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Brazing of Si_3N_4 to Metals with Al-Si Filler Metals†

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Abstract

The wettability of molten Al-Si (0–50 mass%) alloys was investigated by measuring the contact angle of alloys on Si_3N_4 in vacuum. The silicon doesn's change the equilibrium contact angle of aluminum at 1373 K and exhibits the angle below 50 degree, although the addition of silion promotes the weeting rate of aluminum. Al-Si alloys wet Si_3N_4 and are applicable to the filler metals for joining Si_3N_4.

Si_3N_4 was brazed to a variety of metals such as Nb, Ti, and SUS304 using Al-10mass% Si filler. The addtion of silicon to aluminum improves the mechanical properties of filler metal itself and also the intermediate phases formed in the filler in the joint. This provides the superior strength of Si_3N_4/metal joint with Al-10Si filler, compared with that of Si_3N_4/metal joint Al filler.

KEY WORDS: (Ceramic-Metal Joning) (Joining) (Brazing) (Wettability) (Silicon Nitride) (Aluminum-Silicon Alloy) (Filler Metal)

1. Introduction

The worse workability of ceramics requires the joining of ceramics to metals in the practical engineering. Alminum posesses the two superior properties of the filler metal for the joining of ceramic to metals. First, the molten aluminum has the high wettability against ceramics such as alumina[1,2] and zirconia[3] and Si_3N_4[4]. Secondly, aluminum is a soft metal which relaxes the stress arising from the difference in the thermal expansion between the ceramics and metal in joints. Then, aluminum[5-10] and aluminum-copper[11,12] alloys often have been used as the brazing filler for ceramic/metal joining. This work, in succesive, from the previous papers[9,10,12] reports the effect of silicon on the wellability of aluminum on Si_3N_4, and applies Al-10 mess% Si filler to join Si_3N_4 to metals.

2. Experimental Procedure

The materials were pressureless sintered Si_3N_4 containing a few percent of Al_2O_3 and Y_2O_3, and Al-Si alloys with silicon content up to 50 mass % as shown in **Table 1**.

The wettability of the molten alloy was evaluated by measuring the contact angle between the peripheral surface of 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, and were heated at the rate of about 1.3 $K \cdot sec^{-1}$ in a vacuum below 1.33 mPa. The molten drops on the ceramics were then photographed at regular time intervals.

Table 1 Chemical composition and liquidus temperature of Al-Si alloy filler used.

	Si (mass%)	Al (mass%)	Liquidus temperture (K)
Al	-	bal.	933
Al- 4Si	4	bal.	908
Al-10Si	10	bal.	863
Al-30Si	30	bal.	1093
Al-50Si	50	bal.	1323

S_3iN_4 of 15 mm in diameter and 3 mm in thickness was lapped to Si_3N_4 of 6 mm diameter and 3 mm thickness under a loading of 10 g with Al-Si filler of 100 μm thickness. The thickness of the filler in Si_3N_4/Si_3N_4 was about 25 μm after joining.

Si_3N_4 of 15 mm in diameter and 3 mm in thickness were also lapped to metal of 6 mm in diameter and 3 mm thickness with Al-10 mass% filler. First, the metallizing of Si_3N_4 with the filler was conducted at 1373 K for 3.6 ks in 1.33 mPa, and then the lap joint with the filler thinned down to 0.1 mm thickness was made in the joining condition of 973 K to 1272 k and 300 s where SUS304 was Ni-plated.

The joining strength of the lap joint was determined by fracture shear loading using a crosshead speed of 1.7×10^{-2} mm/s. The microstructures and element distribution of joints were determined by means of a

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scanning electron microscope and an energy dispersive microanalyser, respectively.

3. Results and Discussion

3.1 Wetting behavior of Al-Si alloys

Figure 1 shows the change in contact angle of molten Al-Si alloys on Si_3N_3 with time 1373 K. The Al-Si alloys with silicon content up to 50 mass% represent the time dependence of contact angle, and the contact angles of alloys reach the equilibrium values at 3.6 ks.

The change in contact angle of molten metal on ceramics with time is expressed by the first law of time according to Newman[13].

$$\frac{d(\cos\theta_t)}{dt} = b(\cos\theta_\infty - \cos\theta_t) \qquad (1)$$

where b is a rate constant, θ_t and θ_∞ are a contact angle at time t and a equilibrium contact angle, respectively. From eq. (1)

$$\cos\theta_t = (\cos\theta_\infty)\,[1 - a\exp(-bt)] \qquad (2)$$

The contact angle of Al-Si alloys on Si_3N_4 is expressed using eq. (2) in **Fig. 2**.

