Wetting of Silicon Nitride by Copper-Titanium or Copper-Zirconium Alloys†

Masaaki NAKA* and Ikuo OKAMOTO**

Abstract

The sessile drop technique has been used to measure the contact angle of molten copper-0-60 at% titanium or copper-0-60 at% zirconium alloys with Si_3N_4 as a function of time and temperature over the range 900° to 1100°C using time-lapse photography in vacuum condition.

The temperature dependence of contact angle of copper alloys containing 30 at% titanium or more is large although the dependence of alloys containing 20 at% titanium is small. The drops of containing 30 at% titanium or more largely spread. Since the time dependence of contact angle of alloys containing 30 at% titanium is quite large, the alloys show photographically small time dependence of the contact angle. On the other hand, the contact angle of Cu-20 at% Ti alloy changes from 40° to 10° after 120 min holding at 1100°C. At 1100°C for 30 min the contact angles of alloys containing 30 at% or more titanium show the small value of 8°. This is attributable to the formation of intermediate layer mainly composed of TiN in thickness of 10 μm or more. The Cu-Ti alloys are applicable to the filler metal for joining of Si_3N_4.

The contact angle of copper-zirconium alloys at 1100°C for 30 or 60 min decreases extremely at zirconium content of 30 at% or more. This is attributable to the formation of ZrN at the interface between Cu-Zr drops and Si_3N_4. The copper-zirconium alloys is, however, not applicable to the filler metal for joining of Si_3N_4.

KEY WORDS: (Wetting), (Silicon Nitride), (Ceramics), (Joining), (Copper-Titanium Alloys), (Copper-Zirconium Alloys), (Work of Adhesion), (Contact Angle), (Interfacial Energy), (Surface Energy), (Filler Metal)

1. Introduction

The use of ceramics in structural component has received increasing attention in recent years. In particular, silicon-based ceramics such as silicon nitride (Si_3N_4) possess significant benefits for use in hot components for gas turbine engines because of their excellent high temperature strength and oxidation resistance. However, the inherent brittleness that arises from the ionic or cobalent boding in the ceramics requires the joining of ceramics to metals.

The joining methods of ceramics to metals are, in general, divided into solid state bonding and brazing methods[1]. Since the brazing of ceramics often necessiates the use of molten alloys, knowledge of the wetting behavior of alloys with ceramics is important.

It is the purpose of the present work to study the wetting of silicon nitride (Si_3N_4) by Cu-Ti or Cu-Zr alloys.

2. Experimentals

Pressureless sintered silicon nitride (Si_3N_4) (Kyoto Ceramics Co. Ltd) used contains a few percent of Al_2O_3 as bonding materials, and impurities of, Y, W and Fe. The nominal composition and melting point of Cu-Ti and Cu-Zr alloys used is presented in **Table 1**. The sessile drop technique was used to evaluate wetting behavior by measuring contact angle Θ of molten drop which was photographically taken at a constant heating rate of 12°C/min or at regular time intervals at constnat temperature in 1×10^{-5} torr as shown in **Fig. 1**. The sessile drop apparatus is shown in **Fig. 2**.

3. Results and Discussion

Fig. 3 shows the temperature dependence of molten Cu-Ti alloys with Si_3N_4 at the heating rate of 12°C/min. While the temperature dependence of Cu-20 at% Ti alloy is small, the dependence of Cu-Ti alloys containing 30 at% Ti or more is large. The contact angle of the alloys becomes small with spreading on Si_3N_4 at 1100°C.

