Title	Wetting of Alumina by Molten Aluminum and Aluminum-Copper Alloys(Welding Physics, Process & Instrument)
Author(s)	Naka, Masaaki; Hirono, Yutaka; Okamoto, Ikuo
Citation	Transactions of JWRI. 1984, 13(2), p. 201-206
Version Type	VoR
URL	https://doi.org/10.18910/8504
rights	
Note	

Wetting of Alumina by Molten Aluminum and Aluminum-Copper Alloys[†]

Masaaki NAKA*, Yutaka HIRONO* and Ikuo OKAMOTO****

Abstract

The sessile drop technique has been conducted to measure the contact angle of molten aluminum and aluminum-copper alloys with alumina. The contact angle of aluminum alloys decreases with increasing time at temperatures above 1000°C. The process of wetting of the molten alloys is interpreted in terms of first order of kinetics, and may be dominated by the chemical reaction between molten aluminum and alumina etc. The work of adhesion of molten aluminum-copper alloys slightly increases from 1297 ergs/cm^2 for pure aluminum up to 1360 ergs/cm^2 for Al-30wt%Cu alloy, and markedly decreases to 517 ergs/cm^2 for pure copper at 1100°C.

KEY WORDS: (Wetting) (Joining) (Brazing) (Alumina) (Aluminum) (Aluminum-Copper) (Contact Angle)

1. Introduction

An understanding of those factors responsible for good adhesion between metals and ceramics is not only of scientific interest but also of considerable technological importance. The strength of interface in ceramics and metal depends critically on the ability of the metal to wet the ceramics and a good deal of effort has been directed towards understanding the wetting process. The same factors are also important in the production of vacuum tight joint between metal and ceramics components.

Several works have investigated aluminum/alumina or sapphire wetting behavior. Champion et al.[1)] studied the wetting of alumina by molten aluminum over a temperature range 800° to 1500°C. They found that a rapid increase in contact area occured at temperatures above 900°C. Wolf et al.[2)] have reported the wetting of aluminum on sapphire (α-alumina) over a temperature range 700° to 1150°C. The contact angle of molten aluminum decreases with increasing temperature and a wetting condition occurs at temperatures above 1038°C. The studies of wetting behavior of aluminum on alumina have so far been focused on only pure aluminum. The effect of alloying elements on wetting behavior of aluminum also have to be made clear.

The object of the present work is to study in more detail the wetting and spreading of molten aluminum and aluminum-copper alloys on aluminum oxide over the temperature range 900° to 1250°C.

2. Experimentals

The composition of alumina in this work was 99.6wt% Al_2O_3, 0.1wt%SiO_2 and others. The purities of aluminum used was 99.99wt%. Aluminum-copper alloys containing nominal compositions of 4, 10, 30 and 60wt% copper were also used. Aluminum samples of 0.2 g in weight were placed on alumina plate of 15 mm diameter and 3 mm thickness that polished mechanically with silicon carbide paper to No. 1000. The sessile drop technique was used to evaluate wetting behavior by measuring contact angle θ and base diameter d of molten drop which were photographically taken at regular time intervals at constant temperature as shown in **Fig. 1**. The heating rate up to desired temperature was about 85°C/min in 2×10^{-5} torr. The sessile drop apparatus is shown in **Fig. 2**. Typical example of sessile drop of Al-30wt%Cu alloy cooled down from 1100°C, 30 min. is shown in **Fig. 3**.

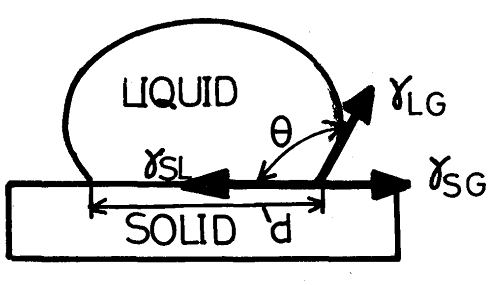

Fig. 1 Schematic of contact angle of liquid drop on solid surface.

