Joining of Silicon Nitride Using Amorphous Cu-Ti Filler Metal†

Masaaki NAKA*, Tasuku TANAKA*** and Ikuo OKAMOTO**

Abstract

Joining of Si_3N_4 to Si_3N_4 was conducted using amorphous $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ amorphous filler metals which were produced by liquid quenching, where pressureless sintered Si_3N_4 was used. The fracture shear testing was carried out at room temperature. The joining strength of Si_3N_4 using $Cu_{66}Ti_{34}$ filler is higher than that of Si_3N_4 using other Cu-Ti fillers at any brazing temperature except for brazing temperature of 1273 K. Thus, the joining strength of $Cu_{66}Ti_{34}$ filler shows the maximum value of 313.8 MPa at brazing temperature of 1323 K. The Si_3N_4 joint using $Cu_{50}Ti_{50}$ filler exhibits the gradual decrease in the elevated temperature strength from 199.1 MPa at 373 K to 105.9 MPa at 973 K. During brazing Ti in molten $Cu_{50}Ti_{50}$ filler reacts with Si_3N_4 and forms TiN, Ti_5Si_3 and Cu-Si phase at the joining layer. The activation energy for growth of TiN at the joining interface is 206.3 kJ/mol, and the growth of TiN is dominated by the diffusion of N in TiN.

KEY WORDS: (Joining) (Brazing) (Ceramics) (Silicon Nitride) (Amorphous Filler) (Copper-Titanium Alloy)

1. Introduction

Over the past decade or so on, ceramic technology for structural materials has been established and has been grown on the material science. In particular, silicon base ceramics such as Si_3N_4 and SiC which are composed of cobalent bonding have attracted the intensive interests as high temperature materials because of their superior mechanical properties. The several joining methods of oxide ceramics to metal have been reported; that are refractory-metal metallizing method[1], active metal method[2] and metal-oxide eutectic-utilizing method[3]. On the other hand, the studies of joining of silicon-base ceramics to metal has not been satisfactorily reported.

In this report Si_3N_4 was joined with Si_3N_4 using amorphous Cu-Ti filler metal, which adds the simplicity and reliability to the joining method[4,5], and the joining mechanism was made clear.

2. Experimental

Table 1 shows the physical properties of amorphous $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ alloy fillers used. The number attached to the fillers designates the atomic percent of element. The liquid alloy of desired composition which was first prepared by argon arc melting of high pure Cu and Ti was ejected onto the outer wheel surface in a rotating speed of about 83 rps[6]. The amorphous fillers 1 cm wide and 45μm thick were prepared.

Table 1 Physical properties of amorphous Cu-Ti alloy fillers.

	Nominal composition(at%)		Liquidus temperature(K)	Thickness(μm)
	Cu	Ti		
$Cu_{66}Ti_{34}$	66	34	1148	45
$Cu_{50}Ti_{50}$	50	50	1248	50
$Cu_{43}Ti_{57}$	43	57	1228	45

The sessile drop tests were conducted to investigate the wettability of molten alloys as measure of joining ability. The Cu-Ti sample of about 0.2 g in weight was placed on Si_3N_4 of 15 mm diameter and 3 mm thickness which was polished mechanically with silicon carbide paper to No. 1000. The contact angles of molten alloys were photographically measured in a vacuum condition of 1.33×10^{-3} Pa or below at 1373 K.

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, which were polished with silicon carbide paper to No. 1000, were made a lap joint inserted with the amorphous filler metal of 6 mm diameter and 45μm thickness. The brazing of Si_3N_4/Si_3N_4 joint was conducted in 1.33×10^{-3} Pa with a heating rate of 0.33 K/s, and then a cooling rate of 0.33K/s down to 873K and 1.7×10^{-2} K/s to room temperature. The joining strength of the lap joint was evaluated by fracture shear loading using a cross head speed of 1.67×10^{-2} mm/s.

The microstructures and element distribution of specimens joined were determined by means of scanning electron microscope and EDX, and EPMA microanalyser, respectively. The phases in the microstructure were also

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determined by X-ray diffractometory of the fracture surface with Cu · Kα X-ray.

3. Results and Discussion

3.1 Wetting of molten Cu-Ti alloys on Si_3N_4

Knowledge of wetting of molten on ceramics is necessary for brazing ceramics. **Fig. 1** shows the change in equilibrium contact angle of Cu-Ti alloys on Si_3N_4 with copper content at 1373 K. The times for attaining the equilibrium contact angles were 3.6, 7.2 ks for Cu, Cu-20 at% Ti alloy and 1.8 ks for Cu-30 at%Ti alloy, respectively. The equilibrium contact angle of Cu-Ti alloys lowers with increasing titanium content, and reaches 8 (degree) at titanium content of 30 at% or more. The formation of intermediate phases resulted from the reaction between Si_3N_4 and the alloy accounts for the decrease in the contact angle with titanium content. In fact, the Ti compounds such as TiN and Ti_5Si_3 were observed at Cu-Ti/Si_3N_4 as described below. Similarly, the formation of TiO_x in Cu-Ti/Al_2O_3[7], and $CaZrO_2$ in Cu-Zr/ZrO_2[8] system resulted in the decrease in contact angle of Cu alloys. The Cu-Ti alloys containing Ti content of 30 at% or more wett markedly Si_3N_4, and are applicable to the fillers for joining of Si_3N_4.

