

The wetting, reaction and bonding of silicon nitride by Cu–Ti alloys

D. H. KIM*[‡], S. H. HWANG[§], S. S. CHUN*

* *Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, PO Box 150, Cheong Ryang, Seoul, Korea*

§ *Welding Design and Fabrication Laboratory, Korea Research Institute of Ship and Ocean Engineering, PO Box 1, Daeduk Science Town, 305-606 Daejeon, Korea*

The wettability and reactivity of pressureless sintered Si_3N_4 by powdered Cu–Ti alloy were investigated using sessile drop tests conducted in a vacuum. Bonding of Si_3N_4 to itself was also carried out and joint strength was evaluated by compressive shear testing. The correlation of wetting behaviour with reaction and bond strength was interpreted. The wettability of Cu–Ti alloys on Si_3N_4 was improved greatly by addition of titanium up to 50 wt%. However, the reaction-layer thickness was increased up to 10 wt% and thereafter decreased up to 50 wt%. We propose the dovetail model which describes the reaction-layer growth behaviour with titanium. As the titanium content was increased, it tended to form a continuous thin reaction layer which greatly improved the wettability. From metallographic and XRD analyses, TiN and Ti silicide were found in the reaction layer. The thermodynamic reaction for TiN formation was suggested to be $\text{Si}_3\text{N}_4(\text{s}) + 4\text{Ti}(1 - \text{sol}) = 4\text{TiN}(\text{s}) + 3\text{Si}(\text{s})$. Ti-silicide might be formed during cooling by the reaction with Ti and Si which had been decomposed from Si_3N_4 , diffused to and dissolved in the liquid Cu-rich alloy. The reaction layer growth was controlled by diffusion of nitrogen or titanium in the reaction layer according to the titanium concentration. The shear strength of Si_3N_4 to Si_3N_4 was affected by the morphology and thickness of the reaction layer rather than the wettability. As the titanium content increased, shear strength also increased rapidly up to 5 wt% and then slowly up to 50 wt%. As the reaction temperature and time were increased, shear strength was lowered due to the greater thickness of the reaction layer despite improved wettability.

1. Introduction

Ti-added active alloy has been widely used as a brazing filler metal for ceramics because it can improve wettability. However, the wetting and bonding mechanism becomes complicated because titanium reacts with the ceramics. Although the bonding of Si_3N_4 by active metal brazing has been recently studied [1, 2], the influence of titanium on the wetting behaviour and the bonding mechanism are not yet fully understood.

It is generally known that the wetting of ceramics is greatly influenced by the reaction with titanium. It has frequently been suggested that the improvement of wettability is caused by the lowering of interfacial energy due to the formation of the reaction product at the interface between the active alloy and the ceramics, such as oxides [3–5] and carbides [6–9].

Therefore, it is expected that the active alloy can improve the wettability to Si_3N_4 by reducing the interfacial energy caused by the reaction at the interface. Attempts [1, 2, 7, 10] have been made to correlate the wetting tendency with interfacial reactions. But this is not yet clearly elucidated for Si_3N_4 and Ti-added active alloys. It is expected that the effects of the

reaction on the wetting vary with reaction-layer thickness [1, 2] and morphology as well as with the composition of the reaction layer [7, 10, 11]. Several results of thermodynamic studies on the formation of the compound by the interfacial reaction are reported [1, 12, 13]. And moreover, to get a quantitative understanding of the formation of the reaction layer, kinetic studies were also performed [1, 14]. But the details of the growing process of the reaction layer are not yet specified.

Although the chemical reaction at the interface is expected to cause the bonds to be strong, there are many points of disagreement on the effect of wetting and reaction on the bond strength. In order to evaluate the bond strength from the experimental results of wetting and reaction, work of adhesion (WAD) [15, 16] and push-off tests [17–19] have been used. Neither the WAD nor the push-off test results can estimate the effect of wetting and reaction on the bond strength [15, 19, 20]. However, the experimental results [20] showing that bond strength is largely affected by the reaction rather than the wettability were also reported.

[‡] *Present address:* Welding Metallurgy Laboratory, Korea Research Institute of Ship and Ocean Engineering (as above).

The objective of this study was to investigate the effects of titanium concentration and bonding conditions, such as temperature and time, on the bonding of Cu–Ti alloy and Si_3N_4 . The correlation of wettability and reaction was analysed, and the bonding mechanism related to the formation and the growth of the reaction layer was also discussed. Finally, the effects of wetting and reaction on the bond strength were illustrated by comparing with wettability, variation of the composition, morphology and thickness of the reaction layer.

2. Experimental procedure

2.1. Materials and apparatus

The pressureless-sintered Si_3N_4 (PLS- Si_3N_4) used was manufactured by Kyocera (No. SN220), Kyoto, Japan, and contained a few per cent of Al₂O₃ and Y₂O₃. This material was obtained in the form of 15 mm diameter discs approximately 5 mm thick. Cu–Ti alloys containing 0.5, 1.0, 3.0, 5.0, 10, 15 and 50 wt % titanium made from high-purity copper (more than 99.5%) and titanium (more than 98.5%) powder were used. Fig. 1 shows the apparatus for the wettability test. This apparatus was composed of graphite plate resistance furnace, vacuum chamber and diffusion pumps. Maximum attainable temperature and degree of vacuum was 1500 °C and less than 1×10^{-5} torr. The graphite element was connected to water-cooled copper electrodes by graphite holders. Quartz glass viewing ports were mounted onto the door of vacuum chamber. Under these conditions, the oxidation of molten Cu–Ti alloy during a test did not appear to be a problem.

2.2. Wettability test

Before the wettability test, Si_3N_4 was polished mechanically with silicon carbide paper to No. 1200 and cleaned using ultrasonic vibration in acetone. Copper and titanium powder were weighed to about 0.2 g in accordance with the alloy composition and mixed

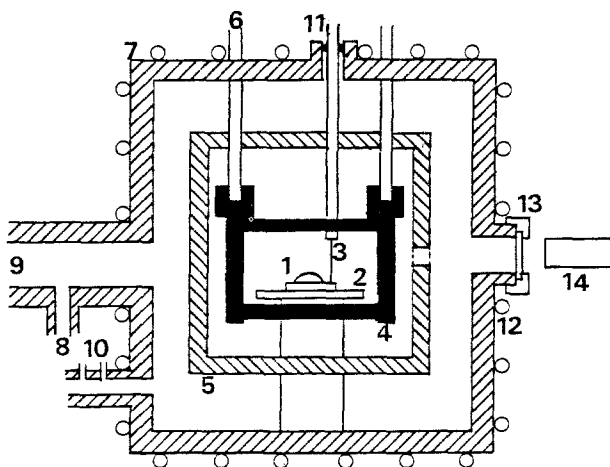


Figure 1 Schematic diagram of apparatus for wettability test. 1, Sample; 2, Alumina die; 3, Thermocouple; 4, Graphite plate and holder; 5, Heat shield; 6, Copper electrode; 7, Vacuum chamber; 8, Rotary pump; 9, Diffusion pump; 10, Vacuum gauge; 11, Rubber O-ring; 12, Cooling coils; 13, Viewing port; 14, Telescope.

uniformly. Then the mixed powders were kneaded using paraffin liquid and moulded into a cylindrical shape. The paraffin binder was burnt away during the heating process and had no influence on the wetting behaviour of the melt. This Cu–Ti alloy was placed on a Si_3N_4 substrate plaque and set onto the flat surface of an alumina plate, which was fitted in a vacuum furnace so that they could be viewed through observation ports.

After loading, the furnace was evacuated to less than 5×10^{-5} torr and the temperature was raised to 800 °C at a heating rate of $13 \text{ }^\circ\text{C min}^{-1}$. The samples were then heated to 940–1160 °C at a heating rate of $7 \text{ }^\circ\text{C min}^{-1}$ and held for the required time to establish equilibrium conditions. The wettability of the molten metal was evaluated by measuring the contact angle between the peripheral surface of a small sessile drop of molten metal and the horizontal surface of the ceramic substrate. The sessile drop outline was photographed at regular time intervals with a 35 mm camera for 60 min from the moment the drop was completely molten, after which it was furnace-cooled to room temperature. Equilibrium as defined by a constant contact angle was generally attained in under 30 min. Contact angles were measured from the series of photographs projected onto the screen of a Nikon profile projector using a protractor.

The contact angle, θ , is determined by the interplay of the various surface energies which are related by the Young–Dupré equation as

$$\Gamma_{sv} = \Gamma_{lv} \cos \theta + \Gamma_{sl} \quad (1)$$

where Γ_{sv} is the solid substrate–vapour–surface energy, Γ_{lv} is the liquid–vapour–surface energy, and Γ_{sl} is the interfacial energy between the liquid metal and solid substrate.