---

† Received on October 31, 1984

* Associate Professor

** Professor

*** Graduate Student

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

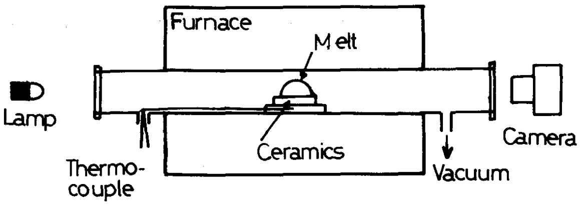

Fig. 2 Sessile drop technique apparatus.

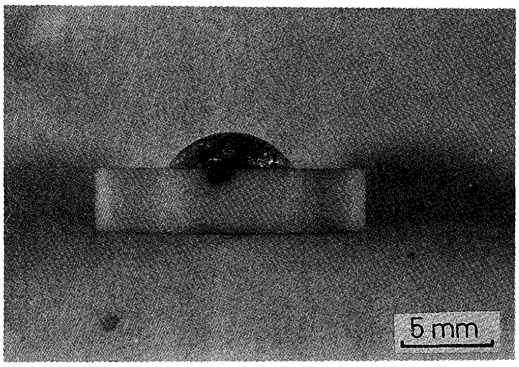

Fig. 3 Sessile drop of Al-30wt%Cu alloy cooled down from 1100°C, 60 min.

3. Results

The contact angles between aluminum and alumina over temperature range 900° to 1250°C are presented in **Fig. 4**. Although the contact angle at 900°C does not change with time, the angle at temperatures above 1100°C decreases with an increase in time. The contact angle at temperatures above 1100°C rapidly changes at the initial time of contact whereas it decreases slowly with time at 1000°C. Mori et al.[3] reported that the contact angle of molten aluminum does not change at temperatures below 900°C. The contact angles at 60 min are taken as the equilibrium values because they reach the final steady values. The equilibrium contact angle between aluminum and alumina decreases with an increase in temperature as shown in **Fig. 5**. Also shown in the figure for comparison are the results of Champion et al.[1], Wolf et al.[2] for aluminum on sapphire and Mori et al.[3] for aluminum on alumina. The temperature dependence of equilibrium contact angle in the present work is steeper than that of other works. The present works at temperatures above 1100°C are lower than that of other works, and the values at 1000°C are almost same. The difference of contact angle values may come from the purity of alumina ceramics. However, in theoretical, Okamoto[4] stated that the temperature dependence of equilibrium contact angle is a hyperbolic function.

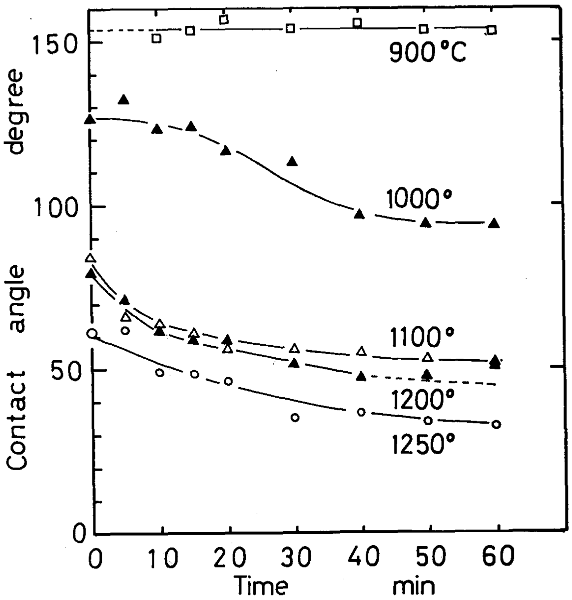

Fig. 4 Time dependence of contact angle for pure aluminum on alumina at temperatures 900° to 1250°C.