3.2 Joining strength of Si_3N_4 to Si_3N_4 joint

The joining of Si_3N_4 to Si_3N_4 was conducted using $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers in **Table 1. Fig. 2** shows the joining temperature dependence of Si_3N_4 joints brazed at the brazing time of 1.8 ks using amorphous fillers. The fracture took place at the interface or near the interface for the joints brazed with $Cu_{66}Ti_{34}$ and $Cu_{50}Ti_{50}$ fillers at temperatures up to 1373 K, and also for the joints brazed with $Cu_{43}Ti_{57}$ filler at joining temperatures up to 1323 K. Further, at the higher joining temperatures the fracture took place at the inner parts of the fillers. The every joint exhibits the maximum joining strength at the brazing temperature around 1323 K. The maximum strength is 313.8 MPa for the joint brazed with $Cu_{66}Ti_{34}$ filler. The joining strength of joint brazed with copper rich $Cu_{66}Ti_{34}$ filler is higher than that of joint brazed with $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers at all joining temperatures except 1237 K. The below-described structure observation indicates that the low value of joint using $Cu_{66}Ti_{34}$ filler at 1273 K is arisen from the insufficient reaction of the filler against Si_3N_4. The joining strength of joints using $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers significantly decreases with increasing brazing temperature above 1423 K, and the downward trend of strength is appreciable in the joint with titanium rich $Cu_{43}Ti_{57}$ filler. For instance, the joining strength of joint with $Cu_{43}Ti_{57}$ filler

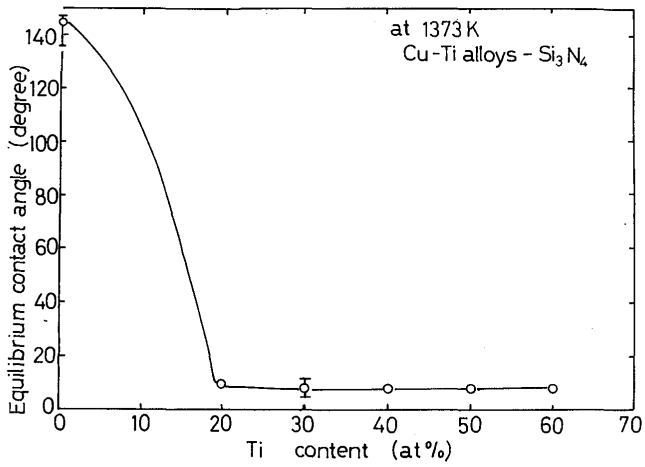

Fig. 1 Titanium content dependence of equilibrium contact angle of molten Cu-Ti alloys on Si_3N_4 at 1373 K.

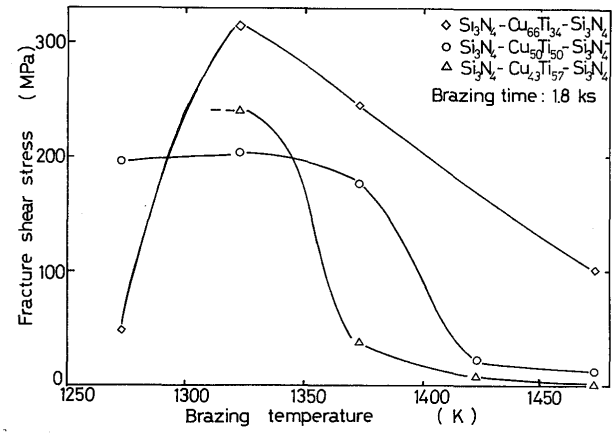

Fig. 2 Brazing temperature dependence of joining strength of Si_3N_4/Si_3N_4 joint using $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers.

is extremely low at the joining temperature of 1473 K. The effect of copper content in the filler on the joining strength of joints will be later discussed in connection with the structure observation of joints.

Fig. 3 shows the brazing time dependence of joining strength for Si_3N_4 joint with $Cu_{50}Ti_{50}$ at the brazing temperature of 1373 K. The strength changes through the maximum of 176.5 MPa at the brazing time of 1.8 ks down to 19.6 MPa at the brazing time of 7.2 ks.

