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TECHNICAL NOTE

Wetting of Zirconia by Cu-Zr Alloys†

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KEY WORDS: (Wetting) (Zirconia) (Copper-Zirconium Alloys) (Work of Adhesion) (Interfacial Energy) (Surface Energy) (Joining) (Filler Metals)

Brazing is used extensively in the joining of ceramics with metals. The wetting of ceramics by liquid phase is a major factor in producing an effective bond of ceramics with metals. The wetting behavior between ceramics and molten alloys can be measured in terms of the contact angle between the peripheral surface of a small sessile drop of molten alloy and the horizontal surface of the ceramic substrate as indicated in **Fig. 1**.

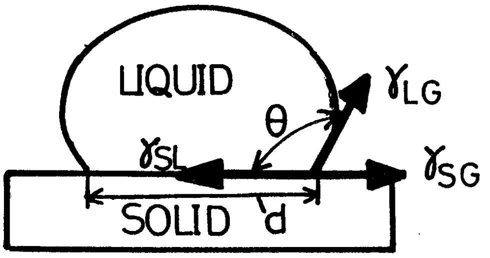

Fig. 1 Schematic of contact angle of liquid drop on ceramics.

This angle, θ, is related to the solid and liquid surface energies, γ_{SG} and γ_{SL} and the solid-liquid interfacial energy, γ_{SL} by the Young's equation,

$$\gamma_{SG} = \gamma_{LG} \cos\theta + \gamma_{SL} \qquad (1)$$

The zirconia substate was in the form of 15 mm diameter disk 3 mm thick. The zirconia was polished up to No. 1000 with silicon carbide paper. The composition of zirconia used was 91 wt%ZrO_2, 5.5 wt%CaO and others and the structure strabilized with CaO was cubic. The nominal compositions of copper-zirconium alloys were 0, 30, 50 and 60 at% zirconium. In sessile drop apparatus as shown in **Fig. 2** the alloys were placed on zirconia plate and the contact angles of molten drops were photographycally taken at regular time intervals at 1150°C. The heating rate up to desired temperature was about 85°C/min in 2×10^{-5} torr.

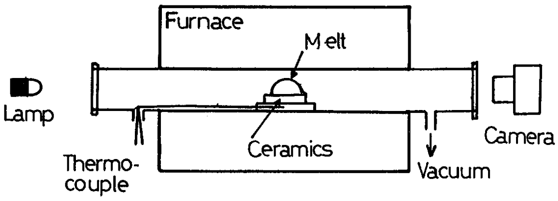

Fig. 2 Sessile drop apparatus.

Fig. 3 shows the time dependence of contact angle of copper and copper-zirconium alloys at 1150°C. The contact angles of drops reach the equilibrium values at 60 min. The zirconium content dependence of the equilibrium contact angles of copper-zirconium alloys at 1150°C is shown in **Fig. 4**. The contact angles of the alloys change from 91° for copper to 45° for $Cu_{45}Zr_{60}$ alloy. In contrast to the effect of titanium content on the contact angles of Cu-Ti alloys on alumina, the effect of zirconium content is not effective in decreasing the contact angles of alloys on zirconia, The copper-zirconium alloys can be said to be in wetting state because the equilibrium contact angles are below 90°. The work of adhesion, W_{ad}, which is the work required to separate a unit area of solid-liquid interface into two surfaces is provided by Young-Duprè equation as follows,

$$W_{ad} = \gamma_{LG} (1 + \cos\theta) \qquad (2)$$

where γ_{LG} is the liquid surface energy in Fig. 1. For liquid copper γ_{LG} = 1300 erg/cm^2 (1083°C) and the temperature dependence, $d\gamma_{LG}/dT = -0.45$$^{1)}$, γ_{LG} of copper

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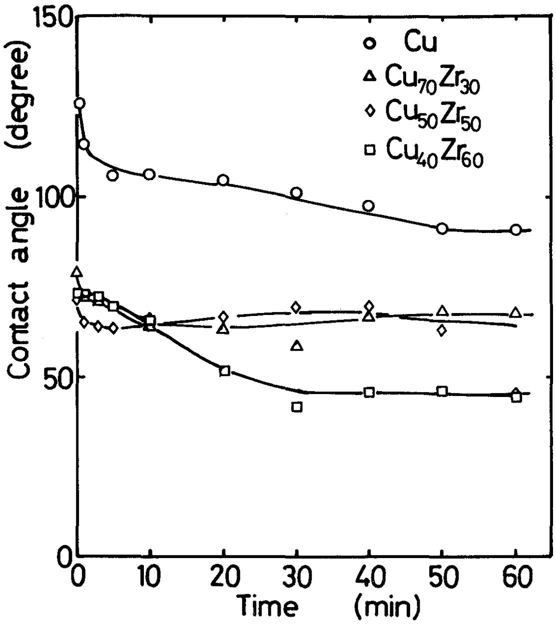

Fig. 3 Time dependence of contact angle of Cu-Zr alloys on ZrO2 at 1150°C.