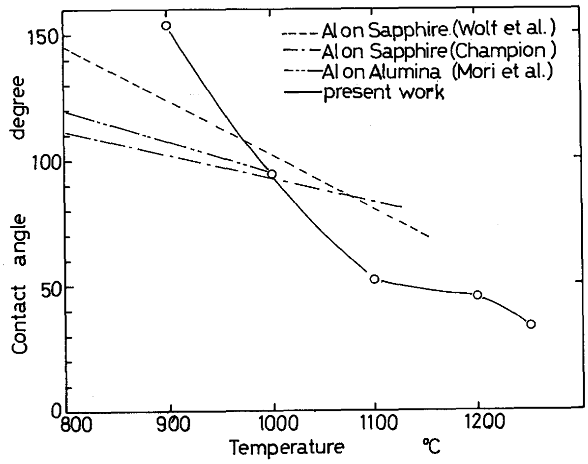

Fig. 5 Temperature dependence of equilibrium contact angle for pure aluminum on alumina.

In general, at the contact angle between 0° and 90°, the shape of melt is convex and the melt is said to be wetting state and at the contact angle between 90° and 180° the shape becomes to swell and the melt is said to be non-wetting state. The wetting of aluminum on alumina begins at temperatures above 1010°C as seen in Fig. 5. The value at 1250°C is relatively lower than that extrapolated from values at lower temperatures. An observation of sessile drop after wetting experiment at 1250°C shows the decrease in aluminum volume and the evaporation of aluminum during wetting. These results indicate that the front edge of the melt on alumina recedes during wetting, and the observed contact angles correspond to the contact angles during receding of melts on alumina.

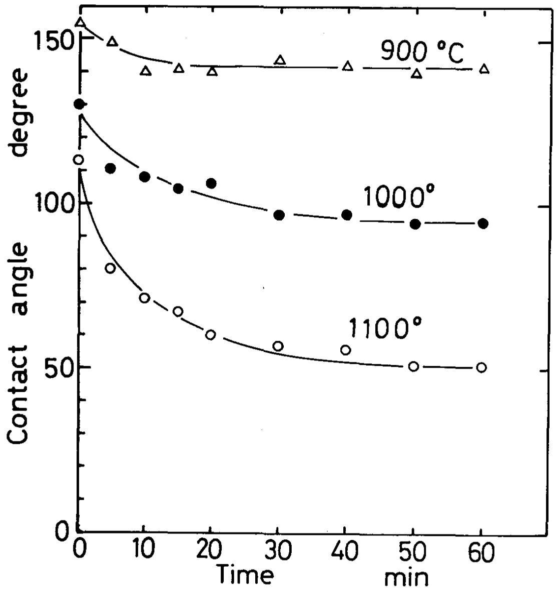

Fig. 6 Time dependence of contact angle for aluminum-30wt%-copper alloy on alumina at temperatures 900° to 1100°C.

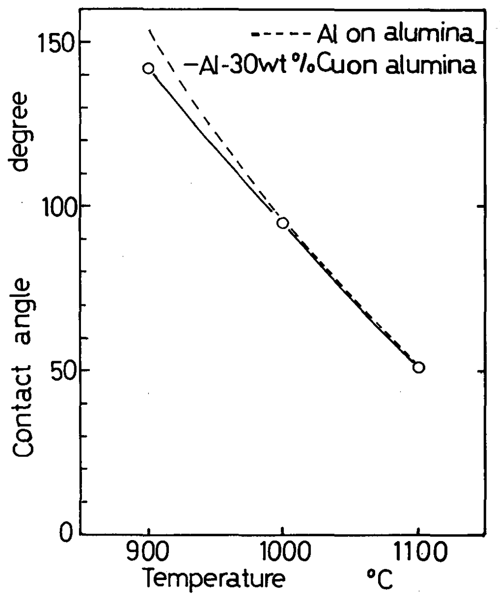

Fig. 7 Temperature dependence of equilibrium contact angle for aluminum-30wt%copper alloy on alumina.