Taking into account the heat resistant properties of Si_3N_4, the strength of Si_3N_4 joint using Cu-Ti filler have to be investigated at elevated temperatures. **Fig. 4** shows the testing temperature dependence of joining strength of Si_3N_4 brazed at 1373 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler. The strength gradually decreases through the maximum of 199.1 MPa at 373 K to 105.9 MPa at 973 K. Thus, the strength of the joint does not remarkably decrease with decreasing the testing temperature. The distribution of TiN nitride (Hv = 2000) and Ti_5Si_3 silicide (Hv = 986) with the high hardness in the filler is attributable to the maintenance of the elevated temperature strength up to

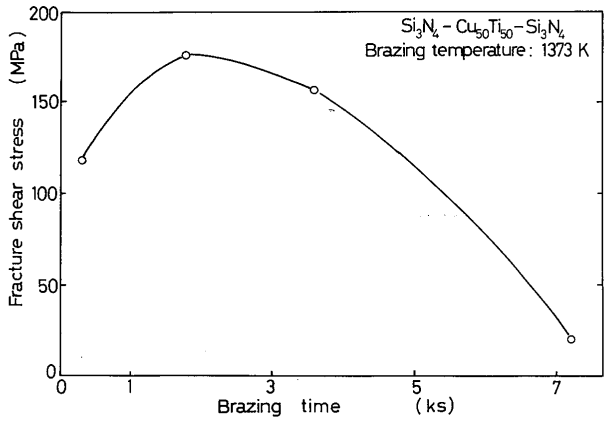

Fig. 3 Brazing time dependence of joining strength of Si_3N_4/Si_3N_4 joint using $Cu_{50}Ti_{50}$ filler at brazing temperature of 1373 K.

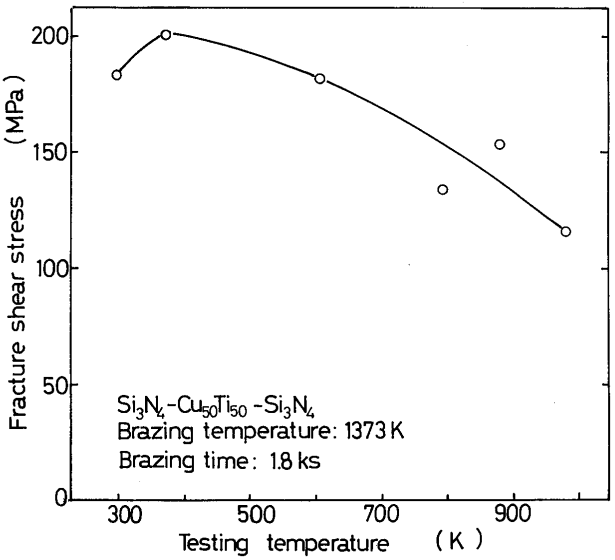

Fig. 4 Testing temperature dependence of joining strength of Si_3N_4/Si_3N_4 joint brazed at 1373 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler.

973 K.

3.3 Structure observation of joining interface and element distribution

The joining strength of Si_3N_4 joints was investigated as described above. Further, the structure observation of joining interface by means of scanning electron microscope, and the line and spot analyseser, and line analysis of N by means of EPMA microanalyser were conducted.

Fig. 5 shows the microstructure and the line analyses of Ti, Cu and Si for Si_3N_4/Si_3N_4 joint brazed at 1373 K for 1.8 ks. The joining layer is divided into several layers. The titanium rich layer with Si and Cu poor content is formed at the layer that is adjacent to Si_3N_4. The EPMA analysis of N in **Fig. 6** demonstrates that this layer possseses the higher N content than that of Si_3N_4, and N peak corresponds to the Ti peak in the analysis. These line analyses in Figs. 5 and 6, and the X-ray diffraction analysis in **Fig. 7** indicate that TiN is formed at the joining

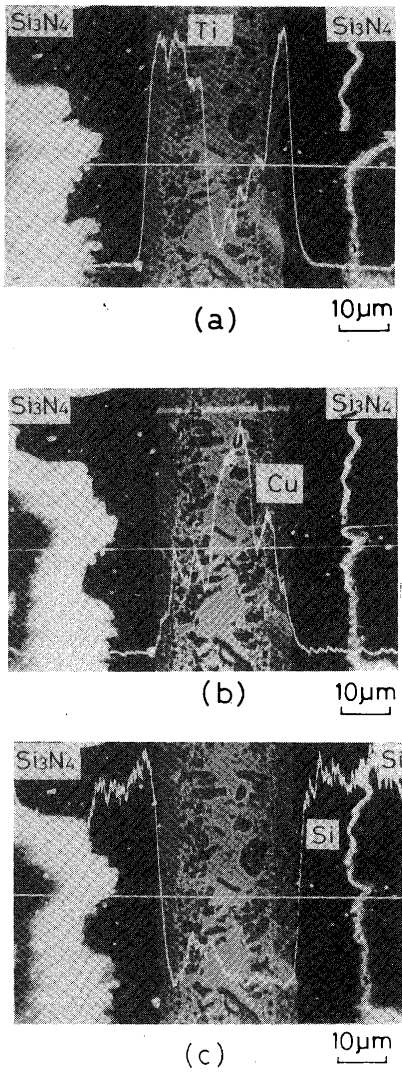

Fig. 5 Microstructure and line analyses for Ti, Cu and Si of Si_3N_4/Si_3N_4 joint at 1373 K for 1.8 ks.