Fig. 4 represents the change in contact angle of Cu-Ti alloys with time after reaching 1100°C. The Cu-Ti alloys

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Table 1 Nominal composition of Cu-Ti and Cu-Zr Alloys used

	Nominal Composition(at%)		Liquidus Temperature(°C)
	Cu	Ti	
Cu	100	–	1083
$Cu_{80}Ti_{20}$	80	20	970
$Cu_{70}Ti_{30}$	70	30	905
$Cu_{60}Ti_{40}$	60	40	925
$Cu_{50}Ti_{50}$	50	50	975
$Cu_{40}Ti_{60}$	40	60	965
$Cu_{70}Zr_{30}$	70	30	1080
$Cu_{60}Zr_{40}$	60	40	895
$Cu_{50}Zr_{50}$	50	50	930
$Cu_{40}Zr_{60}$	40	60	965

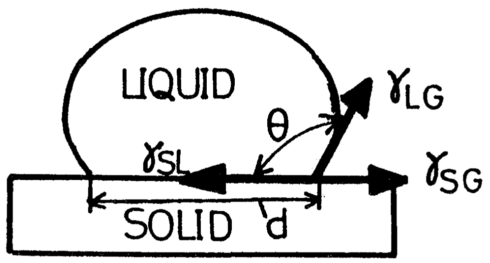

Fig. 1 Schematic of contact angle of liquid drop on ceramics.

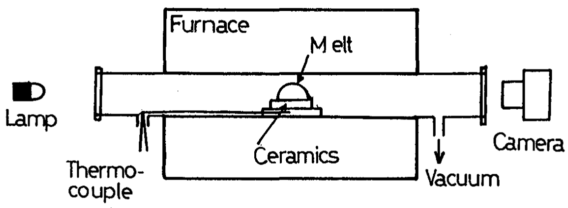

Fig. 2 Sessile drop apparatus.

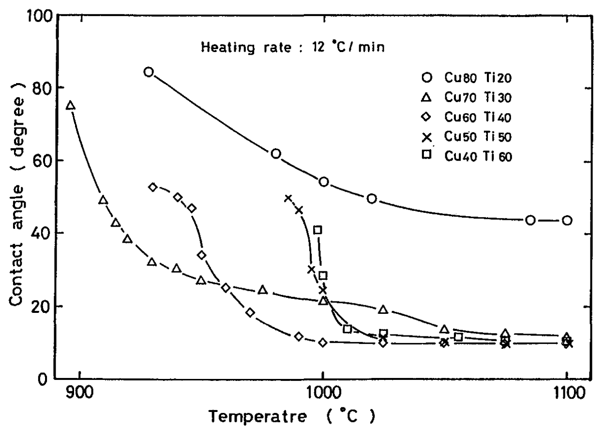

Fig. 3 Temperature dependence of contact angle of Cu-Ti alloys on Si_3N_4.

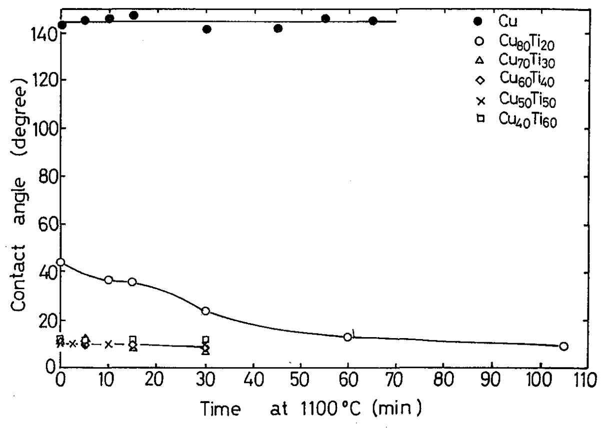

Fig. 4 Time dependence of contact angle of Cu-Ti alloys on Si_3N_4.

containing 30 at% Ti or more spread rapidly during heating, and show the small time dependence of contact angle. On the other hand, Cu-20 at% Ti alloy provides the time dependence, and changes from 40° after melting at 1100°C to 10° after 120 min that is the same as that of Cu-30 at% Ti alloy. Pure copper does not show the time dependence of contact angle, and 145° at 1100°C. In general, at the contact angle between 0° and 90°, the shape of melt is convex and the melt is said to be in wetting state[2]. The molten Cu-Ti alloys containing 20 at% or more are in the wetting state because the contact angles of the alloys are 90° or below.

Fig. 5 represents the change in contact angle of Cu-Ti alloys at 1100°C for 30 min with titanium content. These contact angles except for that of Cu-20 at% Ti alloy reach the equilibrium values, and the values of alloys containing 30 at% Ti or more provide 8 ~ 10°.