2.3. Bonding experiment

Two pieces of Si_3N_4 disc, 15 mm diameter and 5 mm thick, were used for a lap joint. The bonding was conducted with powdered Cu–Ti alloy containing the same titanium content as that of the wettability test. Copper and titanium powders of 0.2 g in weight were mixed uniformly and kneaded with paraffin liquid, and inserted uniformly between the Si_3N_4 couple.

After loading this assembly, the furnace was evacuated to less than 5×10^{-5} torr and heated to 980–1160 °C for 0 to 120 min. The heating rate up to bonding temperature was the same as that of the wettability test. After bonding, the specimen was cooled slowly down to room temperature with the cooling rate of $13 \text{ }^\circ\text{C min}^{-1}$ to 600 °C, $3 \text{ }^\circ\text{C min}^{-1}$ to 300 °C and $1.7 \text{ }^\circ\text{C min}^{-1}$ to room temperature. The bonded joint was shown in Fig. 2a.

2.4. Microstructural analysis of joint interface

The wetted specimens were sectioned perpendicular to the metal– Si_3N_4 interface using a diamond cut-off wheel, and mounted in bakelite. Samples were then polished with silicon carbide paper to No. 1200 and alumina powder to 0.05 μm . Then samples were

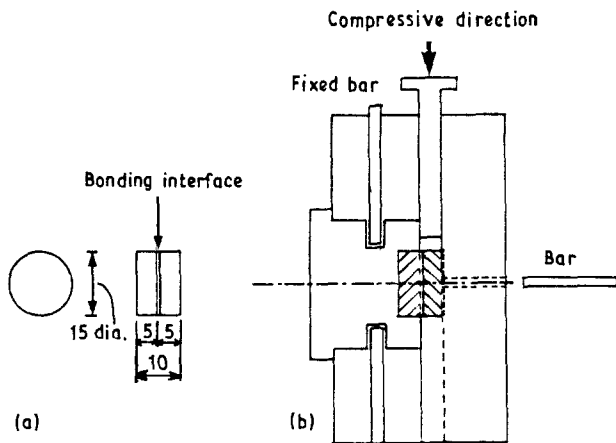


Figure 2 (a) Bonded Si_3N_4 - Si_3N_4 assembly and (b) test fixture used for shear test.

cleaned in ultramet sonic cleaning solution for 30 min using ultrasonic vibration and washed with distilled water.

The reaction layer thickness at the joint interface of the etched same sample was examined using an optical microscope. The microstructure and element distribution of the joint interface were determined by means of a scanning electron microscope (SEM) and an energy dispersive microanalyser (EDX), and nitrogen was determined with an electron probe microanalyser (EPMA). Finally after eliminating solidified metal from the sessile drop by mechanical and chemical means, reaction products of the joint interface were identified with an X-ray diffractometer (XRD).

2.5. Shear strength test

The bonding characteristics of the Cu-Ti alloy and Si_3N_4 were assessed as the shear strength. Shear tests by compressive loading were performed at room temperature at a crosshead speed of 0.5 mm min^{-1} using the fixture manufactured as shown in Fig. 2b. The shear strength of the lap joint was determined by dividing the fracture load by the cross-sectional area of the joint.

3. Results

3.1. Wetting of Cu-Ti alloys on Si_3N_4

Fig. 3 shows the variation of contact angle with titanium concentration of the Cu-Ti alloy. Contact angle decreased remarkably as titanium concentration increased. It is observed that the wetting state is reached when titanium is added more than 3 wt %, and it spreads over the Si_3N_4 surface with a titanium concentration above 15 wt %. It is suggested that the reason Cu-Ti alloy wets Si_3N_4 is due to the reaction between Si_3N_4 and titanium [1, 2, 9, 13], and results in the formation of a titanium-rich compound. It is evident from Equation 1 that wettability is improved when Γ_{lv} decreases and Γ_{sv} increases or Γ_{sl} decreases. But it can be seen that Γ_{sv} of Si_3N_4 in vacuum heating is nearly constant, and Γ_{lv} of the alloy in which titanium is added to copper is also constant [21, 22]. Hence the improvement of wettability is mostly caused by the decrease in Γ_{sl} . When reaction products are formed at the interface, Equation 1 can be modi-

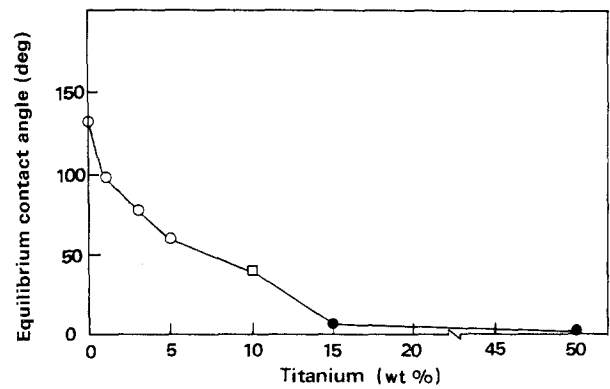
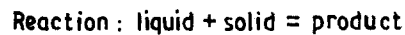


Figure 3 The effect of titanium additions on the wetting of Si_3N_4 by Cu-Ti alloys for 1800 s (○ 1160; □ 1100; ● 1000 °C).



Vapour

Liquid

Rx. layer

Solid

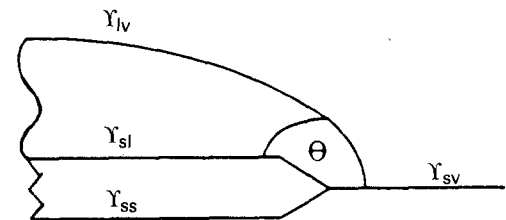


Figure 4 Schematic diagram of solid wet by liquid with reaction [13].

fied [13] into the following equation

$$\Gamma_{sv} - (\Gamma_{sl} + \Gamma_{ss}) + A\Delta G = \Gamma_{lv} \cos \theta \quad (2)$$

where Γ_{ss} is the interfacial energy between the solid substrate and the reaction layer, as is shown in Fig. 4. ΔG is the Gibbs energy for the reaction, and A is a constant related to the modes of product formed for unit extension of the drop on the solid. It is evident from the equation that Γ_{sl} and Γ_{ss} are decreased when reaction products are formed, and consequently the wettability is improved.

The microstructure of the interface at the temperature and time where the equilibrium contact angle was reached, is shown in Fig. 5. When titanium concentration is extremely low, the reaction layer formed discontinuously, and with the increment of titanium concentration, reaction products gradually grew into a thick layer. However, when titanium concentration was higher than 15 wt %, reaction layer thickness decreased considerably despite a remarkable improvement in wettability, as shown in Fig. 3.

Therefore it is difficult to find a proportional relationship between the reactivity and titanium concentration. Takeda *et al.* [23] demonstrated that when the initial titanium concentration is low, the reaction is not uniform and proceeds by the concentrating of titanium to the interface, but when the excess titanium exists initially, a stable thin layer is formed uniformly and the reaction does not proceed any further. Therefore it can be supposed that the formation of a reaction layer at the interface between the Cu-Ti alloy and Si_3N_4 is described by the dovetail model proposed by King *et al.* [24].