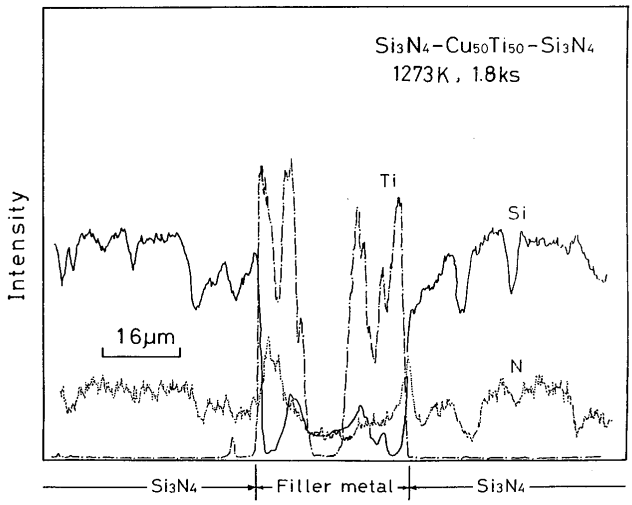

Fig. 6 Electron microprobe analyses of Ti, Si and N in Si_3N_4/Si_3N_4 brazed at 1373 K for 1.8 ks with $Cu_{50}Ti_{50}$ filler.

interface of Si_3N_4 joint where the X-ray diffraction lines of Si_3N_4 are eliminated. The spot analyses in the joining

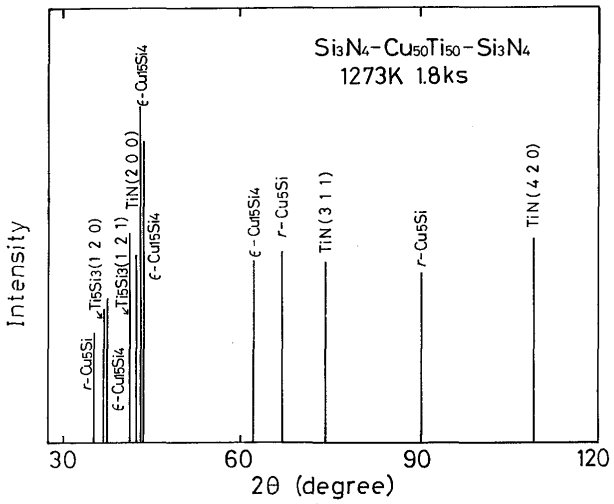

Fig. 7 X-ray diffraction pattern of fracture surface of Si_3N_4/Si_3N_4 joint at brazed at 1373 K for 1.8 ks with $Cu_{50}Ti_{50}$ filler.

layer and the standard specimen of Ti-Si alloys reveal that the massive and granular intermediate phases are identified as Ti_5Si_3. The copper rich phase is observed at the space between those massive and granular Ti_5Si_3, and also at the central part in the joining layer. The X-ray diffraction analysis in Fig. 7 indicates that the copper rich phases are composed of γ-Cu_5Si and ϵ-$Cu_{15}Si_4$.

Further, the change in microstructure of Si_3N_4 joint using $Cu_{50}Ti_{50}$ with brazing temperature or time is investigated. The change in microstructure of Si_3N_4 joint brazed at brazing time of 1.8 ks with brazing temperature is shown in **Figs. 8** to **10**. At the joining condition of 1273 K and 1.8 ks in **Fig. 8** the thickness of TiN layer is thin as shown in the Si-deficient layer that is identified by the Si line analysis. The most parts of Ti_5Si_3 are observed in the granular shape without the massive shape, and the copper rich phases gathers in the central part of the joining layer. **Fig. 9** represents the point analyses of joining layer in Fig. 8. (i), (ii) and (iii) in Fig. 9 correspond to TiN, Ti_5Si_3 and $TiSi_2$, respectively where the phases observed were identified from the comparison of the spot analyses measured with that of standard silicides prepared. As below-discussed the thermodynamic instability of titanium silicides may be attributable to the small amounts of $TiSi_2$ in the joining filler. At the higher brazing temperature of 1423 K at the brazing time of 1.8 ks in **Fig. 10** the thickness of TiN becomes thicker, and the amounts of granular and massive Ti_5Si_3 increase. In particular, the massive Ti_5Si_3 gathers, and are in contact with each other. The defects in the joining layer were originated from the phenomena of liquid-spilit, that is, the capillary phenomena of the molten filler. The defect in the contact parts between the massive Ti_5Si_3 grains are attributable to the degradation of joining strength at brazing temperatures above 1273 K in Fig. 3.