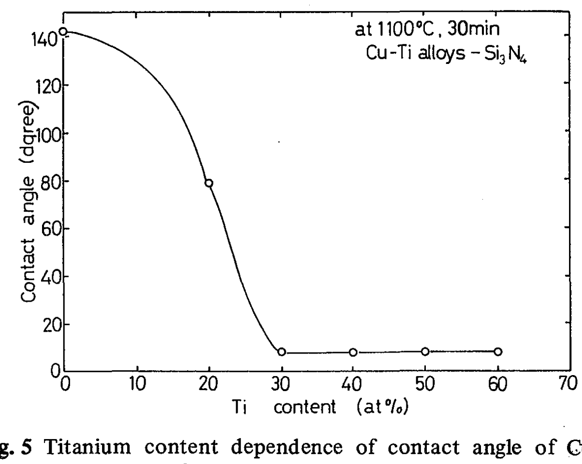

Fig. 5 Titanium content dependence of contact angle of Cu-Ti alloys at 1100°C for 30 min.

The work of adhesion, W_{ad}, that is often used as a measure of joining is defined by Durprè's equation as,

$$W_{ad} = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \qquad (1)$$

where γ_{SG} is the solid-gas surface energy, γ_{LG} is the liquid-gas surface energy and γ_{SL} is the interfacial (liquid-solid) energy. The vectorial addition of the surface energies gives Young's equation in Fig. 1 as,

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\Theta_{\infty} \quad (2)$$

where Θ_{∞} is the equilibrium contact angle. Eqs. (1) and (2) give Young-Durprè equation of W_{ad} as follows,

$$W_{ad} = \gamma_{LG}(1 + \cos\Theta_{\infty}) \quad (3)$$

Using γ_{LG} = 1300 erg/cm^2 at 1083°C, it's temperature dependence of d γ_{LG}/dT = –0.45[3] and the present result of Θ = 145° with Si_3N_4 at 1100°C for pure copper, the work of adhesion of liquid copper, W_{ad} (Cu/Si_3N_4, 1100°C) is calculated to be 234 erg/cm^2. This value is smaller than 517 erg/cm^2 of W_{ad} (Cu/Al_2O_3, 1100°C) for pure copper with Al_2O_3[4]. From the small difference between the surface tension of Al_2O_3, γ_{SG} = 905 erg/cm^2 (1850°C)[5] and the surface tension of Si_3N_4, γ_{SG} = 1154 erg/cm^2 (1430°C)[6], the difference in these work of adhesions is attributable to the difference in solid-liquid interface energies, γ_{SL}. The interface between Cu and Al_2O_3 is stabler than that between Cu and Si_3N_4.

The decrease in interface energy arises from the adsorption of alloying element[7] or the formation of intermediate phase at the interface between metal and ceramic. For instance, TiO_x is formed at the interface between molten Cu-Ti alloy and Al_2O_3[8]. In this work the intermediate phase is investigated at the cross section of a sessile drop cooled down. **Fig. 6** shows the change in contact angle and the thickness of intermediate phase with titanium content at temperatures above 50° from melting points of alloys. The contact angle markedly decreases at titanium content of 30 at% or more, and the thickness of the intermediate layer becomes 10 μm or more. **Fig. 7** exhibits the microstructure of the interface between $Cu_{50}Ti_{50}$ drop and Si_3N_4 at 1025°C for 30 min.

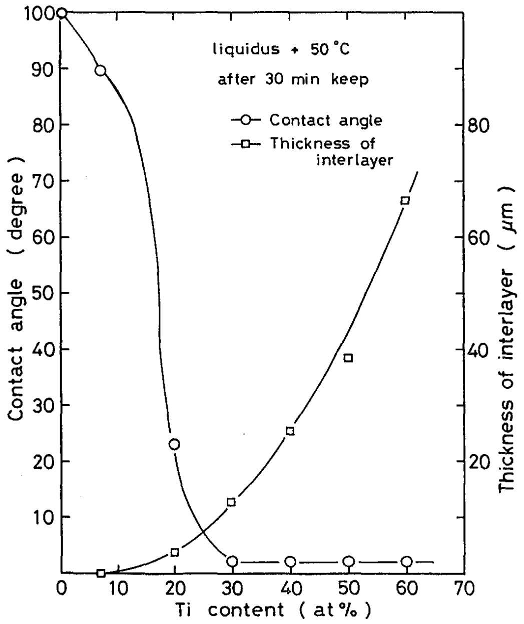

Fig. 6 Contact angle and intermediary layer thickness of Cu-Ti alloys at liquidus temperature + 50°C for 30 min.