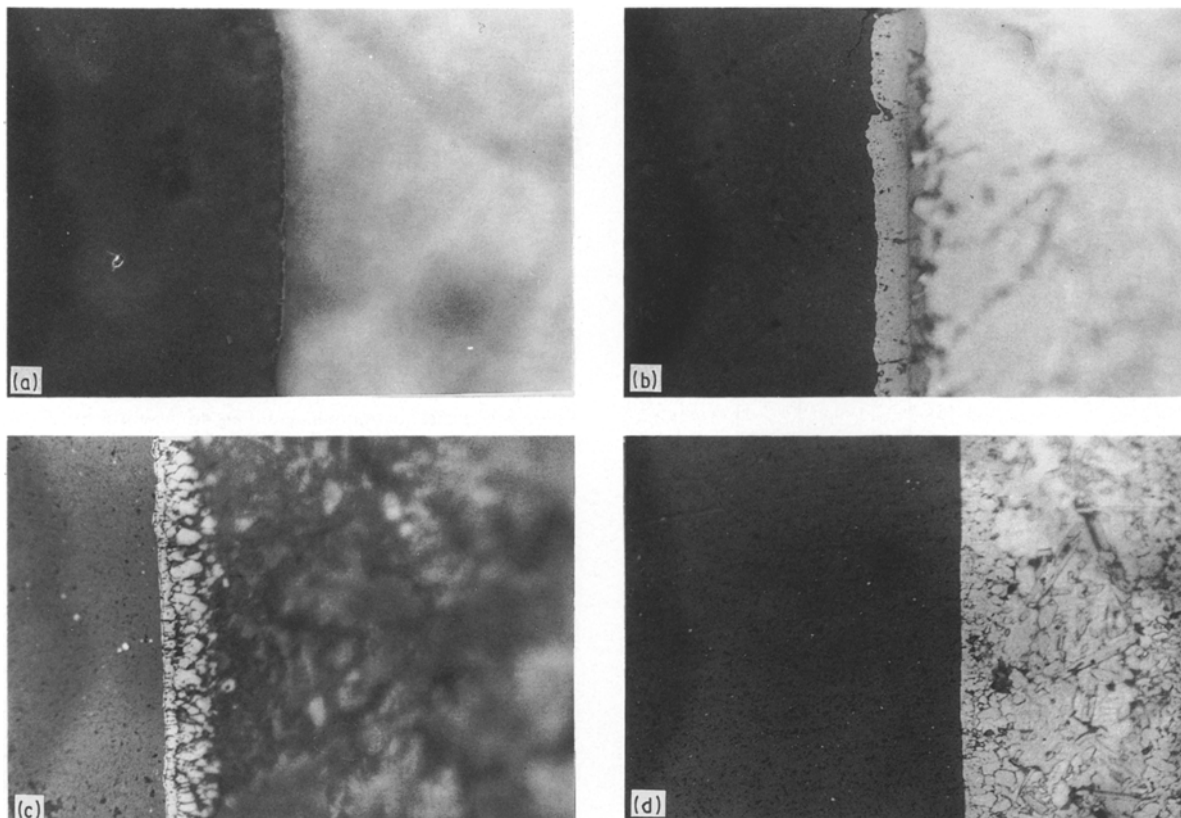


Figure 5 Difference of interfacial reaction layer morphology at equilibrium wetting temperature and time ($\times 400$). (a) $\text{Cu}_{99}\text{Ti}_1$; (b) $\text{Cu}_{95}\text{Ti}_5$ (both 1130°C , 1800 s); (c) $\text{Cu}_{85}\text{Ti}_{15}$; (d) $\text{Cu}_{50}\text{Ti}_{50}$ (both 1000°C , 1800 s).

Fig. 6 shows the change of contact angle as a function of time at the temperature conditions that, the variation in contact angle is slight. For the alloys with low titanium contents, the change of contact angle with the lapse of time was small, but the changing rate increased gradually with the increase of titanium concentration. That is, the more titanium participating in the reaction, the higher the reaction rate, and the contact angle decrease. However, when a low-titanium-content alloy is heated for long time, the reaction layer grows considerably. On the other hand, the reduction of the contact angle is small. Hence it is difficult to estimate the wettability simply by the thickness of the reaction layer. When titanium concentration is higher than 15 wt %, the change of contact angle with time was not observed because the equilibrium wetting state is obtained once the continuous thin and stable reaction product formed at the initial reaction stage. Therefore it can be asserted from the observation of the variation in the morphology of the reaction layer with time that the growth of the reaction layer is independent of the contact angle.

3.2. Reaction of Cu-Ti alloys with Si_3N_4

Fig. 7 shows the elemental distribution at the interface of alloy $\text{Cu}_{95}\text{Ti}_5$ and alloy Si_3N_4 when the holding time was varied. The distribution of Si shows large variation with the increment of the holding time. At 0 s, Si was detected in the reaction layer or in the vicinity of reaction layer. At 7200 s, Si was scarcely detected in the reaction layer or in the alloy adjacent to the reaction layer. This is thought to be the result of

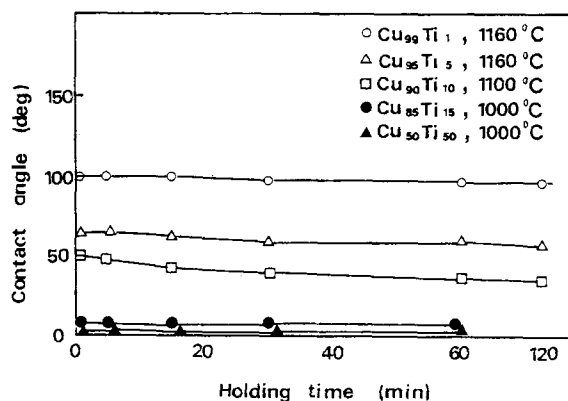


Figure 6 The effect of holding time on the contact angle of Cu-Ti alloys on Si_3N_4 .

the diffusion of Si into the melted alloy during the long time reaction at high temperature. Therefore it is suggested that Ti reacted preferentially with N, originated from the decomposed Si_3N_4 , to form TiN in the liquid phase, and Si was dissolved into the Cu-rich alloy.

When it is held for a long time at high temperature, the decomposition of Si_3N_4 continues and the quantity of TiN increases. Accordingly, the reaction layer grows considerably and Si diffuses into the alloy, hence most of Ti-silicide is formed in the alloy side after cooled.

Fig. 8 shows the results of SEM-EDX analysis of the interface between $\text{Cu}_{50}\text{Ti}_{50}$ and Si_3N_4 . No continuous thin layer was detected and it was seen that a very thin layer formed. The growth of Cu-Ti intermetallic compound from the interface into the

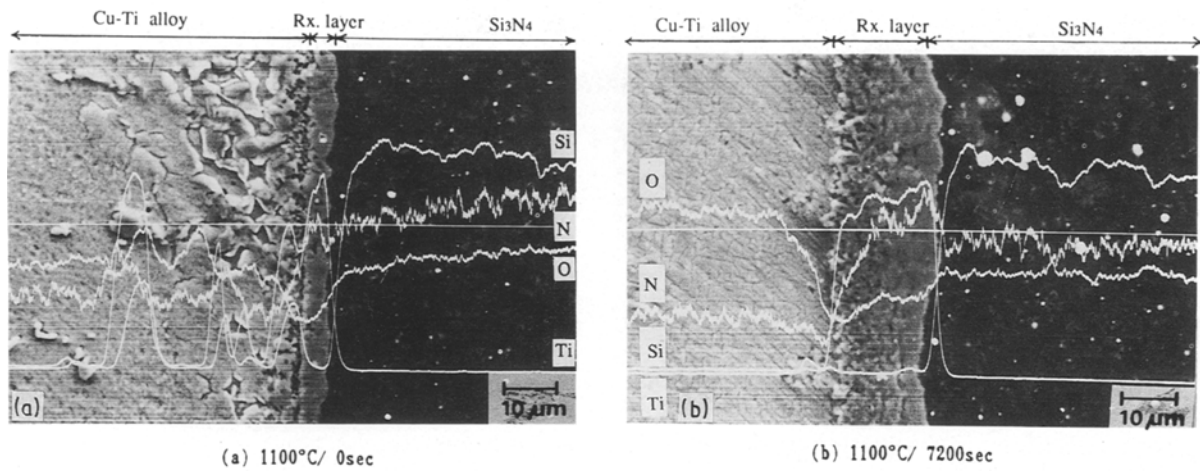


Figure 7 Cross-sectional SEM photographs and EPMA line scanning of $\text{Cu}_{95}\text{Ti}_5\text{-Si}_3\text{N}_4$ joint interface with holding time. (a) 1100 °C, 0 s; (b) 1100 °C, 7200 s.

alloy is remarkable, and it is also observed that Ti-silicide appeared in a mixed form with Cu-Ti intermetallic compound. For the Cu-Ti alloy with high Ti content, once a continuous thin layer formed, it is difficult for Ti to diffuse further toward the interface. Therefore, further reaction is restricted and because of the excessive Ti in liquid alloy, Cu-Ti nucleates at the interface and grows into the alloy during the cooling process. Ti-silicide is also inferred to be formed by the reaction between Ti and the dissolved Si in the liquid alloy during the cooling process. It was observed from the analysis of the point designated by A in Fig. 8e that the atomic ratios of Cu, Ti and Si were 13, 79 and 8, respectively. Hence it was confirmed that Ti-rich Cu and Si compounds formed simultaneously and co-existed at the same position. When it is held for a long time (3600 s) the reaction layer thickness was larger than for shorter times, and the elemental distribution was not so different from that shown in (f). That is, Ti-silicide and a Cu-Ti intermetallic compound were also formed in the mixed form in the vicinity of the interface. This result indicates that dissolved Si existed mostly in the vicinity of the interface, and hardly diffused into the alloy fully even over a long time. Then Ti and Si, which are abundant in the interface area, reacted in the cooling process and formed Ti-silicide. Fig. 9 shows the result of XRD analysis of the interface of Cu-Ti alloys and Si_3N_4 . From the results, the reaction layer is observed to be composed of TiN and Ti_5Si_3 , in agreement with other results [1, 9, 13, 14]. CuSiTi was also identified in the high-titanium-content alloy and it is thought that this product is not included in the reaction layer.