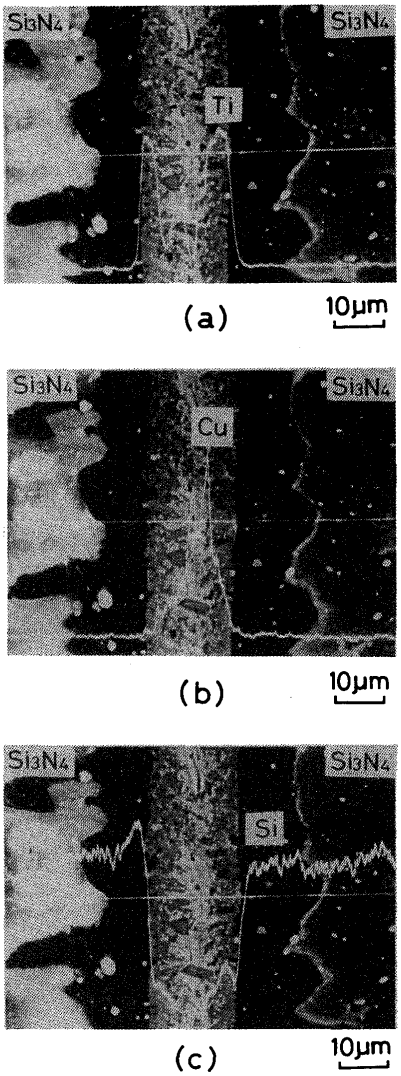

Fig. 8 Microstructure and line analyses of Ti, Cu and Si of Si_3N_4/Si_3N_4 joint brazed at 1273 K for 1.8 ks with $Cu_{50}Ti_{50}$ filler.

During changing the brazing time at the brazing temperature of 1373K the arrangement of intermediate phases in the joining layer does not change. On the other hand, the microstructure in the joining time of 7.2 ks in Fig. 11 indicates that the thickness of TiN and the joining layer become larger with the joining time. In the middle parts of the joining layer, the amounts of Cu-Si alloys increase with decreasing the amounts of Ti_5Si_3. Moreover, the change in Si content for Cu-Si phases in the joining layer with increasing the joining temperature at the joining time of 1.8 ks was determined from the EDX spot analyses of the joints and the standard specimens of Cu-Si alloys. **Fig. 12** shows the silicon content in the copper alloy in the joining layer increases with increasing the brazing temperature. Hence, the sequence of the intermediate phase in the joining layer with the increase in the brazing temperature is Cu solid solution at 1273 K, γ-Cu_5Si + ϵ-$Cu_{15}Si_4$ at 1373 K and ϵ-$Cu_{15}Si_4$+ η'-(Cu, Si) phases at 1473 K. These results are also confirmed by the X-ray

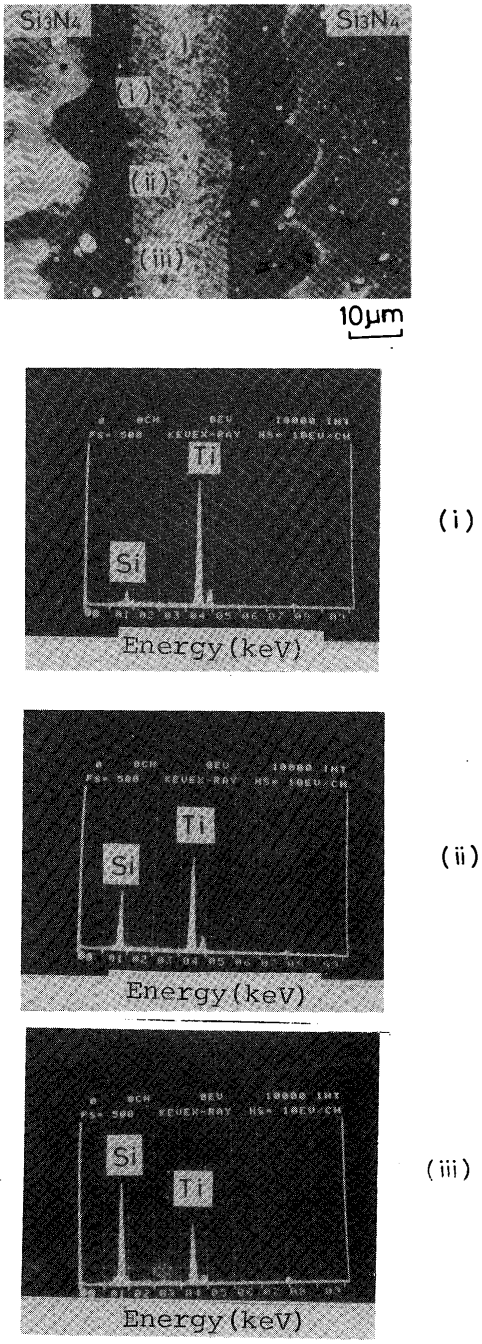

Fig. 9 Microstructure and spot analyses of TiN (i), Ti_5Si_3 (ii) and $TiSi_2$ (ii) brazed at 1273 K for 1.8 ks.