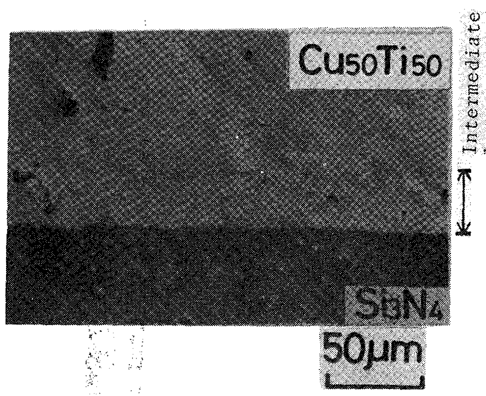

Fig. 7 Intermediate layer formed at interface between $Cu_{50}Ti_{50}$ and Si_3N_4 at 1025°C for 30 min.

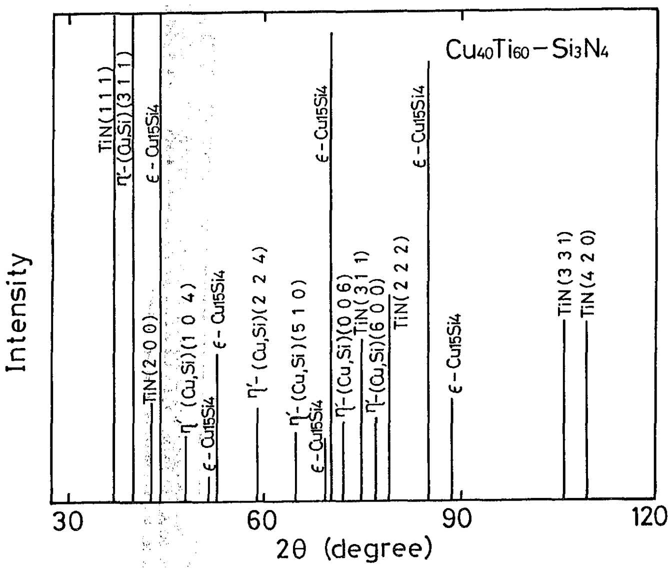

Fig. 8 X-ray diffraction pattern of separated surface of $Cu_{40}Ti_{60}$ drop after sessile drop testing at 1020°C for 30 min.

X-ray diffraction pattern of the interface of Cu-60 at% Ti alloy drop separated from Si_3N_4 after cooling down indicates the formation of TiN, ϵ-$Cu_{15}Si_4$, η'-(Cu, Si) as shown in **Fig. 8**. From the melting points of the intermediate phases, copper silicides is in the molten state and TiN is in the solid state at the sessile drop measurement. TiN may be formed by the following reaction. Since Si_3N_4 and TiN are formed by eqs. (4) to (6)[9),10),11)],

$$3Si(s) + 2N_2(g) = Si_3N_4(s)$$
$$\Delta G^{\circ} = -17280 + 75.3T \quad (4)$$

$$Ti(l) + 1/2N_2(g) = TiN(s)$$
$$\Delta G^{\circ} = -81380 + 21.6\ T \quad (5)$$

where g, l and s are denoted as gas, liquid and solid, respectively, and liquid titanium is used in stead of liquid Cu-Ti alloys. From eqs. (4) and (5),

$$Si_3N_4(s) + 4Ti(l) = 4TiN(s) + 3Si(s)$$
$$\Delta G^{\circ} = -152719 + 15.9\ T \quad \text{cal/mol} \quad (6)$$

The ΔG° value of -13.1 kcal/mol of eq. (6) at 1100°C and the X-ray diffraction pattern of TiN of the separated surface of Cu-Ti drop suggest the reaction of eq. (6) takes place and the silicon separated is thought to react with copper in the Cu-Ti alloys. The results of sessile drop measurements demonstrate that Cu-Ti alloys containing titanium content of 30 at% or more are applicable to the filler metals for joining of Si_3N_4.