The values of b for Al-Si alloys are estimated from the slopes in Fig. 2. The silicon dependence of b is shown in **Fig. 3** in which the values of b for Al-Cu alloys are also included[2]. The b of Al-Si alloys rises definitely with increasing the silicon content up to 30

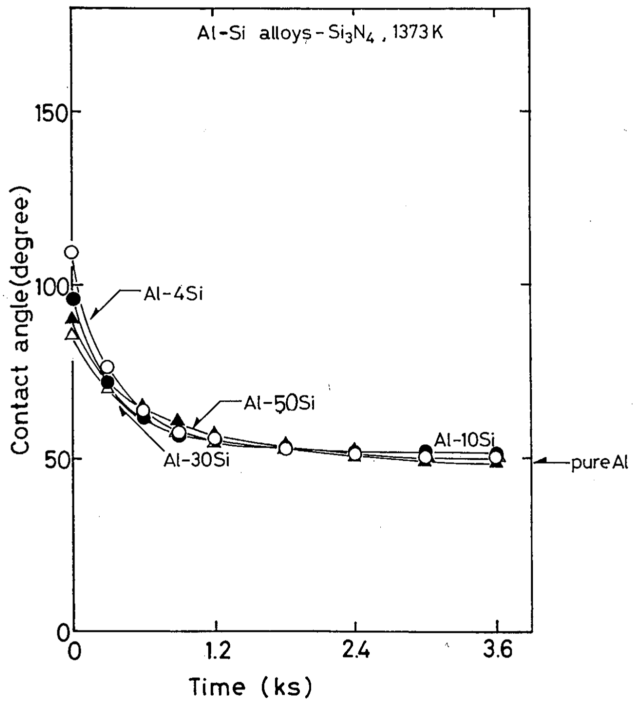

Fig. 1 Change in contact angle of Al-Cu alloys on Si_3N_4 with time at 1373 K.

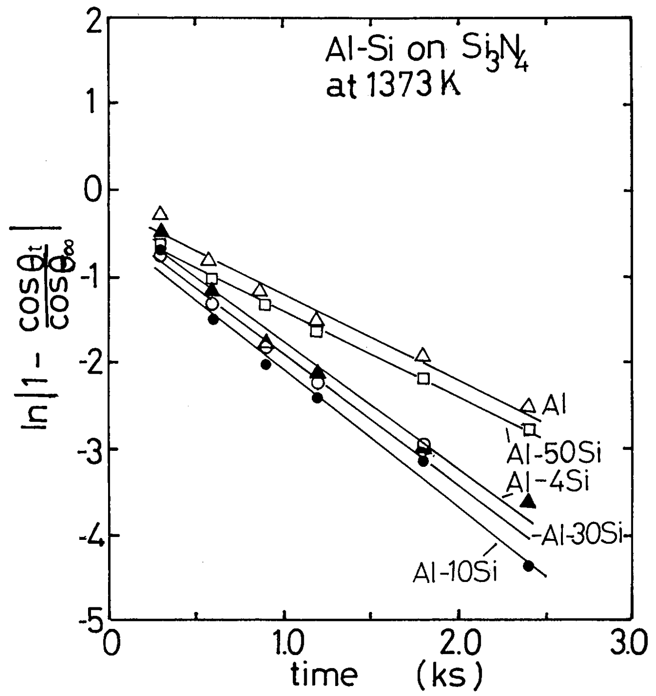

Fig. 2 $\ln|\,1-\cos\theta/\cos\theta_\infty\,|$ vs t, for Al-Si alloys at 1373 K.

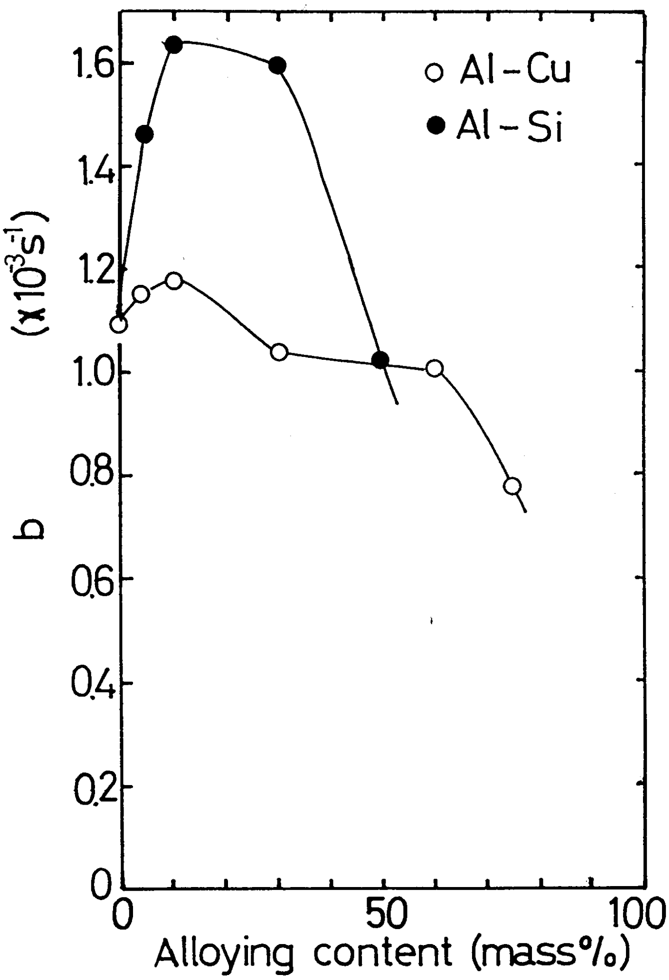

Fig. 3 Silicon content of dependence of b for Al-Si alloys on Si_3N_4 at 1373 K.