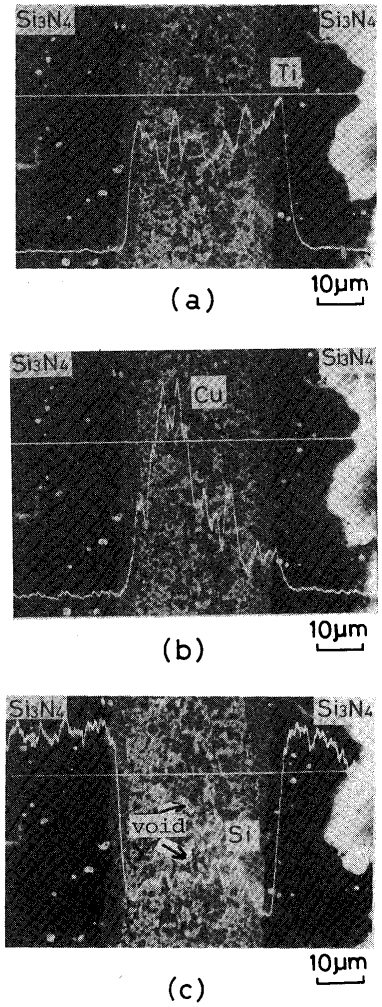

Fig. 10 Microstructure and line analyses of Ti, Cu and Si of Si_3N_4/Si_3N_4 joint at 1423 K for 1.8 ks with $Cu_{50}Ti_{50}$ filler.

diffraction analyses of the fracture surface of Si_3N_4 joints.

3.4 Thermodynamic stability of intermediate phases

The formation conditions for intermediate phases in the joining layer are considered thermodynamically. The formation reactions of Si_3N_4 and TiN are expressed as the following equations[9,10] where ΔG^0 (kJ/mol) is the standard free energy for the reaction.

$$3Si\,(s) + 2N_2\,(g) = Si_3N_4\,(s)$$

$$\Delta G^0 = -723 + 0.315T \qquad (1)$$

$$Ti\,(s) + 1/2\,(g) = TiN\,(s)$$

$$\Delta G^0 = -335.8 + 0.093\,T \qquad (2)$$

, where the symbols of s, 1 and g denote the state of solid, liquid and gas, respectively.

The formation of energies of Ti silicides are expressed as the following reactions.

$$5/3\,Ti\,(s) + Si\,(g) = 1/3\,Ti_5Si_3\,(s)$$

$$\Delta G^0 = 667.7 + 0.172\,T \qquad (3)$$

$$Ti\,(s) + Si\,(g) = TiSi\,(s)$$

$$\Delta G^0 = -610.9 + 0.172\,T \qquad (4)$$

$$1/2\,Ti\,(s) + Si\,(g) = 1/2\,TiSi_2\,(s)$$

$$\Delta G^0 = -538.4 + 0.150\,T \qquad (5)$$

Further, the liquid Ti (1) is used instead of the liquid Cu-Ti alloys as follows[11].

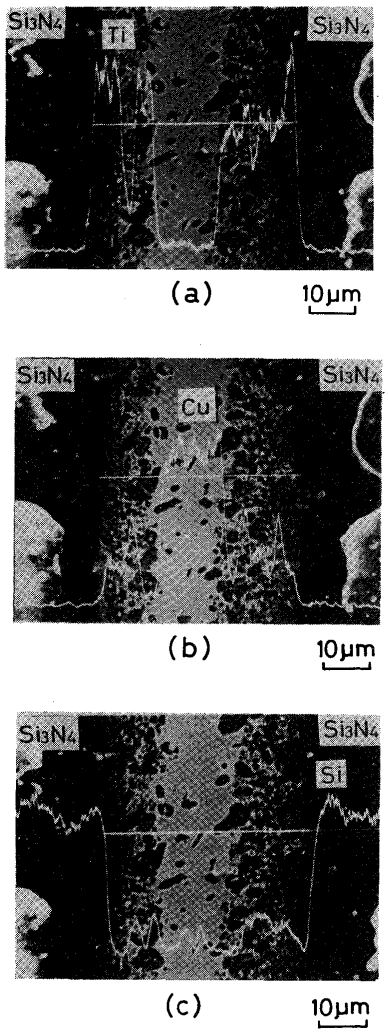

Fig. 11 Microstructure and line analyses of Ti, Cu and Si of Si_3N_4/Si_3N_4 joint brazed at 1373 K for 7.2 ks with $Cu_{50}Ti_{50}$ filler.