In order to make clear the wetting behavior of copper alloys with Si_3N_4, we investigate the wetting behavior of copper-zirconium alloys. Fig. 9 shows the change in contact angle of Cu-Zr alloys with time at 1100°C. The alloys containing zirconium up to 30 at% exhibit no time

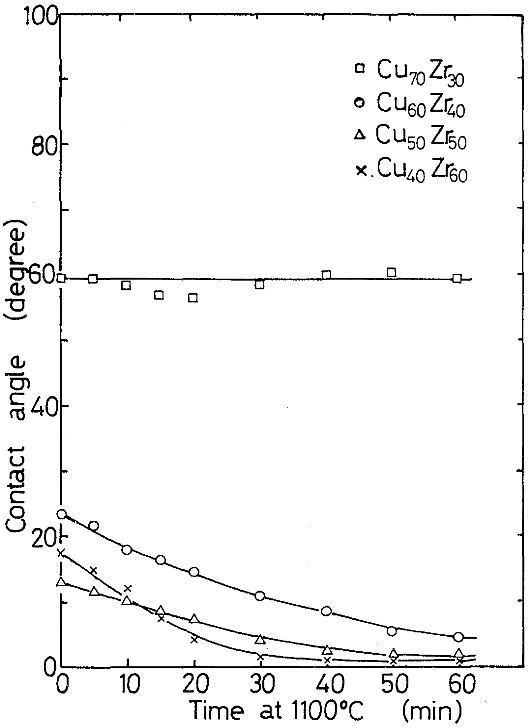

Fig. 9 Time dependence of contact angle Cu-Zr alloys on Si_3N_4 at 1100°C.

dependence of contact angle, and the alloys containing zirconium content of 40 at% or more show the time dependence.

That change in contact angle of liquid metal on solid with time is often interpreted in terms of Newman's equation as follows[12],

$$\cos\Theta_t = (\cos\Theta_\infty)\,\{1 - a\exp(-bt)\} \quad (7)$$

where Θ_∞ is the equilibrium contact angle and Θ_t is the contact angle at time t. From eq. (7), the rate of wetting is obtained as,

$$\frac{d(\cos\Theta_t)}{dt} = b\,(\cos\Theta_\infty - \cos\Theta_t) \quad (8)$$

Eq. (8) indicates that b is the apparent ratè constant of

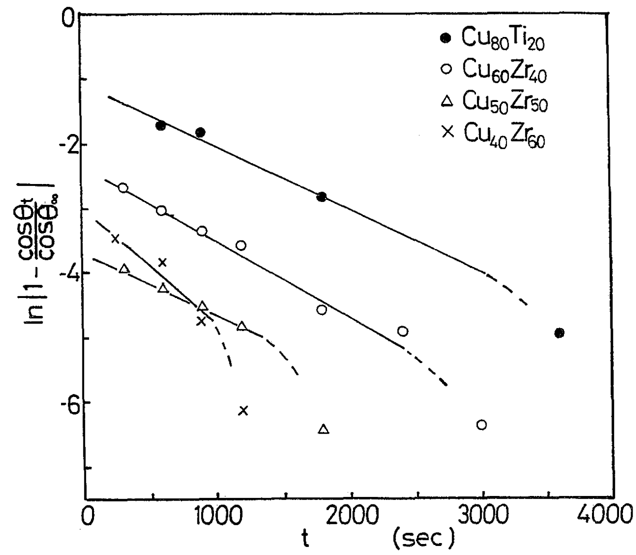

Fig. 10 Time dependence of contact angle, ln $|1-\cos\Theta_t/\cos\Theta_\infty|$ vs t, for copper-20 at% titanium and copper-zirconium alloys at 1100°C.