Fig. 10 shows the change in reaction layer thickness with variation in temperature and time. The thickness of the layer increased with the increment of temperature and time, but the rate of increment reduced as the time became longer. Wagner [25] illustrated that the growth of the reaction layer in this process can be represented by the following equation,

$$X = KDt^{1/2} \quad (3)$$

where X is reaction layer thickness, and K is a material constant. The relationship of Equation 3 was

confirmed from the result of Fig. 11. Therefore the growing rate of the reaction layer obeys the parabolic rate law, and the growth of the reaction layer is governed by the diffusion of participating elements. The values of K are calculated from the slopes of the $X^2 = f(t)$ straight lines at each temperature condition. Generally, the thermal variation of K follows on the Arrhenius law,

$$K = K_0 \exp\left[-\frac{Q}{RT}\right] \quad (4)$$

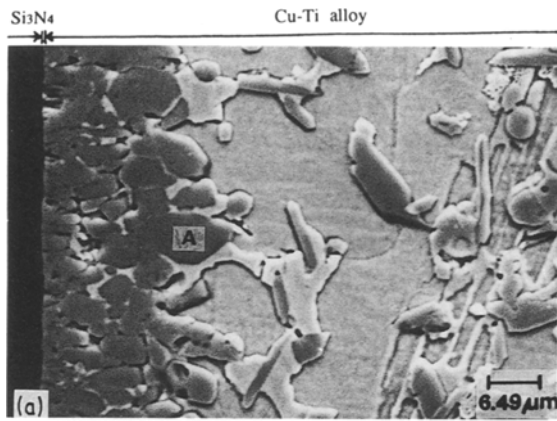
where Q is the activation energy, K_0 is a material constant, T the absolute temperature and R the gas constant ($R = 8.31 \text{ J mol}^{-1} \text{ K}$). The logarithm of the reaction rate constant K plotted against $1/T$ is shown in Fig. 12 and the activation energy was calculated from the slope of each line.

It is evident from Equations 3 and 4 that X^2 is proportional to t as long as the temperature remains constant. Therefore for $\text{Cu}_{85}\text{Ti}_{15}$ alloys, the activation energy can be obtained from the relation between $\ln X^2$ and $1/T$ since X^2 is proportional to time, t . It can be seen from the calculated results that activation energy varied with titanium concentration. The activation energy is listed in Table I, together with the estimated controlled process. The activation energy of $\text{Cu}_{95}\text{Ti}_5$ and $\text{Cu}_{90}\text{Ti}_{10}$ alloy were 202 and 223 KJ mol^{-1} , respectively. This is nearly the same as the activation energy of the diffusion of N in TiN as reported in the literature [1, 26, 27].

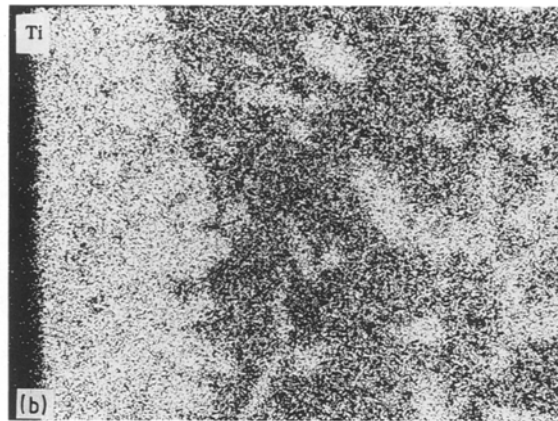
Hence the growth of the reaction layer for the Cu-Ti alloy containing 5 and 10 wt % titanium could have been controlled by the diffusion of N in TiN from the Si_3N_4 to the liquid alloy. On the other hand, the activation energy of the $\text{Cu}_{85}\text{Ti}_{15}$ alloy was 332 KJ mol^{-1} , nearly the same as that of diffusion of Ti in the reaction layer reported in the literature [14]. Hence the growth of the reaction layer for high-titanium-content alloys up to 15 wt % could have been controlled by the diffusion of Ti in the reaction layer from the liquid alloy to Si_3N_4 .

3.3. Shear strength of $\text{Si}_3\text{N}_4\text{-Si}_3\text{N}_4$ joint

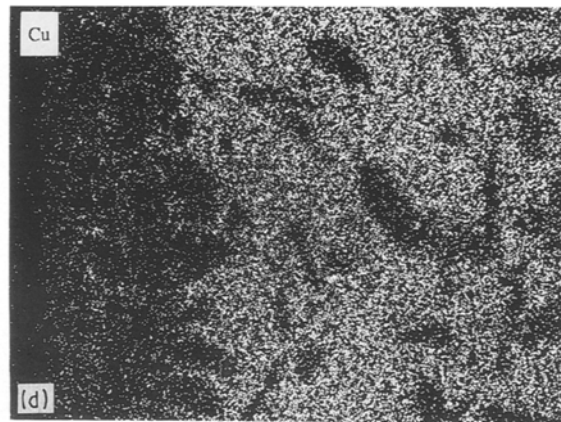
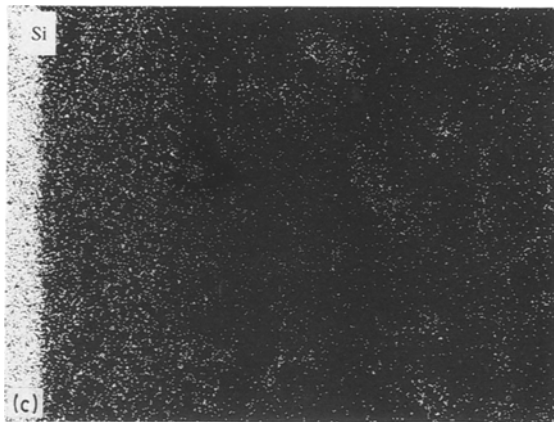
The variation in shear strength of the $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ joint produced using the Cu-Ti alloy at 1020 °C



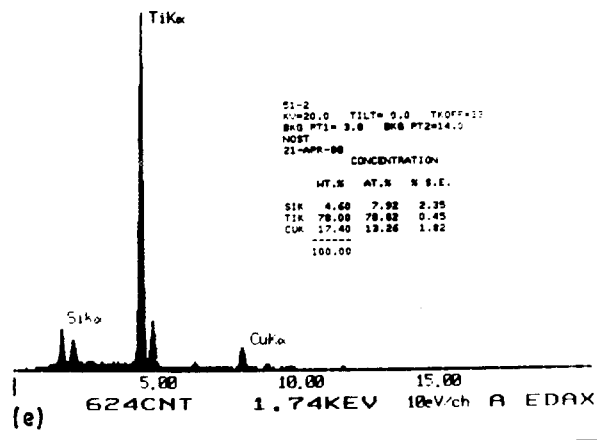
(a) Cross-sectional interface



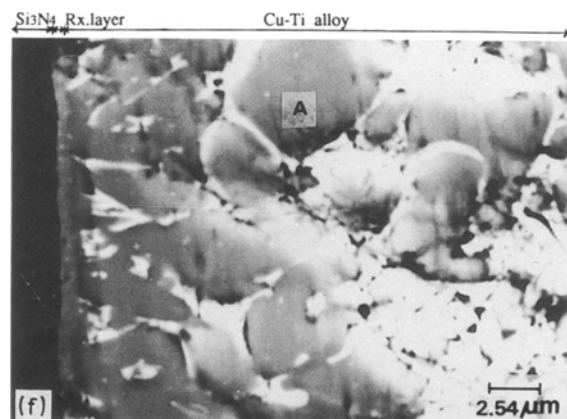
(b) Ti



21-APR-88 11:05:57 EDAX READY
 RATE- 8594CPS TIME- 21LSEC
 FS- 5639CNT PRST- OFF
 A -51-2



(e) Point A



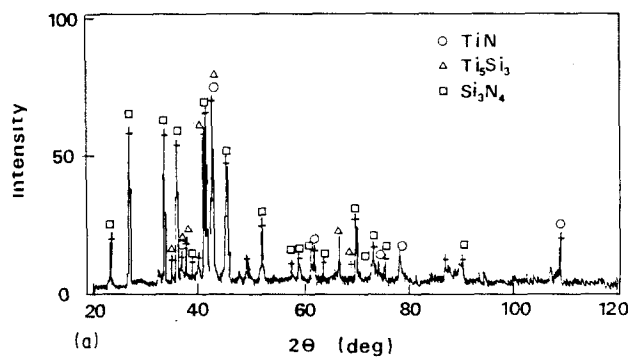
(f) Cross-sectional interface

Figure 8 Cross-sectional SEM photographs, compositional maps of $\text{Cu}_{50}\text{Ti}_{50}\text{-Si}_3\text{N}_4$ joint interface and spot analysis of point A. (a-e) 1000 °C, 1800 s, (f) 1000 °C, 3600 s. (a) cross-sectional interface; (b) Ti; (c) Si; (d) Cu; (e) point A.