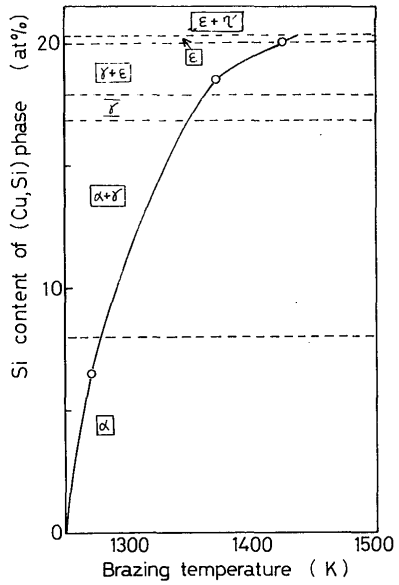

Fig. 12 Influence of brazing temperature on Si content of Cu-Si phase in the joining layer of Si_3N_4/Si_3N_4 with $Cu_{50}Ti_{50}$ at the brazing time of 1.8 ks.

$$Ti(s) = Ti(l)$$

$$\Delta G^0 = 4728 - 2.47\,T \qquad (6)$$

The reaction of Ti in Cu-Ti liquid with Si_3N_4 is given using eqs. (1), (2), (3) and (6).

$$Si_3N_4(s) + 4Ti(s) = 4TiN(s) + 3Si(s)$$

$$\Delta G^0 = -639 + 0.652\,T\ (kJ/mol) \qquad (7)$$

$$Si_3N_4(s) + 9Ti(s) = 4TiN(s) + Ti_5Si_3(s)$$

$$\Delta G^0 = -130.9 + 0.152T\ (kJ/mol) \qquad (8)$$

At 1373K, ΔG^0 values of (7) and (8) are negative values of -54.8 and -131.0 kJ/mol respectively. From the above-described observation of TiN and Ti_5Si_3 in the joining layer, the both reactions of (7) and, in particular, (8) will take place during joining Si_3N_4 to Si_3N_4

The stabilities of various Ti silicides under the presence of excess Ti (1) are given in the following reactions using eqs. (3) – (6).

$$TiSi(s) + 2/3\,Ti(l) = 1/3\,Ti_5Si_3(s) \qquad (9)$$

$$\Delta G^0 = -60.0 + 0.00218\,T = -57.0\ kJ/mol\ (at\ 1373\ K)$$

$$TiSi_2(s) + 7/3\,Ti(l) = 2/3\,Ti_5Si_3(s) \qquad (10)$$

$$\Delta G^0 = -273.1 + 0.0477\,T = -20.8\ kJ/mol\ (at\ 1373\ K)$$

$$TiSi(s) + Ti(l) = 2TiSi(s) \qquad (11)$$

$$\Delta G^0 = -153.0 + 0.0435\,T = -93.3\ kJ/mol\ (at\ 1373\ K)$$

The above calculations indicate that the sequence of stability for the silicides under the excess Ti (1) at 1383 K is Ti_5Si_3, TiSi, $TiSi_2$, and at joining Si_3N_4 using $Cu_{50}Ti_{50}$ filler at the joining time of 1.8 ks, the small amounts of TiS_2 at the lowest joining temperature of 1273 K and the most parts of silicides are Ti_5Si_3 at the higher joining temperature.

3.5 Growth mechanism of TiN intermediate phase

The growth of TiN at joining interface of Si_3N_4 joint is dominated by Fick'law. The thickness x of TiN is given as follows,

$$x = k\sqrt{Dt} \qquad (12)$$

, where k is constant. By involving eq. (12) to the second power,

$$x^2 = k^2 t D_0 \exp(-Q/RT) \qquad (13)$$

, where D_0 and Q are the frequency factor, and the

activation energy for diffusion, respectively. At the constant joining temperature, x^2 is proportional to t. In joining Si_3N_4 using $Cu_{50}Ti_{50}$ filler at 1373 K, the thickness x of TiN was obtained by means of EDX and SEM analyser, and x^2 is proportional to the joining time t as shown in **Fig. 13**. In the figure the extrapolated point does not intersect with zero point. This indicates that the time from the beginning of melting was spent to attain the brazing temperature during joining.

At the constant joining time of 1.8 the following reaction is obtained using eq. (13),

$$\ln (x^2) = -Q/RT + \ln K \qquad (14)$$

, where K is constant. The activation energy Q of 206.3kJ/mol obtained from the slope in **Fig. 14** is comparable to the activation energy for diffusion of N in TiN, Q^N_{TiN} = 217.6 kJ/mol[12], in other words, the growth of TiN formed during joining Si_3N_4 is dominated by the diffusion of N into TiN.