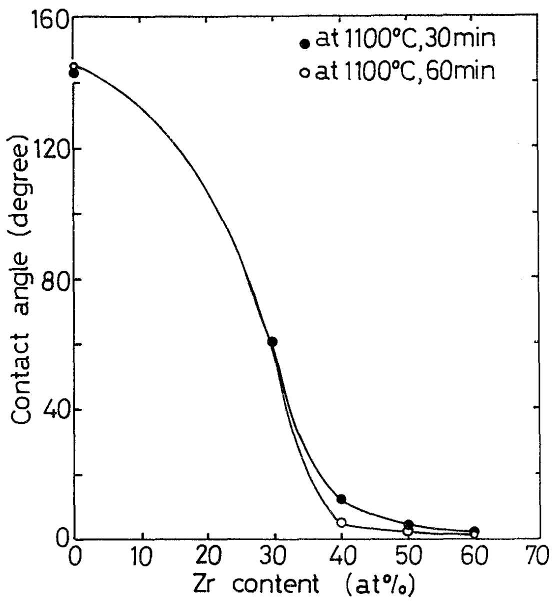

Fig. 11 Change in contact angle of Cu-Zr alloys on Si_3N_4 with zirconium content at 1100°C for 30 min or 60 min.

wetting during a primary spreading process. Using Newman's equation the contact angles of copper-zirconium alloys containing 40 at% zirconium or more and copper-20 at% titanium alloy at 1100°C are analysed as shown in **Fig. 10.** The contact angles of Cu-Zr alloys at 60 min are took as the equilibrium values since the angles of the alloys reach the final values. For Cu-20 at% Ti alloy the value at 120 min is taken as the equilibrium value. The initial stage of wetting can be applicable to Newmann's equation as the figure. In Cu-Ti alloys b is 0.95×10^{-3} sec^{-1}, and increases with titanium content. b of Cu-Zr alloys containing zirconium content of 40 at% or more is $(0.9 \sim 1.8) \times 10^{-3}$ sec^{-1}. These values are comparable to the b values of Al-Cu alloys against Al_2O_3[4]. Thus the rate of wetting of molten Cu-Zr alloys on Si_3N_4 is comparable to that of molten Al-Cu alloys on Al_2O_3.

In **Fig. 11** are shown the changes in contact angles of alloys at 1100°C for 30 min or 60 min with zirconium content. The alloys containing zirconium content of 30 at% or more provide the value of 2° or less. The decrease in contact angle with zirconium content is attributable to the intermediate phases at the interface between alloys and Si_3N_4. The intermediate phases are ZrN, Zr_5Si_3, Zr_3Si_2, ϵ-$Cu_{15}Si_3$ and η'-(Cu, Si) which are idntified by X-ray diffraction pattern of the interface of $Cu_{50}Ti_{50}$ drop separated from the sessile drop in **Fig. 12**. ZrN may be formed by the following reactions[9), 10), 11)],