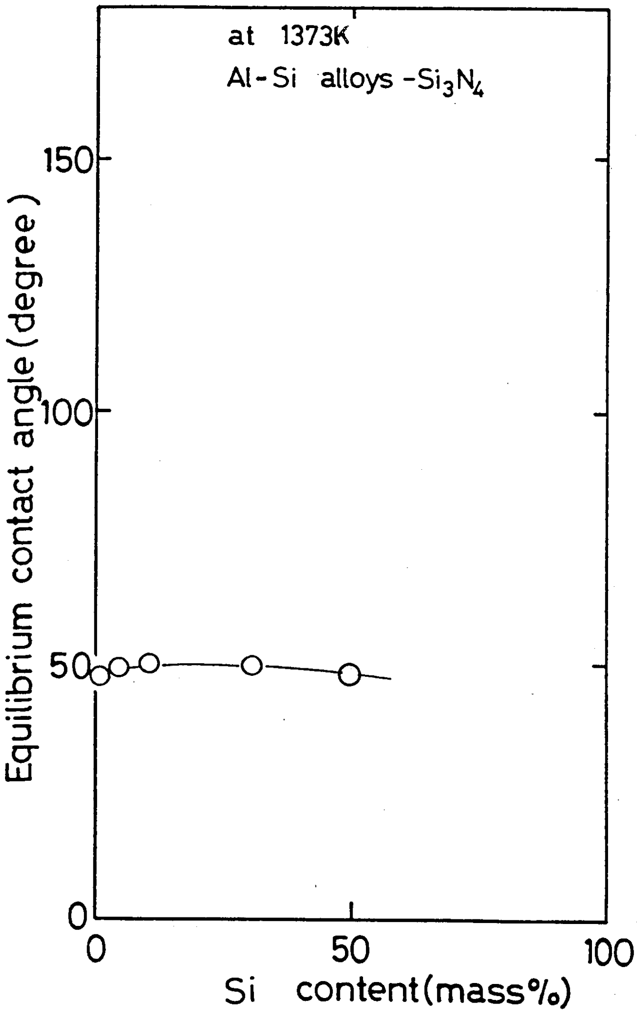

Fig. 4 Silicon content dependence of equilibrium contact angle for Al-Si alloys on Si_3N_4 at 1373 K.

mass% Si and lowers further with higher Si content. The wetting rate of molten aluminum becomes faster with mixing silicon in alloys. The large amount of silicon of 50 mass% retards the wetting rate of alloys on Si_3N_4. The values of *b* for Al-Si alloys are larger than that for Al-Cu alloys.

The equilibrium contact angle of Al-Si alloy at 1373 K doesen't change with adding silicon to aluminum as shown in **Fig. 4**. Al-Si alloys up to 50 mass% wet Si_3N_4, since the alloys show the angles below 50 degree. The result in Fig. 4 indicate that Al-Si alloys are applicable to filler metals for joining Si_3N_4.

3.2 Strength of Si_3N_4/Si_3N_4 and Si_3N_4/metal joint with Al-10Si filler metals

The joining strength of Si_3N_4 to Si_3N_4 brazed with Al-10Si filler was investigated. **Fig. 5** shows the change in strength of a Si_3N_4 joint at 3.6 ks using Al-10Si filler with brazing temperature. Although the strength of joint is effectively improved around the brazing temperature of 1373 K, the strength of joint is relatively

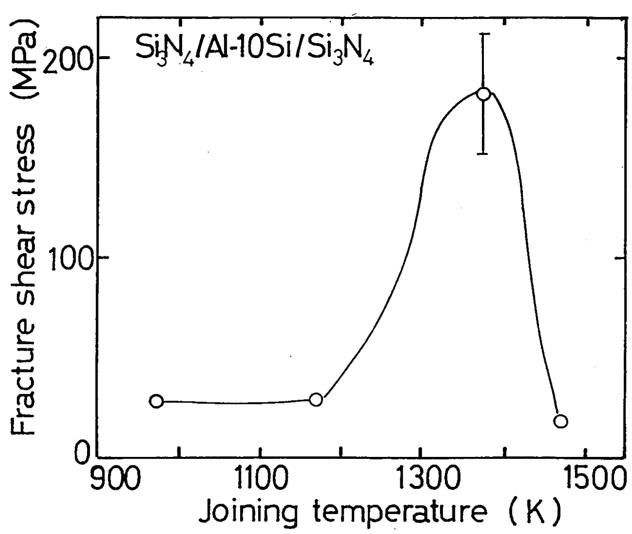

Fig. 5 Change in strength of Si_3N_4 joint using Al-10Si filler at a brazing time of 3.6 ks with brazing temperature.

