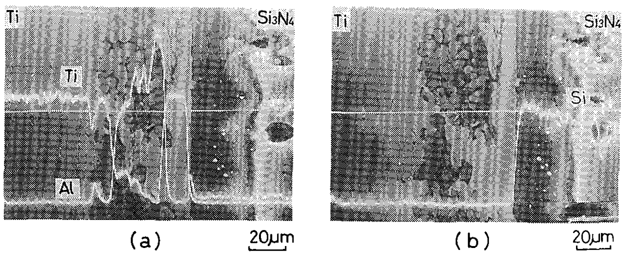

Fig. 11 Microstructure and line analyses for Ti and Al in Si_3N_4/ Nb joint brazed at 1073 K for 300s.

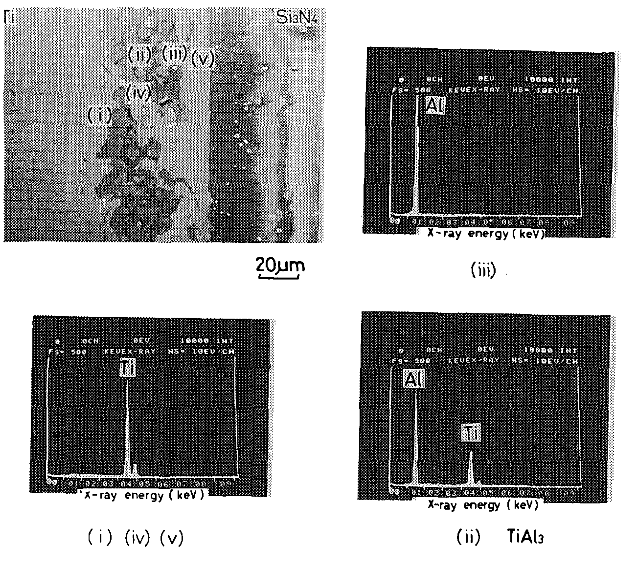

Fig. 12 Microstructure and spot analyses of Si_3N_4/Ti joint brazed at 1073K for 300s.

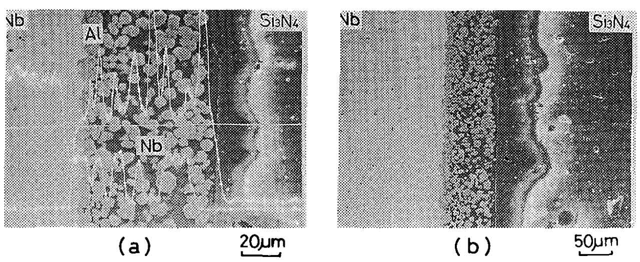

Fig. 13 Microstructure and line analyses for Nb and Al in Si_3N_4/Nb joint brazed at 1273K 300s.

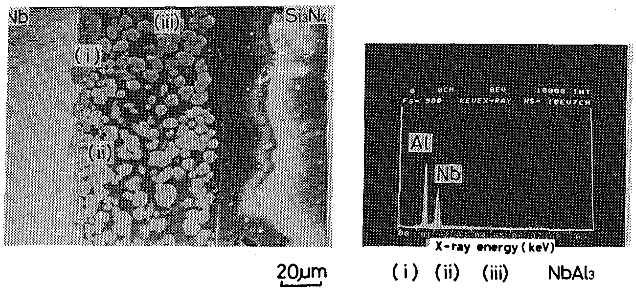

Fig. 14 Microstructure and spot analyses of Si_3N_4/Nb joint brazed at 1273K for 300s.

for Nb and Al in Si_3N_4/Al/Nb joint brazed at 1273K for 300s. The granular intermediate phases are identified as $NbAl_3$ in **Fig. 14** using EDX microanalysis. Since Al filler reacts with Nb during brazing of Si_3N_4 to Nb, the thickness of joining layer becomes 60μm that is thicker than the thickness of 10μm in Si_3N_4/Si_3N_4 joint. Compared with Si_3N_4/Ti joint the microstructure of Si_3N_4/Nb joint is uniform since the intermediate phase of $NbAl_3$ distributes homogeneously in Al matrix. This is attributable to the higher strength of Si_3N_4/Nb joint.

4. Conclusion

The wettability of molten aluminum, copper and silver was evaluated by a sessile drop technique. Further, the brazing of Si_3N_4 to Si_3N_4, and Si_3N_4 to Nb or Ti was conducted using Al filler in a vacuum. The joining strength and the microstructure at interface of Si_3N_4 joints were investigated by shear fracture loading, transmission electron microscopy and EDX microanalysis, respectively.

Aluminum among the three metals shows the lowest equilibrium contact angle with the highest temperature dependence of the angle, and the work of adhesion of aluminum definitely increases with increasing temperature. The formation of AlN sialon at the interface of Si_3N_4 and Al accelarates the wetting of molten aluminum. These results indicate the molten aluminum is applicable for the brazing filler of Si_3N_4.

The joining strength of Si_3N_4/Si_3N_4 joint brazed with Al filler is 210MP at room temperature, and shows the maximum at elevated temperature. The decrease in strength of Al filler is attributable to the decrease in the strength of Si_3N_4/Si_3N_4 joint.

The joining strength of Si_3N_4/Nb or Ti joint brazed with Al filler is about half the joining strength of Si_3N_4/ Si_3N_4 joint.

The stress arisen from the difference of thermal expansion coefficient between Si_3N_4 and metal accounts for the decrease in joining strength of Si_3N_4/metal joint. The homogeneous distribution of intermediate phase of $NbAl_3$

in Al matrix is attributable to the higher joining strength of Si_3N_4/Nb joint.

Acknowledgement

The authors thank Ass. Prof. H. Mori in High Voltage Electron Microscope Center of Osaka University for the observation of microstructure at aluminum/silicon nitride interface by transmission electron microscopy.

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