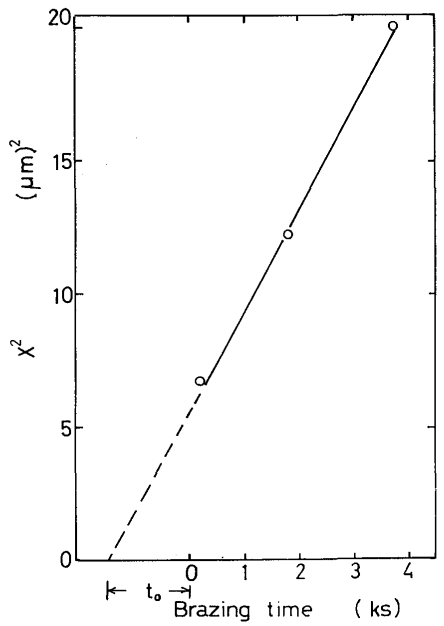

Fig. 13 Relationship between thickness of TiN layer (X) and brazing time in Si_3N_4/Si_3N_4 joint brazed at brazing temperature of 1373 K.

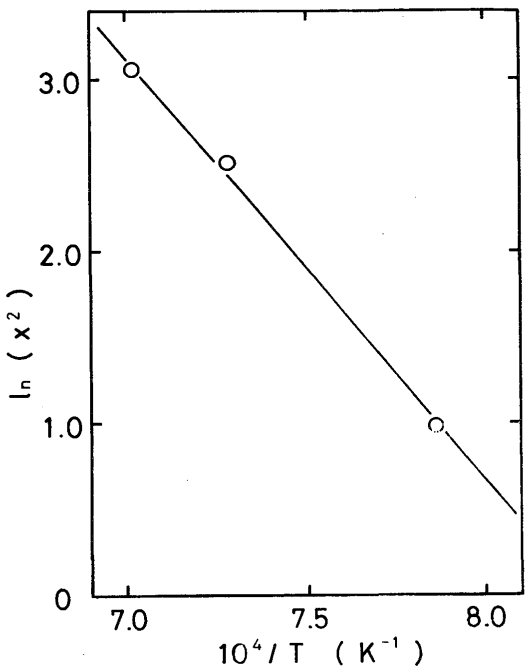

Fig. 14 Relationship between thickness of TiN layer (X) and brazing temperature in Si_3N_4/Si_3N_4 joint brazed at brazing time of 1.8 ks.

4. Conclusion

Si_3N_4/Si_3N_4 joint was made using $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ amorphous filler metals, where pressureless sintered Si_3N_4 was used. The joining strength of Si_3N_4 joint was measured by fracture shear testing, and the joining mechanism was investigated by microstructure observation with SEM, and elements analyses at the joint interface with EDX and EPMA.

The results obtained are summarized as follows.

(1) The molten Cu-Ti alloys containing 20 at% Ti or more exhibit the equilibrium contact angle of about 8 degree, and are applicable to the filler metal for joining of Si_3N_4.

(2) The joining strength of Si_3N_4 using $Cu_{66}Ti_{34}$ filler is higher than that of Si_3N_4 using other Cu-Ti fillers at any brazing temperature except for brazing temperature of 1273 K. Thus, the joining strength of Si_3N_4 with $Cu_{66}Ti_{34}$ filler shows the maximum value of 313.8 MPa at brazing temperature of 1323 K. At the brazing temperature of 1373 K, Si_3N_4 joint with $Cu_{50}Ti_{50}$ filler shows the maximum value of 176.5 MPa at brazing time of 1.8 ks, and gradually decreases with longer brazing time, and to 19.6 MPa at brazing time of 7.2 ks. The elevated temperature fracture shear strength of Si_3N_4 joint brazed at 1373 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler increases to 199.1 MPa at 373 K, and gradually decreases to 105.9 MPa at 973 K.

(3) During brazing Ti in molten $Cu_{50}Ti_{50}$ filler reacts with Si_3N_4 by the following reactions. $Si_3N_4(s) + 4Ti(l) = 4TiN(s) + 3Si(s)$, and $Si_3N_4(s) + 9Ti(l) = 4TiN(s) + Ti_5Si_3(s)$. TiN at the interface between Si_3N_4 and the filler, Ti_5Si_3, and Cu-Si phase at the central part of the filler are formed. The activation energy for growth of TiN at the joining interface is 206.3 kJ/mol, and the growth of TiN is dominated by the diffusion of N in TiN. The silicon content of the Cu-Ti phase increases about 7 at%Si to about 20 at%Si

with increasing the brazing temperature.

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