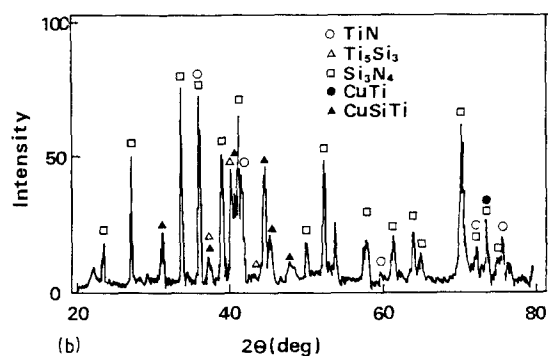
and/or 1100 °C as a function of titanium concentration is shown in Fig. 13. The equilibrium contact angle and the reaction layer thickness are also plotted. With titanium concentration less than 5 wt %, the shear strength increased rapidly up to 12.5 kg mm⁻² with the increment of titanium concentration. However, it increased gradually when titanium concentration is higher than 5 wt % and reached 17.5 kg mm⁻² at 50 wt %. The equilibrium contact angle reduced from

135° to about 0° as titanium concentration increased from 0 to 50 wt %.

The thickness of the reaction layer showed its maximum value of 15 μm at the titanium concentration of 5 wt %, but further increase of titanium concentration reduced the thickness of the reaction layer. However, shear strength was steeply increased in range I, where the reaction-layer thickness was also steeply increased up to 15 μm with the increment of titanium concentra-



(a) Cu₉₅Ti₅ (1130°C/1800sec)



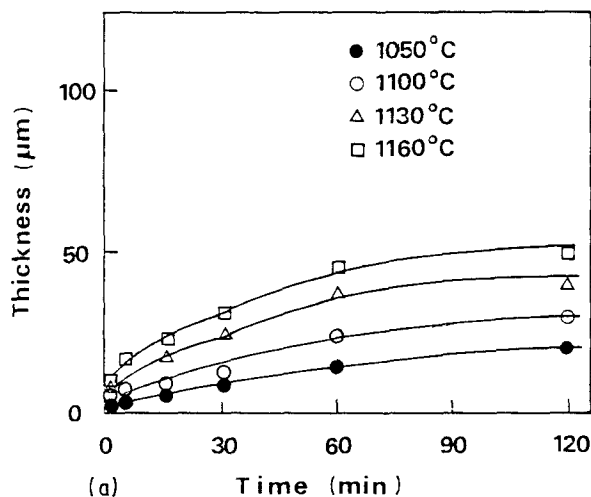
(b) Cu₅₀Ti₅₀ (1000°C/1800sec)

Figure 9 X-ray diffraction pattern from the joint interface of Cu-Ti alloy-Si₃N₄. (a) Cu₉₅Ti₅ (1130°C, 1800s); (b) Cu₅₀Ti₅₀ (1000°C, 1800s).

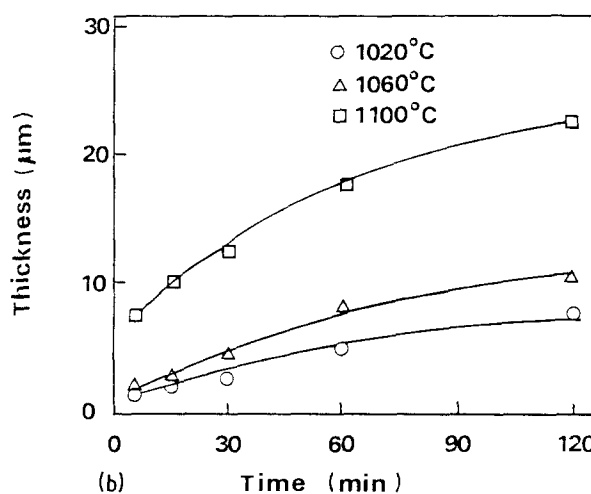
tion. On the contrary, strength was gradually increased in range II, where the reaction-layer thickness was decreased to less than 1 μm with increasing titanium concentration. Therefore higher strength is associated with the continuous thin reaction layer condition formed at higher titanium concentrations, and accompanied by an improvement in wettability.

Fig. 14 shows the variation of the shear strength with a temperature of Cu₉₅Ti₅ alloy in relation to the contact angle and reaction layer thickness. It can be seen that the contact angle remains about 60° above 1060°C. The reaction layer thickness increases from 8 μm at 1060°C to 30 μm at 1160°C. Maximum shear strength is obtained at 1060°C and thereafter strength slightly decreased with rising temperature. That is, sufficient strength is guaranteed if only a reaction layer with a certain thickness (8 μm) is formed.

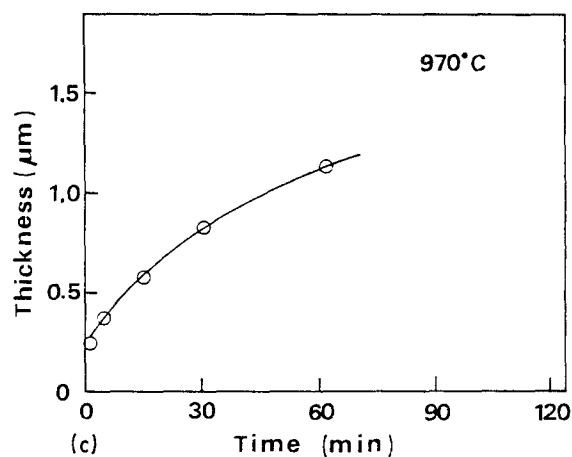
The variation of the shear strength with the holding time for the Cu₉₅Ti₅ alloy is shown in Fig. 15. The change of contact angle and the reaction layer thickness are also plotted. The initial value of the contact angle is about 60°, but it was reduced to about 55° after 7200 s and changed little with time. On the other hand, the reaction-layer thickness increased heavily with time and it is about six times as large as the initial value after 7200 s. As the contact angle decreases and approaches the equilibrium value, it is expected to contribute to the shear strength, but the results are opposed to the expectation. Therefore the change in shear strength is almost independent of the contact angle, and is mainly influenced by the change in



(a) Time (min)



(b) Time (min)



(c) Time (min)

Figure 10 The effect of reaction temperature and holding time on the reaction layer thickness at the Cu-Ti alloy-Si₃N₄ joint interface (a) Cu₉₅Ti₅; (b) Cu₉₀Ti₁₀; (c) Cu₈₅Ti₁₅.

reaction-layer thickness. That is, the maximum shear strength is obtained in the initial stage of reaction (in a short holding time) when the reaction-layer thickness is relatively small, about 10 μm thick.

4. Discussions

4.1. Wetting and reaction of Cu-Ti alloy

It was observed from the results of this study that titanium concentration affects the interfacial reaction and the wetting behaviour. However, it is difficult simply to correlate the variation of contact angle and