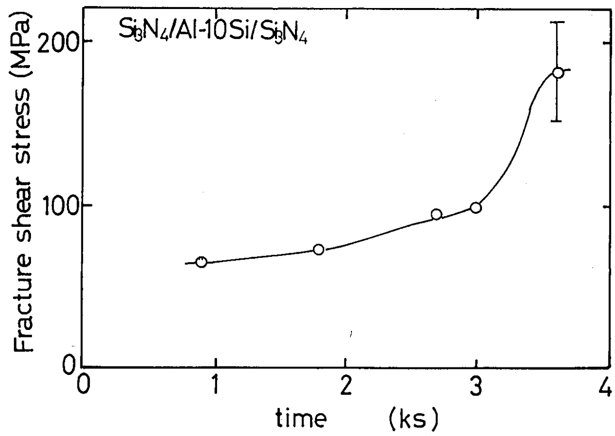

Fig. 6 Change in strength of Si_3N_4 joint using Al-10 Si filler at brazing temperature of 1373 K with brazing time.

low at the lower or higher brazing tempertures. At the brazing temperatures below 1173 K the oxidation film of molten Al-Si filler surpresses the wetting of alloys on Si_3N_4, and at a higher brazing temperature of 1473 K the evaporation of the filler degrades the joining of Si_3N_4 to the filler.

Figure 6 indicates that the brazing time of 3.6 ks at 1373 K requires to join to Si_3N_4 with Al-10Si filler. The brazing time to reach the saturated strength of Si_3N_4 joint using Al-10Si in Fig. 6 also corresponds to the wetting time to reach the equilibrium contact angle of the alloy in Fig. 1. This implies that the sufficient wetting of molten filler gives the high strength of Si_3N_4 joint.

Figure 7 shows the change in strength of Si_3N_4 joint brazed at 1373 K 3.6 ks with silicon content in the filler. The addition of silicon content improves the strength of the joint, and in particular, the Si_3N_4 joint brazed with Al-10Si filler shows the maximum value of 180

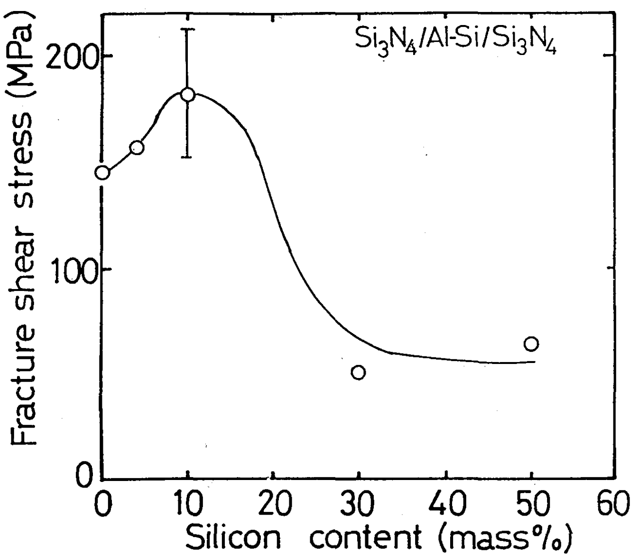

Fig. 7 Change in strength of Si_3N_4 joint using Al-Si alloy filler brazed at 1373 K for 3.6 ks with silicon content of the filler.

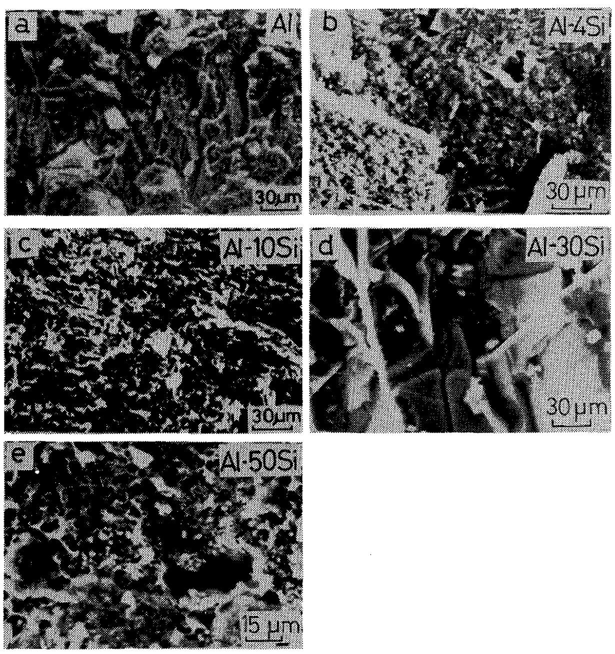

Fig. 8 Fracture structure of Si_3N_4 joint brazed at 1373 K for 3.6 ks with Al-Si alloy filler.
(a) Al, (b) Al-4Si, (c) Al-10Si, (d) Al-30Si, (e) Al-50Si

MPa. Further, the strength of the joint lowers with increasing silicon content up to 50 mass% in the filler. **Fig. 8** represents the structure of the fracture for Si_3N_4 joints brazed at 1373 K for 3.6 ks with Al-Si alloy fillers. The structures of the joints with Al-Si fillers containing a silicon content up to 10 mass% Si are 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 surfaces of Si_3N_4 joints with Al-30 and Al-50 mass% Si fillers shows the brittle