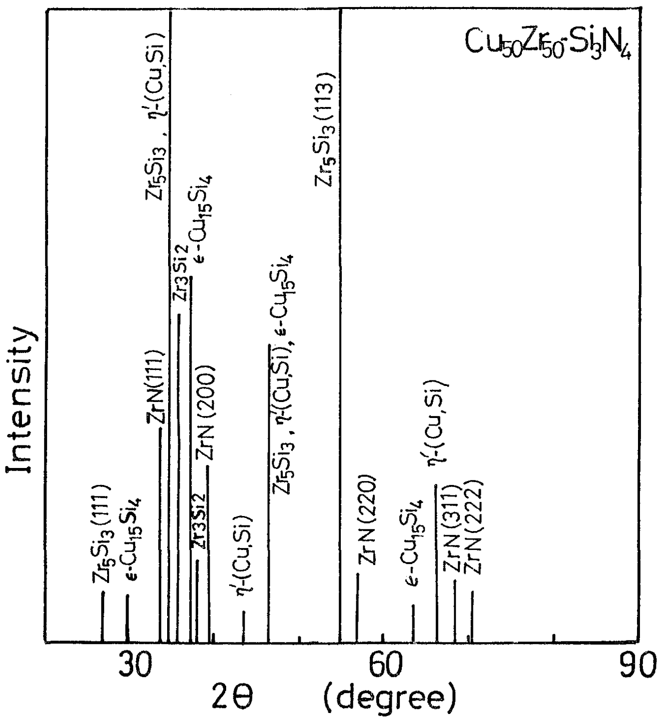

Fig. 12 X-ray diffraction pattern of separated surface of $Cu_{50}Zr_{50}$ drop after sessile drop testing at 1100°C for 60 min.

$$3Si(s) + 2N_2(g) = Si_3N_4(s)$$
$$\Delta G^\circ = -172801 + 75.3\ T \qquad (9)$$

$$Zr(1) + 1/2N_2(g) = ZrN(s)$$
$$\Delta G^\circ = -92655 + 22.3\ T \qquad (10)$$

From eqs. (9) and (10),

$$Si_3N_4(g) + 4Zr(1) = 4ZrN(s) + 3Si(s)$$
$$\Delta G^\circ = -178585 + 22.3\ T \quad \text{cal/mol} \qquad (11)$$

where the liquid zirconium is used instead of liquid Cu-Zr alloys, and g, l and s are denoted as gas, liquid and solid, respectively. The ΔG° value of -16.0 kcal/mol of eq. (11) at 1100°C and the observed X-ray diffraction pattern of ZrN of the alloy drop suggests the occurance of reaction (11). The silicon in eq. (11) may react with Cu and Zr in alloys and form the Cu and Zr silicides. The contact angles of Cu-Zr alloys are small, and the thermal expansion coefficient of ZrN found at the interface between Si_3N_4 and Cu-Zr alloys α: ZrN = 7.9×10^{-6}/°C is the almost same as that of α: TiN = 9.8×10^{-6}/°C for Cu-Ti alloys.[13)] In spite of those values the Cu-Zr alloy drops separated from Si_3N_4 after sessile drop measurements. The contact angles of molten alloys are dominated by small amounts of intermediate phases at the interface between ceramics and alloys, and do not provide the measure of enough amounts of intermediate phases necessary to the joining of ceramics. Those are supported from the following results. In joining Si_3N_4 with Si_3N_4 using $Cu_{50}Zr_{50}$ filler the joining does not take place at 1100°C, but at 1300°C by inceasing the amount of the intermediate phases. The amount of reaction between the ceramics and Cu-Zr alloys is small in comparison with the case of Cu-Ti alloys, and Cu-Zr alloys are not applicable to the filler of joining Si_3N_4.

4. Conclusions

The sessile drop technique has been used to measure the contact angle of molten copper – 0 – 60 at% titanium alloys and copper 0 – 60 at% zirconium alloys with Si_3N_4. Time-lapse photography measurements were made in vacuum condition, and as a function of time and temperature over the temperature range 900° to 1100°C. The temperature dependence of copper-titanium alloys is small for 20 at% Ti alloy, and further large for the alloys containing titanium content of 30 at% or more. The sessile drops of alloys containing 30 at% Ti or more rapidly spread during heating and do not show photographycally the time dependence after reaching 1100°C. At 1100°C for 30 min the contact angles of alloys markedly decrease from 145° for pure copper to about 8° for the copper-titanium alloys containing titanium content of 30 at% or more. This is attributable to the formation of the intermediate phases composed mainly of TiN. Cu-Ti alloys are applicable to the filler of joining Si_3N_4.

The contact angles of Cu-Zr alloys containing zirconium content of 40 at% or more change with time at 1100°C. At 1100°C for 30 min or 60 min, the contact angles markedly decrease at zirconium content of 40 at% or more and exhibit about 2° at zirconium content of 60 at%. This is attributable to the formation of intermediate phases mainly composed of ZrN. However, owing to the small amounts of reaction of the alloys with Si_3N_4, Cu-Zr alloys are not applicable to the filler of joining Si_3N_4.

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