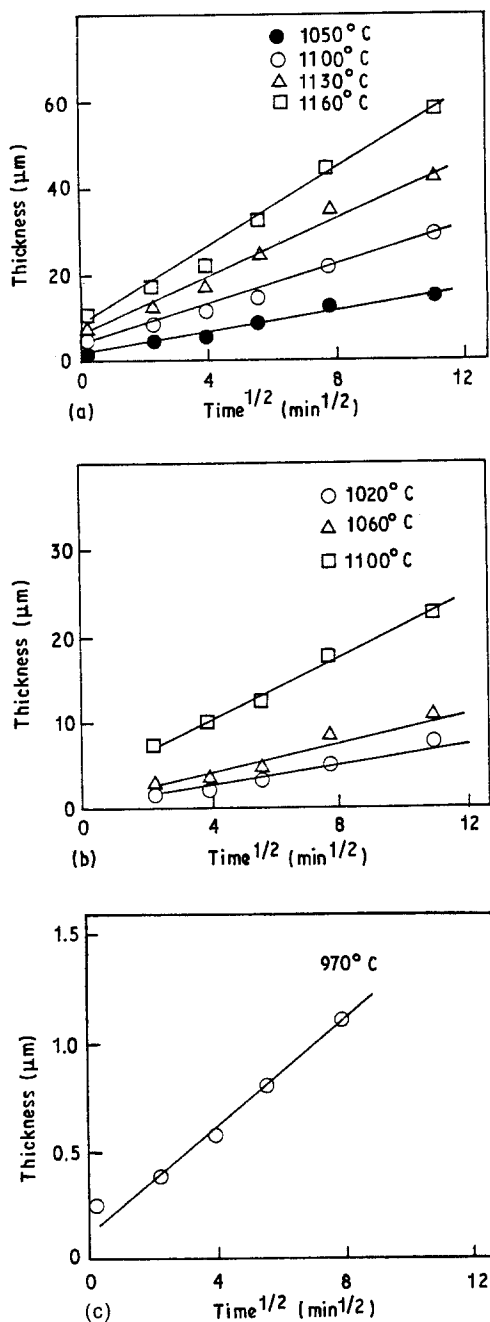


Figure 11 The relation between the reaction layer thickness and holding time of parabolic growth rate at the Cu-Ti alloy-Si₃N₄ joint interface. (a) Cu₉₅Ti₅; (b) Cu₉₀Ti₁₀; (c) Cu₈₅Ti₁₅.

the reaction layer thickness with titanium concentration. There is, however, a correlation utilizing the variation of reaction layer morphology.

When the reaction layer formed at the interface, the interfacial energy changes from the initial value (Γ_{sl}) to the new value (Γ'_{sl}) as is shown previously in Fig. 4. Namely, the sum of Γ_{sl} and Γ_{ss} can be replaced by Γ'_{sl} , which is the total interfacial energy. The wettability is expected to improve as titanium concentration increases, because the amount of reaction product increases and Γ'_{sl} decreases. However, in contradiction, a thin reaction layer showing excellent wettability in high titanium alloys was discovered. It is possible to interpret this contradiction by adopting the dovetail model. When titanium concentration is lower, the wettability does not improve remarkably because the discontinuous reaction products are formed at the

preferential site of the interface, and Γ'_{sl} is not much reduced. As titanium concentration increases, the wettability is much improved because the area where the reaction products are formed is increased, and Γ'_{sl} is further decreased. When titanium concentration is very high, the wettability improves remarkably because the continuous thin layer is formed throughout the interface at the initial stage of reaction, and Γ'_{sl} is reduced to an extremely low value.

In conclusion, the tendency for the formation of the continuous thin reaction layer at high titanium concentrations can be described by the dovetail model, and the formation of a continuous thin reaction layer is expected to have a great influence on the reduction of interfacial energy and consequently enhance the wettability. A schematic illustration of the formation of the reaction layer according to titanium concentration is shown in Fig. 16. It can be seen from the figure that the degree of heterogeneity in the reaction layer is also different. When Si₃N₄ is contacted with a liquid Cu-Ti alloy, the interfacial reaction begins to proceed as the surface of Si₃N₄ is decomposed by titanium. For an alloy with low titanium content, Si₃N₄ is continually decomposed by titanium diffusing through the discontinuous reaction layer to the surface of Si₃N₄, and accompanied by the diffusion of dissociated silicon and nitrogen: consequently the reaction layer continues to grow. Hence the decomposition of Si₃N₄ is expected to proceed vigorously. For an alloy with high titanium content, a continuous thin reaction layer is formed, and the diffusion of titanium through the reaction layer is restricted. The growth of the reaction layer and decomposition of Si₃N₄ are therefore also expected to be limited.

Fig. 17 shows SEM photographs of the Cu-Ti alloy/Si₃N₄ interface illustrating the difference of the decomposed zone size in Si₃N₄ caused by the titanium concentration and holding time. Choh *et al.* [9] asserted that wetting is a decomposition-controlled process, and wetting progresses more and more with the acceleration of the decomposition reaction. In Fig. 17, vigorous decomposition of Si₃N₄ and reaction layer growth are shown for the Cu₉₅Ti₅ alloy which has low wettability compared to the Cu₅₀Ti₅₀ alloy. When the holding time is lengthened to 7200 s, the decomposition of Si₃N₄ and reaction layer growth occurred considerably more than for a holding time of 0 s. But wettability was revealed to be improved only a little (Fig. 6). From these results, it is hard to explain the improvement in wettability if only the reaction layer grows and the accompanied decomposition of Si₃N₄ occurs. Therefore, wettability is thought to be affected by the reaction layer morphology which is varied with titanium concentration as shown in Fig. 16. Since a continuous thin reaction layer tended to form in high-titanium-content alloys, interpreted by the dovetail model, interfacial energy is much reduced and accordingly results in the improvement of wettability.

4.2. Reaction layer formation mechanism

The main reaction product between Si₃N₄ and Cu-Ti alloy is TiN, which was formed regardless of titanium

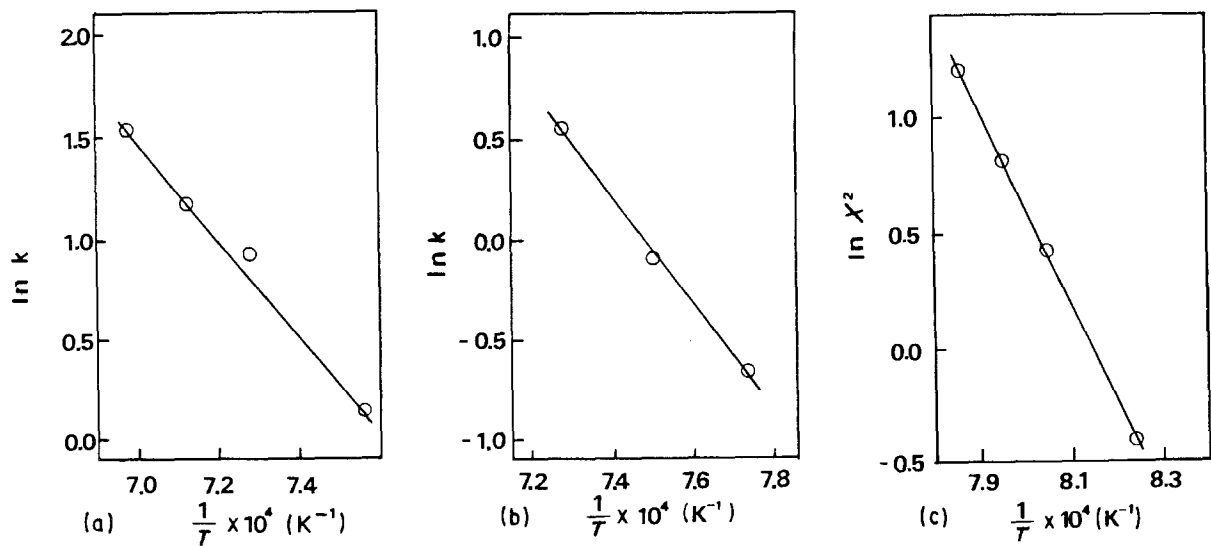


Figure 12 The Arrhenius relationship between the reaction rate constant and the reaction temperature on the reaction layer growth at the Cu-Ti alloy-Si₃N₄ joint interface. (a) Cu₉₅Ti₅; (b) Cu₉₀Ti₁₀; (c) Cu₈₅Ti₁₅.

TABLE I Values of activation energy and estimated rate-controlled process for the reaction layer growth

Alloy composition (wt %)	Reaction product	Activation energy, Q (KJ mol ⁻¹)	Activation energy from the references Q (KJ mol ⁻¹)	Estimated rate controlled process
Cu ₉₅ Ti ₅	TiN	202	206.3 [1]	N in TiN layer
	Ti ₅ Si ₃		217.6 [27]	
			218.6 [28]	
Cu ₉₀ Ti ₁₀	TiN	223		N in TiN layer
	Ti ₅ Si ₃			
Cu ₈₅ Ti ₁₅	TiN	332	318 [14]	Ti in TiN layer
	Ti ₅ Si ₃			
	CuSiTi			

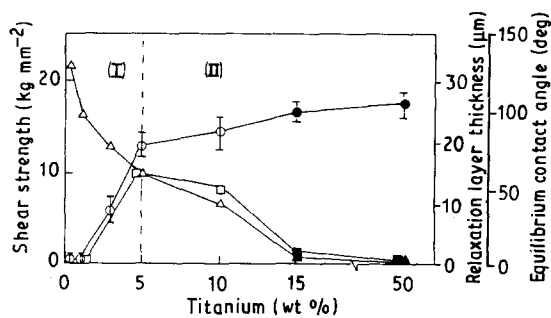


Figure 13 The effect of titanium additions on the shear strength of Si₃N₄-Si₃N₄ joint, equilibrium contact angle and reaction layer thickness of Cu-Ti alloy. ○ Strength; △ angle; □ thickness; white, 1100 °C 1800 s; black, 1020 °C 1800 s.