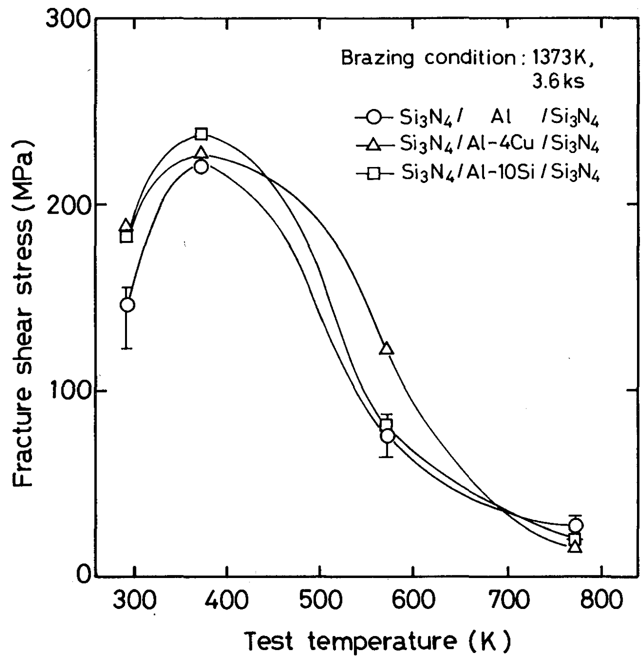

Fig. 9 Effect of testing temperature on strength of Si_3N_4 joints brazed at 1373 K for 3.6 ks using aluminum (○), Al-10Si (□) and Al 4Cu alloy fillers (△).

fracture surface of the filler. The brittle low mechanical properties and the low wettabilities of Al-30 mass% Si and Al-50 mass% Si fillers are attributable to the low strength of Si_3N_4 joints. The results of frigures 7 and 8 indicate that the joints with the fillers that possess the superior wettabilities and mechanical properties give the high strength of joint.

The testing temperature dependence of the strength of Si_3N_4 joints brazed at 1373 K for 3.6 ks with Al-10 mass% Si filler is shown in **Fig. 9**, in which that Al[9] and Al-4 mass% Cu[12] fillers are also included. The release of stress arising from the difference between the thermal expansion of Si_3N_4 and fillers in the joint provides the maximum of strength of Si_3N_4 joint at 373 K.

The change in the fracture structures of Si_3N_4 joints brazed at 1373 K for 3.6 ks using Al-10 mass% Si fillers with testing temperatures is shown in Fig. 10. The fracture structure mixed with the brittle fracture of Si_3N_4 and ductile fracture of the filler at testing temperatures below 373 K and the general ductile fracture structures at temperatures above 573 K are shown in **Fig. 10**. These observation of the fracture surface of joints indicate that the decrease in strength of Al-10 mass% Si filler accounts for the decrease in strength of Si_3N_4 joint.

Si_3N_4 was joined to metals of Ti, Nb, Ni and SUS304 using Al-10 mass% Si filler metal. As shown in **Fig.11**, the combination of Si_3N_4 and Ti provides the highest strength among Si_3N_4/metal joints. The strength of Si_3N_4/metal joint decreases with an increase in $\alpha \cdot E$

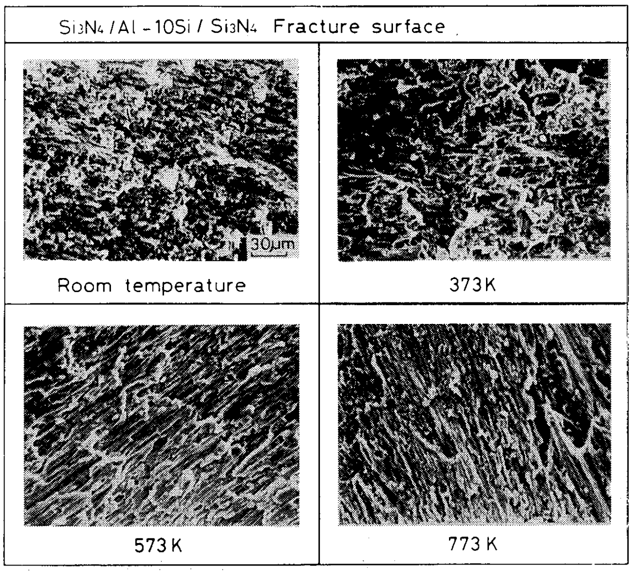

Fig. 10 Change in fracture structure of Si_3N_4 joint brazed at 1373 K for 3.6 ks using Al-10Si alloy filler with testing temperature (a) room temperature, (b) 373 K, (c) 573 K, (d) 773 K.

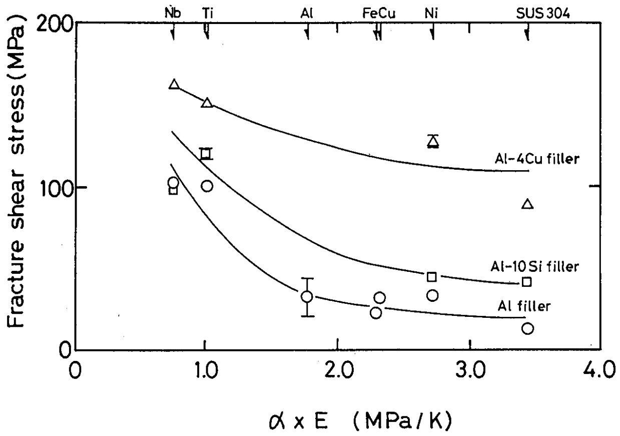

Fig. 11 Strength of Si_3N_4/Al-10Si/Metal joint related to $\alpha \cdot E$

factor, where α and E are the thermal expansion coefficient and elastic modulus of metal, respectively. The stress arisen from the difference of thermal expansion between Si_3N_4 and metal influences the strength of the joint. Included in the figure is the strength of joint using Al[9] and Al-4Cu[12] filler metals.