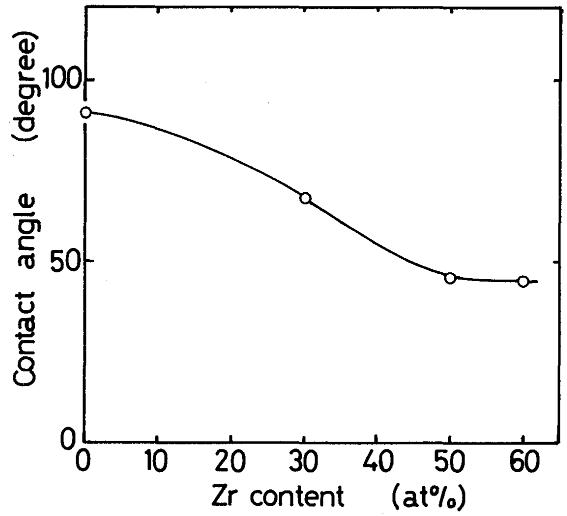

Fig. 4 Zirconium content dependence of contact angle of Cu-Zr alloys at 1150°C for 60 min.

at 1150°C is 1270 erg/cm^2. From the γ_{LG} (at 1150°C) and observed $\theta = 91°$ (at 1150°C) of pure copper, W_{ad} (at 1150°C) of copper against ZrO_2 is 1248 erg/cm^2 (at 1150°C). This value is relatively larger than W_{ad} (517 erg/cm^2) of copper against Al_2O_3 at 1100°C.

W_{ad} is defined by Duprè equation as,

$$W_{ad} = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \qquad (3)$$

Since γ_{SG} (590 erg/cm^2) of ZrO_2 stabilized with CaO at 1850°C is smaller than γ_{SG} (905 erg/cm^2) of Al_2O_3 at 1850°C$^{2)}$, the difference of W_{ad} between Cu/ZrO_2 and Cu/Al_2O_3 comes from the difference of interface energy γ_{SL} between Cu/ZrO_2 and Cu/Al_2O_3. Thus γ_{SL} of Cu/ZrO_2 is smaller than γ_{SL} of Cu/Al_2O_3 and the interface between Cu and ZrO_2 is stabler than that between Cu and Al_2O_3. The decrease in interface between liquid and solid is attributable to the adsorption of special alloying element on the interface or the formation of intermediate phase at the interface. For instance, TiO_X is formed at the interface between Cu-Ti alloy and $Al_2O_3$$^{3)}$. The interface between $Cu_{50}Zr_{50}$ and ZrO_2 was also examined by X-ray diffractometry. **Fig. 5** shows the X-ray diffraction pattern of the interface of ZrO_2 side separated from the sessile drop cooled down from 1150°C for 60 min. The intermediate phase of orthorohmbic $CaZrO_2$ is formed. The copper-zirconium alloys are not applicable to the filler of joining ZrO_2 since the difference of thermal expansion between the alloy and the ceramic causes the separation of the drop from the ceramic after cooling down.

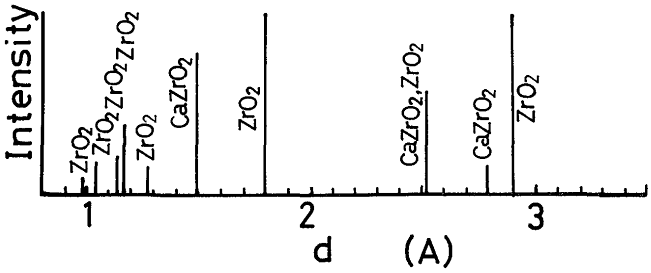

Fig. 5 X-ray diffraction pattern of separated surface of $Cu_{50}Zr_{50}$ drop after sessile drop testing at 1150°C for 60 min.

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