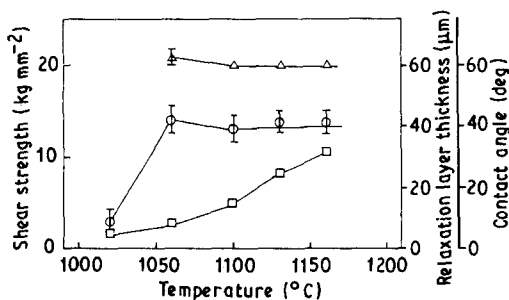


Figure 14 The effect of reaction temperature on the shear strength of Si₃N₄-Si₃N₄ joint, contact angle and reaction layer thickness for 1800 s using Cu₉₅Ti₅ alloy. ○ Strength; △ angle; □ thickness.

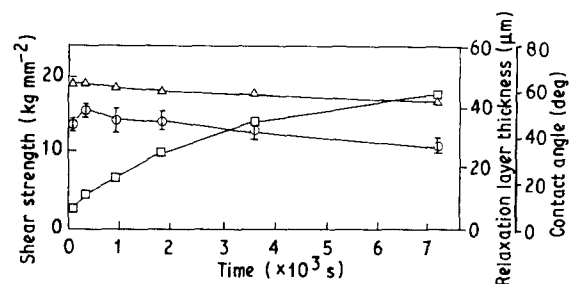
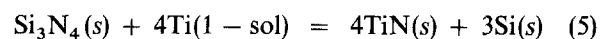


Figure 15 The effect of holding time on the shear strength of Si₃N₄-Si₃N₄ joint, contact angle and reaction layer thickness at 1130 °C using Cu₉₅Ti₅ alloy. ○ Strength, △ angle; □ thickness.

concentration. Ti-silicide was also formed. Ti₅Si₃ was seen to be formed during the cooling process and coexisted with TiN in the reaction layer, while it was also formed in the alloy side out of the reaction layer depending on the titanium concentration and bonding conditions. From the observation of the formation process of TiN and Ti₅Si₃, the reaction for TiN formation can be represented by the following equation [28, 29].



$\Delta G^\circ = -1356 + 0.199 T$ (KJ mol⁻¹) for Cu₉₅Ti₅ alloy. It is inferred from the observation of the formation characteristic of Ti₅Si₃ that the reactions re-

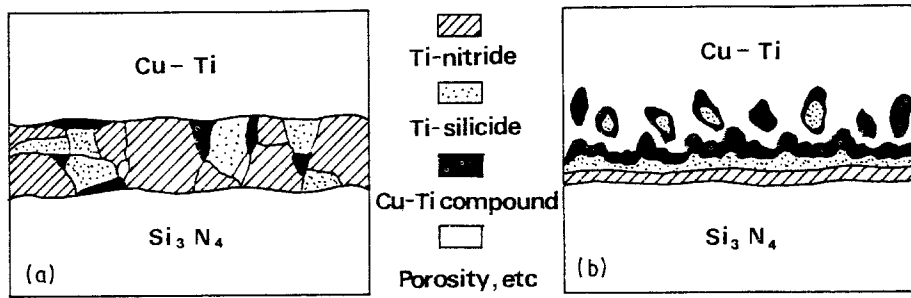


Figure 16 Schematic of reaction layer structure formed at the joint interface of Si_3N_4 and Cu-Ti alloy with (a) lower and (b) higher titanium content.

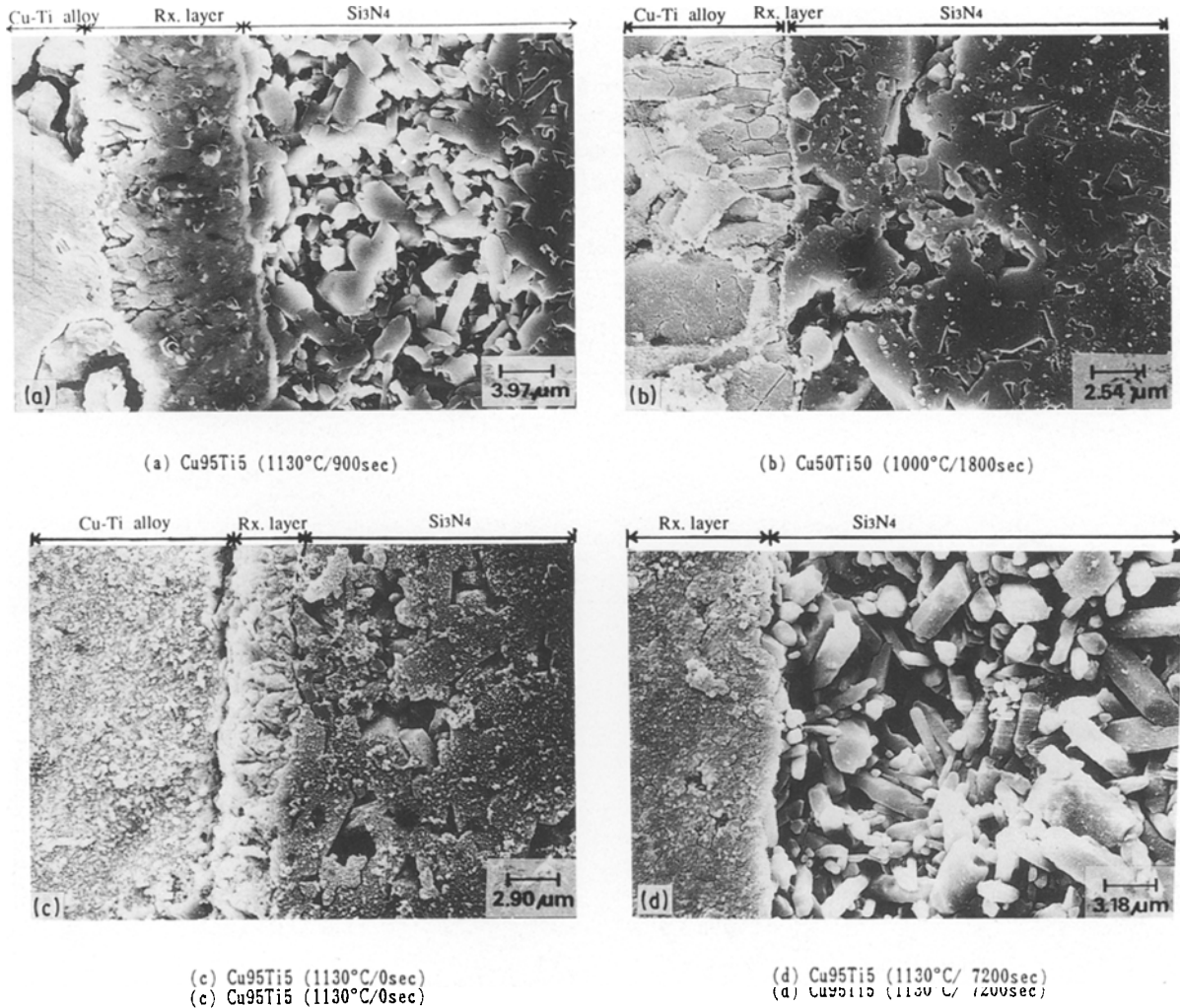
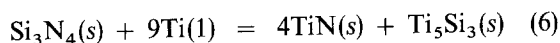
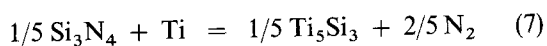


Figure 17 Cross-sectional SEM photographs of the Cu-Ti alloy- Si_3N_4 joint interface (etched by NaOH). (a) $\text{Cu}_{95}\text{Ti}_5$ (1130 °C, 900 s); (b) $\text{Cu}_{50}\text{Ti}_{50}$ (1000 °C, 1800 s); (c) $\text{Cu}_{95}\text{Ti}_5$ (1130 °C, 0 s); (d) $\text{Cu}_{95}\text{Ti}_5$ (1130 °C, 7200 s).

presented by Equations 6 and 7 (recommended by Naka [1] and Loehman [13], respectively) are unlikely to occur in this work.



$$\Delta G^\circ = -130.9 + 0.152 T \text{ (KJ mol}^{-1}\text{)}$$



$$\Delta G^\circ \text{ at } 1200 \text{ K} = -41.0 \text{ KJ}^{-1}$$

It also can be seen from the temperature dependence of isothermal-isobaric potential on the reaction of Ti-silicide that the probability of Equation 7 is low above 600 K [30].