The joints with Al-10Si filler provide the higher strength than that of joints with Al filler, except Si_3N_4/Nb joint, and the lower strength than that of joints wth Al-4Cu filler. The superior mechanical properties of Al-10Si filler is attributable to the higher strength of Si_3N_4/metal joint.

Figure 12 shows the temperature deoendence of strength of Si_3N_4/Ti joint with Al-10Si filler. Included in the figure for comparison is the strength of the joint with Al[9] and Al-4Cu[12] fillers. The strength of the joint with Al-10Si filler is higher than that of the joint

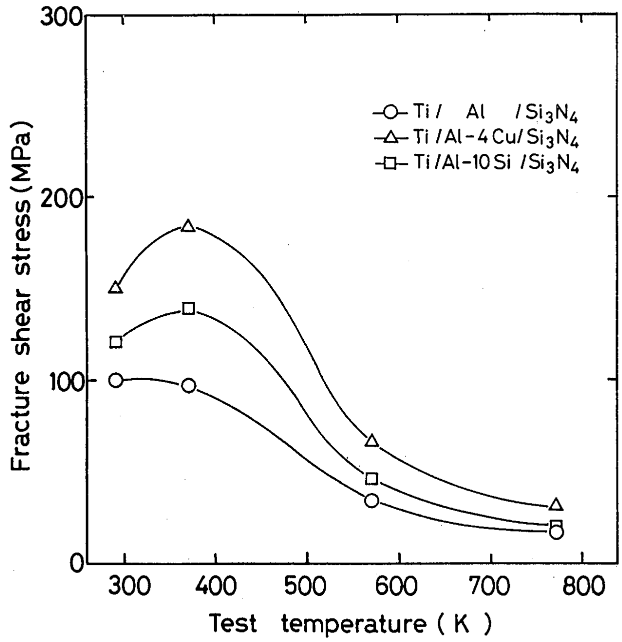

Fig. 12 Change in strength of Si_3N_4/Ti joint using Al-10Si filler with testing temperature.

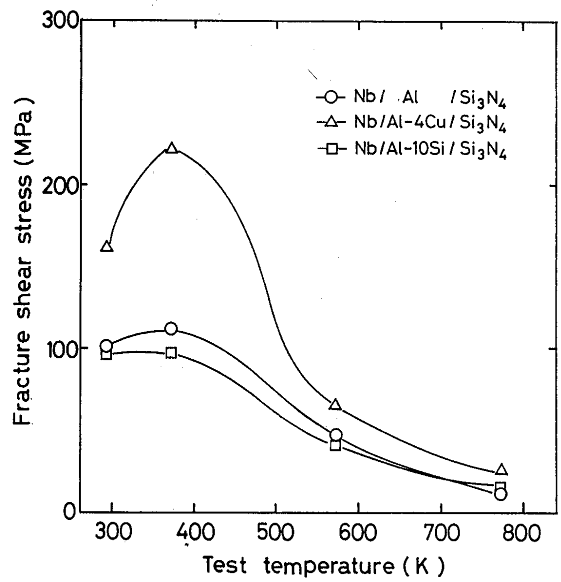

Fig. 13 Change in strength of Si_3N_4/Nb joint using Al-10Si filler with testing temperature.

with Al filler and lower than that of the joint with Al-4Cu filler at all testing temperatures. The strength of the joint with Al-10Si filler gives the maximum of 130 MPa at testing temperature of 375 K. The release of thermal stress at the temperature gives rise to the maximum of the joint.

The strength of Si_3N_4/Nb joint with Al-10Si filler is lower than that of the joint with Al filler at all testing temperatures as shown in **Fig. 13**. Included in this figure for comparison is also the strength of the joint with Al-4Cu fillers. As indicated later, the addition of silicon to Al filler promotes to form the thick layer of $NbAl_3$ intermetallic compound in Nb-Al system. This impares the strength of Si_3N_4/Nb joint with Al-10Si filler.

3.3 Microstructure of Si_3N_4/metal joint with Al-10Si filler metal

Figure 14 shows the microstructure and line analyses of elements in Si_3N_4/Ti joint with Al-10Si filler. At the interface between Ti and the filler the granular $TiAl_3$ is formed. The Al-Si filler remains between $TiAl_3$ and Si_3N_4, and joins soundly with Si_3N_4. Although the intermediate phase at interface between the filler and Si_3N_4 is very thin, Naka et al.[14] reported the formation of AlN type sialon at the interface.

