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Brazing of $\text{Si}_3\text{N}_4$ to Metals with Al Filler (Report I)†
— $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ and $\text{Si}_3\text{N}_4/\text{Ti}$ or Nb Joints —

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Abstract

The wettability of molten aluminum on $\text{Si}_3\text{N}_4$ was investigated by a sessile drop technique in a vacuum. The joining of $\text{Si}_3\text{N}_4$ to $\text{Si}_3\text{N}_4$, and $\text{Si}_3\text{N}_4$ 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 wettability of molten aluminum on $\text{Si}_3\text{N}_4$ increases significantly with increasing temperature, and aluminum definitely wets $\text{Si}_3\text{N}_4$. The joining strength of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint with Al filler exhibits the maximum of 210 MPa at an elevated temperature of 373 K, and decreases with further increasing testing temperature. The strength of $\text{Si}_3\text{N}_4$/Ti or Nb joint with Al filler is about half the strength of $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint. The stress arisen from the thermal difference between $\text{Si}_3\text{N}_4$ and metal provides the detrimental effect on the strength of the $\text{Si}_3\text{N}_4$/metal joint. At the joining layer of $\text{Si}_3\text{N}_4$/Ti or Nb joint the intermediate phase of $\text{TiAl}_3$ or $\text{NbAl}_5$ was formed.

KEY WORDS: (Ceramic-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 Eberhart1) 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 $\text{Si}_3\text{N}_4$ 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 $\text{Si}_3\text{N}_4$ in a vacuum, and the brazing of $\text{Si}_3\text{N}_4$ 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 $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ and $\text{Si}_3\text{N}_4$/metal joints, and observing the microstructure of the joint.

2. Experimental

The pressureless sintered $\text{Si}_3\text{N}_4$ containing a few percent of $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ 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 $\text{Si}_3\text{N}_4$ was evaluated by measuring the contact angle between the peripheral surface of sessile drop and horizontal surface of $\text{Si}_3\text{N}_4$ in a vacuum below 1.33 mPa as shown in Fig. 1. The heating rate up to desired temperature was 1.7 K/s, and the sessile drop apparatus is shown in Fig. 2.

$\text{Si}_3\text{N}_4$ 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 $\text{Si}_3\text{N}_4$ was performed, and Al filler metal was then deposited to form a joint. The joint was then sintered in a vacuum at 1473 K for 30 min.

Fig. 1 Schematic of contact angle of liquid drop on $\text{Si}_3\text{N}_4$.
Si₃N₄ with aluminum was conducted at 1373 K for 3.6 ks in 1.33 mPa, and then the lap joint with Al thinned down to 0.1 mm thickness was made in the joining condition of joining temperatures of 1273 K (for Nb) and 1073 K (for Ti) and brazing time of 300 s 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 \times 10^{-2} \text{ mm s}^{-1}. The microstructure of Si₃N₄/metal was investigated by means of scanning electron microscope and EDX microanalyzer.

3. Results and Discussion

3.1 Wettability of molten aluminum on Si₃N₄

Figure 3 shows the temperature dependence of the equilibrium contact angle of molten aluminum, copper and silver on Si₃N₄. The contact angle of molten metal was taken at 3.6 ks 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 π/2, the shape of the melt is convex and is said to be wetting at contact angles between π/2 and π the melt begins to swell and is said to be in the non-wetting state. The wettability of aluminum on Si₃N₄ begins at temperatures above 1240 K. 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-Dupré equation,

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

where \( \gamma_{LG} \) is the liquid energy. Using the data and their temperature coefficient \( \alpha = \frac{d\gamma_{LG}}{dT} \) available from the literature and the measured \( \theta_{\infty} \) for three metals, the work of adhesion, \( W_{ad} \), of the three metals against Si₃N₄ 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 Al₂O₃ or cubic ZrO₂ is related to the formation energy of
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/Si₃N₄ joint, the microstructure of the sessile drop made at 1473 K for 3.6 ks was observed using a scanning electron microscope and a transmission electron microscope. Figure 5 shows the interface of Al/Si₃N₄ sessile drop, and the intermediate phase between aluminum and Si₃N₄ 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 Si₃N₄. The intermediate phase is composed of fine grains in diameter of 10 nm and grows preferentially in the grain boundaries of Si₃N₄. 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 Al₂O₃ was also observed. The results of Figs. 5 to 6 indicate that aluminum definitely wets Si₃N₄ and is applicable to the brazing filler for Si₃N₄.