Silicon, which was dissolved in the liquid Cu-rich alloy, reacts with titanium during the cooling process and produces Ti_5Si_3 [29]



$$\Delta G^\circ = -1151600 - 16.62 T \text{ (J mol}^{-1}\text{)}$$

After the reaction layer is formed at the interface, the reaction between Si_3N_4 and Ti continues, and the reaction layer grows. The nitrogen which is not reacted with titanium at the interface may diffuse to the alloy solution and there reacts with titanium to form additional TiN outside the reaction layer [14].

From the kinetic studies on the growth of the reaction layer, it was found that the controlled process

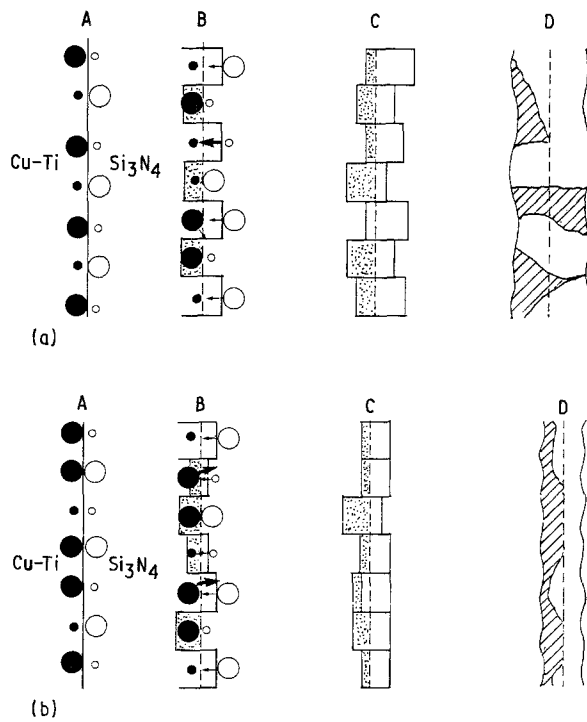


Figure 18 Schematic illustration of the forming procedure of the reaction layer between Cu-Ti alloy and Si_3N_4 with (a) lower and (b) higher titanium. A, physical contact; B, reaction layer forming; C, reaction layer growth; D, structure after cooling. ● Ti; ● Cu; ○ Si; □ TiN; ▨ (Cu, Si); ▩ Ti-Silicide.

changed according to titanium concentration. For the alloy with low titanium content, TiN is formed discontinuously at the initial stage of reaction. Then the reaction layer continues to grow by the formation of TiN resulting from the reaction between Si_3N_4 and titanium diffusing through the reaction layer, or from the reaction between titanium in the liquid alloy and nitrogen diffusing through the reaction layer into the alloy from Si_3N_4 . In this case, diffusion of nitrogen through the reaction layer controls the growth of the reaction layer. Since the titanium and silicon diffuse to the reacting interface through the liquid alloy in contact with the unreacted interface of Si_3N_4 , this process is not considered to act as a controlling process. For the alloy with high titanium content, TiN is formed into a continuous thin layer. Since the diffusion rate of nitrogen and silicon is higher than that of titanium, it can be inferred that the growth of the reaction layer is controlled by titanium diffusion through the TiN layer. A schematic illustration of the formation of the reaction layer, the growing procedure and the final structure of the reaction layer after cooling is shown in Fig. 18.

4.3. Shear strength of Si_3N_4 - Si_3N_4 joint

It was revealed that the shear strength of the Si_3N_4 - Si_3N_4 joint increases with the increment of titanium concentration. Iseki [11] reports that the strength at SiC-SiC joint decreases with the increment of titanium concentration. But the wettability is improved as titanium concentration increases, as in the present work. Iseki [11] interpreted the decrease in strength as the result of the increase in the reaction-

layer thickness. He included the titanium alloy crystal precipitated from the solution during the cooling process in measuring the thickness of the reaction layer. And he interpreted the decrease in strength with the increment of titanium concentration as the result of the existence of the brittle reaction products, such as titanium alloy crystal. In this study, however, the titanium alloy crystal formed during the cooling process was not included in the reaction-layer thickness because it is not formed by the direct reaction with Si_3N_4 . And since the tendency of the continuous thin layer formation is high due to increasing titanium concentration, higher strength is obtained.

The shear strength showed the maximum value when the reaction occurred under a temperature slightly higher than melting point and with a relatively short reaction time. But it decreases with further increment of the reaction time and temperature. On the other hand, the wettability improves and the thickness of the reaction layer increases greatly with the increase in reaction time and temperature. Therefore the shear strength decreases as the reaction layer grows, and is little influenced by the improvement in the wettability.

Scott *et al.* [18] found that maximum strength is obtained when the reaction layer is very thin. Though a continuous reaction layer is formed with the increase of titanium concentration, the flaws develop in the reaction layer and weaken the interface. While the strength of the Si_3N_4 - Si_3N_4 joint can be decreased by the presence of brittle phases in the reaction layer, the strength is mainly governed by the adhesive force between the reaction layer and Si_3N_4 . Generally it was known that a large adhesive force is obtained if the lattice matching between the crystals is good [31].

Ishida *et al.* [32] showed that fine crystals of TiN grow epitaxially in the reaction layer at the Cu-Ti alloy- Si_3N_4 interface. He found that the variation of titanium does not produce a large effect on strength if the titanium concentration ranges from 0.5 to 5 at %, and also confirmed that the failure occurs at the interface, which is in accord with this study. Therefore the improvement of strength cannot be expected only by formation of the reaction products with favourable lattice matching, but the strength can be increased when a continuous thin reaction layer is formed epitaxially throughout the interface.

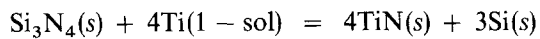
5. Conclusions

Wettability improved with the increment of titanium concentration and no linear proportionality was found between the reaction and the wettability. As titanium concentration increases, a continuous thin layer tends to be formed at the interface and improves the wettability remarkably.

The thickness of the reaction layer was not in proportion to titanium concentration. For a Cu-Ti alloy with low titanium concentration (less than 5 wt %), the initial reaction layer tends to be formed discontinuously and the reaction layer thickness increases with titanium concentration. On the contrary,

in the alloy with high titanium concentration (more than 15 wt %) the reaction-layer thickness decreased as titanium concentration increased, because a continuous thin reaction layer tends to form. The formation behaviour of the reaction layer, which is affected by titanium concentration, can be interpreted with the aid of the dovetail model.

Si_3N_4 and Cu-Ti alloy react directly to each other and form the reaction layer containing TiN as the main product of reaction. The thermodynamic reaction for the formation of TiN is given by the following equation



Dissociated silicon diffused and dissolved in the Cu-rich alloy and reacts with titanium to form Ti-silicide during the cooling process.

Ti_5Si_3 formed and coexisted with TiN in the reaction layer. If titanium concentration is low and the required conditions for the diffusion of silicon are ensured (high temperature and long time), Ti_5Si_3 existed in the alloy side near the reaction layer. However in the alloy of high titanium concentration, CuSiTi also formed in the exterior of the reaction layer regardless of temperature and time.

The activation energy varied with titanium concentration, and it is inferred that the growth of the reaction layer is governed by the different diffusion-controlled process. The activation energies for $\text{Cu}_{95}\text{Ti}_5$, $\text{Cu}_{90}\text{Ti}_{10}$ and $\text{Cu}_{85}\text{Ti}_{15}$ alloys were obtained as 202, 223 and 332 kJ mol^{-1} . Therefore the reaction layer growth of the lower titanium content alloy is thought to be controlled by the diffusion of nitrogen in the TiN layer from Si_3N_4 to the liquid alloy. But in the alloy with high titanium concentration, reaction layer growth is inferred to be controlled by the diffusion of titanium in TiN layer from the liquid alloy to the Si_3N_4 .

The shear strength of the Si_3N_4 - Si_3N_4 joint using Cu-Ti alloy is influenced by reaction layer thickness and morphology. Strength increased with the increment of titanium concentration, and it is also accompanied by improved wettability because the tendency of the continuous thin reaction layer to form increased.

High shear strength is obtained when the reaction-layer thickness is relatively small, which is allowed in conditions of slightly higher temperature than the melting point of the Cu-Ti alloy and relatively short time conditions. When the temperature and time were further increased, bond strength decreased due to the reaction-layer growth, while wettability also improved. Therefore it is inferred that bond strength is largely affected by the reaction-layer morphology rather than the wettability.

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