Figure 15 shows the microstructure and line analyses of elements in Si_3N_4/Nb joint with Al-10Si filler. The thick phase of $NbAl_3$ is observed at the interface between Nb and Al-10Si filler. Since the granular $NbAl_3$ phase was formed in Si_3N_4/Nb joint with Al filler without Si[19], the addition of Si to Al filler promotes the formation of thick $NbAl_3$ layer at the interface between Nb and the filler. This brittle $NbAl_3$ phase leads to impaire the strength of Si_3N_4/Nb joint with Al-10Si filler in **Fig. 11**, although other Si_3N_4/metal joints with Al-10Si filler give the superior strength.

The microstructure and line analyses of elements in Si_3N_4/Ni joints with Al-10Si filler is shown in **Fig. 16**. Two intermediate phases of Ni_2Al_3 and $NiAl_3$ are observed at the interface between Ni and Al-10Si filler. Ni_2Al_3 and $NiAl_3$ form the layer and glanular structures, respectively. Compared with Si_3N_4/Ni joint with Al filler the joint using Al-10Si filler provides the thinner Ni_2Si_3 layer. The decrease in thickness of Ni_2Si_3 phase may improve the strength of the joint.

Two reasons operate for the improvement of strength

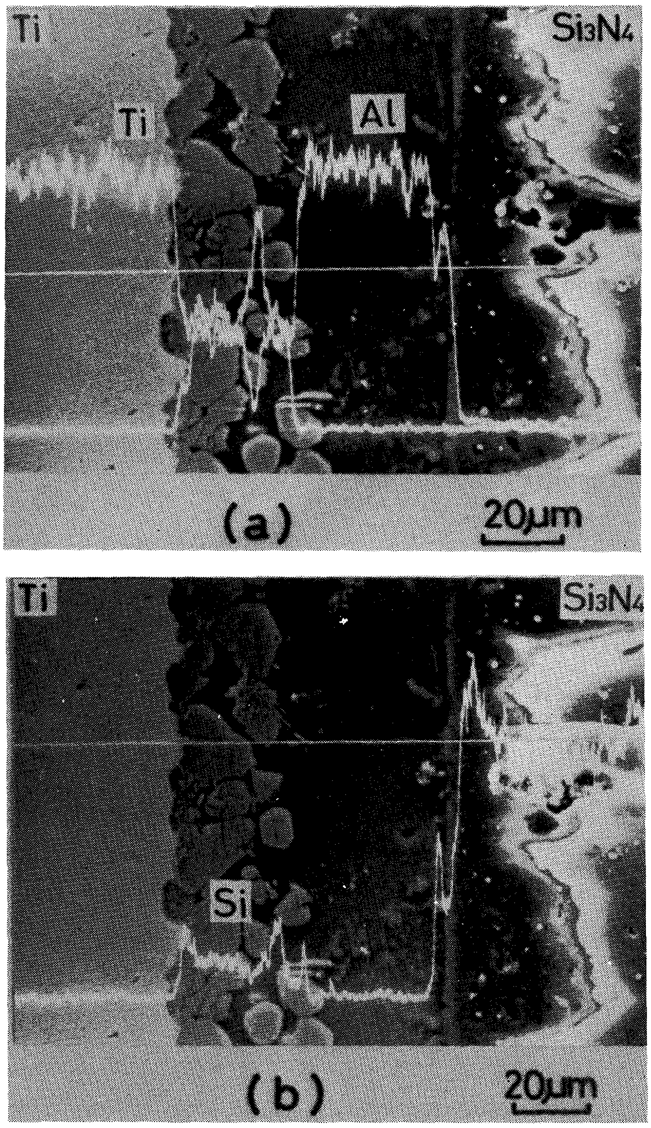

Fig. 14 Microstructure and line analyses of Ti, Al (a) and Si (b) in Si_3N_4/Ti joint with Al-10Si filler.