3.2 Joining strength of Si₃N₄/Si₃N₄ and Si₃N₄/Ti or Nb joints

Figure 7 represents the testing temperature dependence of the strength of Si₃N₄/Si₃N₄ joints brazed at 1373 K for 3.6 ks using Al filler. The strength of Si₃N₄/Si₃N₄ joint shows the maximum value of 210 MPa at 373 K. The release of stress arising from the difference between the thermal expansion of Si₃N₄ and fillers in the joint accounts for the increase in strength of the Si₃N₄ joint at the testing temperature. Furthermore, the strength of the Si₃N₄/Si₃N₄ joint falls with increasing testing temperature.

The change in the fracture structures of Si₃N₄/Si₃N₄ joints brazed at 1373 K for 3.6 ks using aluminum with testing temperature is shown in Fig. 8. The fracture mixed with the brittle fracture structure of Si₃N₄ and ductile fracture structure of the filler below 373 K, and the general ductile fracture structure of the filler above 573 K are shown in Fig. 8. The decrease in strength of aluminum filler accounts for the decrease in strength of the Si₃N₄ joint.
The Si₃N₄/Nb or Ti joint is made using Al filler. Si₃N₄ was metallized with Al filler at 1373 K for 3.6 ks. The metallized Al was thinned down to 0.1 mm in thickness, and then the Si₃N₄ brazed with Nb or Ti by the metallized Al filler.

Figure 7 also shows the change in fracture strength of Si₃N₄/Nb or Ti joint with testing temperature. The strength, 100 MPa, of Si₃N₄/Ti or Nb joint is half the strength of Si₃N₄/Si₃N₄ joint at room temperature. The stress arisen from the difference of thermal expansion coefficient between Si₃N₄ and metal is attributable to the decrease in the strength of the Si₃N₄ joint. The strength of Si₃N₄/Nb joint is a little higher than that of Si₃N₄/Ti joint, and the strength of both joints decreases with increasing testing temperature. As shown in the change in fracture structures of Si₃N₄/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. The decrease in the strength of Al filler is attributable to the decrease in the strength of Si₃N₄/metal joint.

**Fig. 7** Testing temperature dependence of fracture shear strength of Si₃N₄/Si₃N₄ joint brazed at 1373 K for 3.6 ks using Al filler.

**Fig. 8** Change in fracture structure of Si₃N₄/Si₃N₄ joint brazed at 1373 K for 3.6 ks using Al filler with testing temperature.

**Fig. 9** Change in fracture structure of Si₃N₄/Ti joint using Al filler with testing temperature.

**Fig. 10** Change in fracture structure of Si₃N₄/Nb joint using Al filler with testing temperature.
3.3 Joining microstructure of Si$_3$N$_4$/Ti or Nb joint

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

The microstructure and line analyses for Ti, Al and Si in Si$_3$N$_4$/Al/Ti joint brazed with Al filler at 1073 K for 300 s 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$_3$N$_4$ by the dissolution action of aluminum.

Figure 13 shows the microstructure and line analyses for Nb and Al in Si$_3$N$_4$/Al/Nb joint brazed at 1273 K for 300 s. 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$_3$N$_4$ to Nb, the thickness of joining layer becomes 60 µm that is thicker than the thickness of 10 µm in Si$_3$N$_4$/Si$_3$N$_4$ joint. Compared with Si$_3$N$_4$/Ti joint the microstructure of Si$_3$N$_4$/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$_3$N$_4$/Nb joint.

4. Conclusion

The wettability of molten aluminum, copper and silver was evaluated by a sessile drop technique. Further, the brazing of Si$_3$N$_4$ to Si$_3$N$_4$, and Si$_3$N$_4$ to Nb or Ti was conducted using Al filler in a vacuum. The joining strength and the microstructure at interface of Si$_3$N$_4$ 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$_3$N$_4$ and Al accelerates the wetting of molten aluminum. These results indicate the molten aluminum is applicable for the brazing filler of Si$_3$N$_4$.

The joining strength of Si$_3$N$_4$/Si$_3$N$_4$ joint brazed with Al filler is 210 MPa 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$_3$N$_4$/Si$_3$N$_4$ joint.

The joining strength of Si$_3$N$_4$/Nb or Ti joint brazed with Al filler is about half the joining strength of Si$_3$N$_4$/Si$_3$N$_4$ joint.

The stress arisen from the difference of thermal expansion coefficient between Si$_3$N$_4$ and metal accounts for the decrease in joining strength of Si$_3$N$_4$/metal joint. The homogeneous distribution of intermediate phase of NbAl$_3$...
in Al matrix is attributable to the higher joining strength of Si₃N₄/Nb joint.

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References