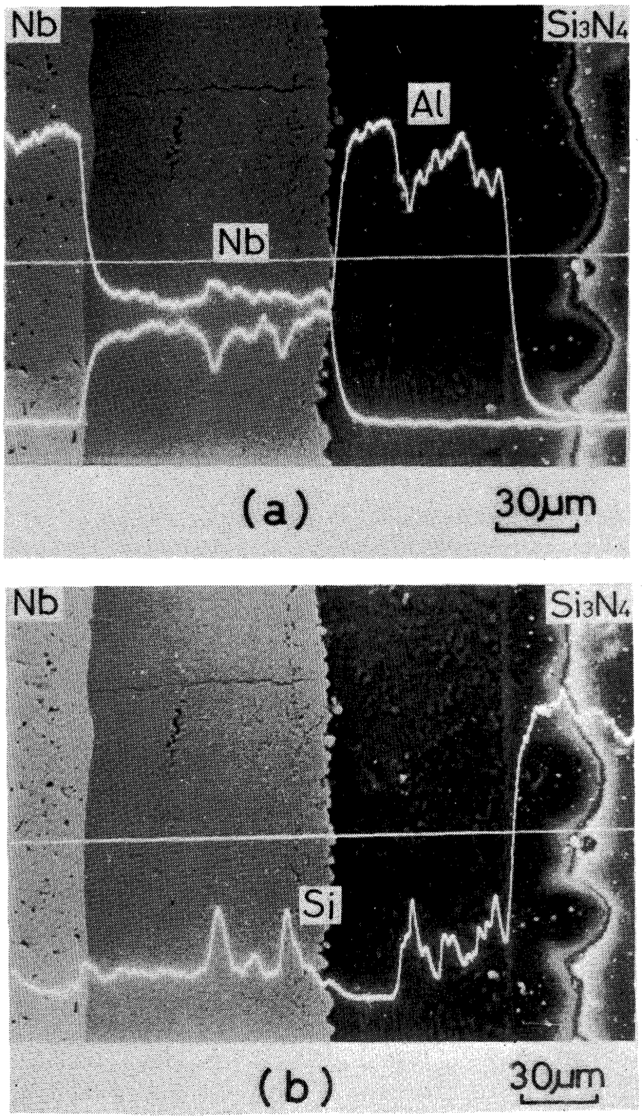

Fig. 15 Microstructure and line analyses of Nb, Al (a) and Si (b) in Si_3N_4/Nb joint with Al-10Si filler.

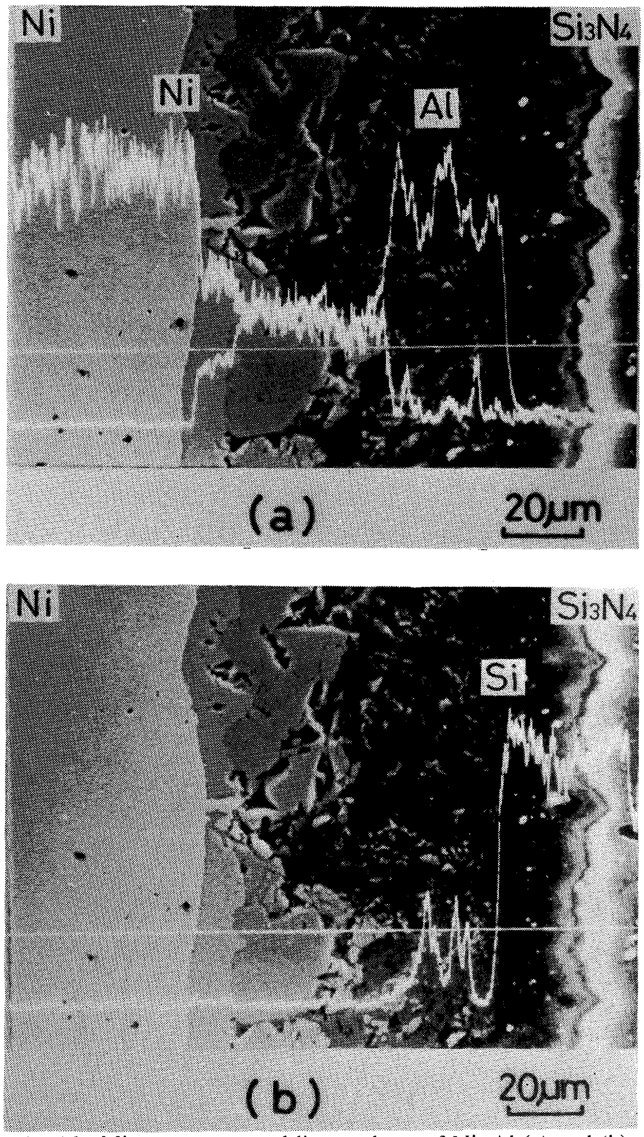

Fig. 16 Microstructure and line analyses of Ni, Al (a) and (b) Si in Si_3N_4/Ni joint with Al-10Si filler.

in Si_3N_4/metal joint with Al-10Si filler. First, the solution of silicon to intermediate phases such as $TiAl_3$ improves the strength of the joint. Second, the Al-10Si filler possesses the superior mechanical properties and larger thermal expansion coefficient, compared with Al filler, and the Al-10Si filler remains between the intermediate phases and Si_3N_4. These gives rise to increasing the strength of the joint.

4. Conclusion

The contact angle of molten Al-Si alloys containing Si content up to 50 mass% on Si_3N_4 was measured at 1373 K in vacuum. The wetting rate of molten aluminum is improved by adding silicon up to 30 mass%. Since Al-Si alloys shows the equilibrium contact angles below 50 degree, the alloys wet well Si_3N_4, and are applicable to the filler metal for joining Si_3N_4. The Al-10 mass% Si filler provides the maximum strength of Si_3N_4 joint.

The joining of Si_3N_4 to metals such as Ti, Nb, Ni and SUS304 was performed using Al-10 mass% Si filler. The combination of Si_3N_4 and Ti provides the highest strength among Si_3N_4 and metal joints. The strength of Si_3N_4/metal joint is related to $\alpha \cdot E$ factor of metal. The stress arisen from thermal expansion between ceramic and metal influences the strength of Si_3N_4 and metal joint.

The addition of Si to Al filler improves the strength of Si_3N_4/metal joint. The superior mechanical properties of Al-10 mass% Si filler improved the strength of Si_3N_4/metal joint.

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