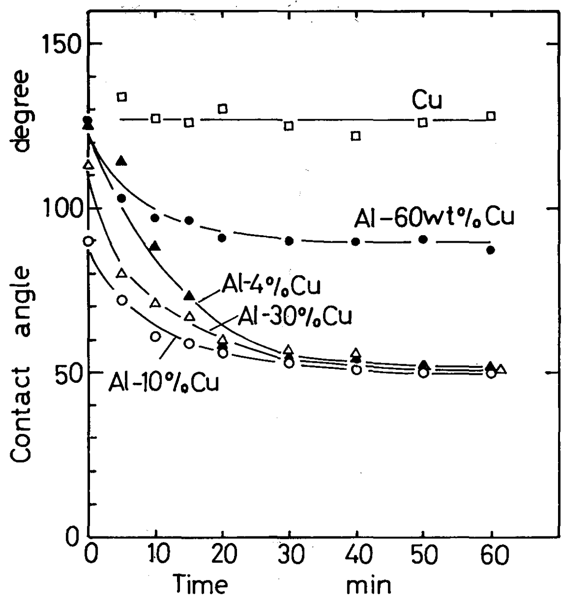

Fig. 8 Time dependence of contact angle for aluminum-copper alloys on alumina at temperatures 1100°C.

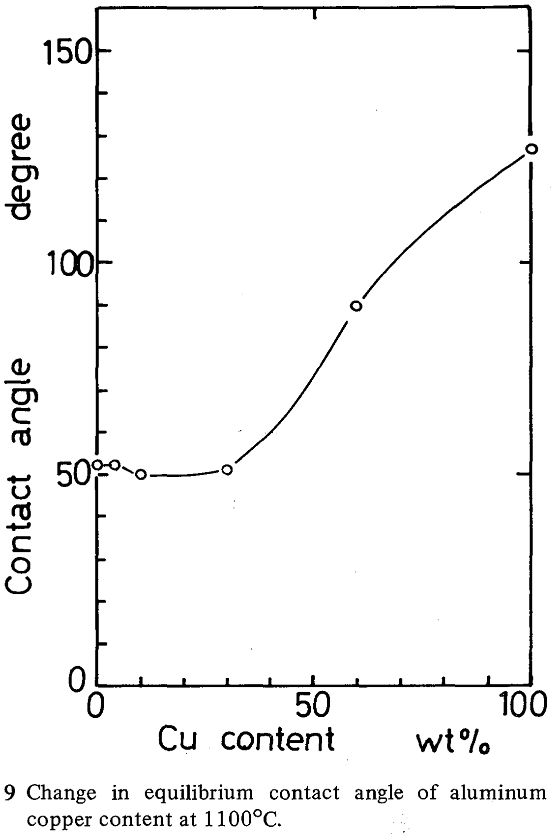

Fig. 9 Change in equilibrium contact angle of aluminum with copper content at 1100°C.

A receding contact angle, in general, is smaller than an advancing contact angle.

Fig. 6 represents the time dependence of contact angle of Al-30wt%Cu alloy at temperatures 900° to 1100°C. In contrast to the case of pure aluminum, Al-30wt%Cu alloy shows the decrease in contact angle at temperatures above 900°C. **Fig. 7** shows the temperature dependence of equilibrium contact angle for the alloy is the almost same as that of pure aluminum. The alloy begin to be wetting state at 1010°C since the contact angle becomes less than 90° at the time. The contact angles of aluminum-copper alloys at 1100°C are plotted as a function of time as shown in **Fig. 8**. The contact angles of alloys except for pure copper decrease with increasing time. The final contact angles of aluminum-copper alloys at 60 min are shown in **Fig. 9**. The aluminum-copper alloys containing copper content below 60wt% are in the wetting state and the contact angles of melts containing copper content below 30wt% exhibit same or a little lower values than that of pure aluminum.

4. Discussion

The change in contact angle of liquid metal on solid with time is often interpreted in terms of Newman's equation as follows[5],

$$\cos\theta_t = (\cos\theta_\infty)\{1-a\exp(-b)\} \tag{1}$$

where θ_∞ is the equilibrium contact angle and θ_t is the contact angle at time t. Using Newman's equation the contact angles of molten aluminum and aluminum-copper alloys at 1100°C were analysed as shown in **Figs. 10** and **11**. The contact angles at 60 min were took as the equilibrium values θ_∞ since the angles reached the final constant values. The initial stage of wetting can be applied to Newman's equation as those figures. The slopes of lines in the figures give b values. From eq.(1) the rate of wetting is obtained,

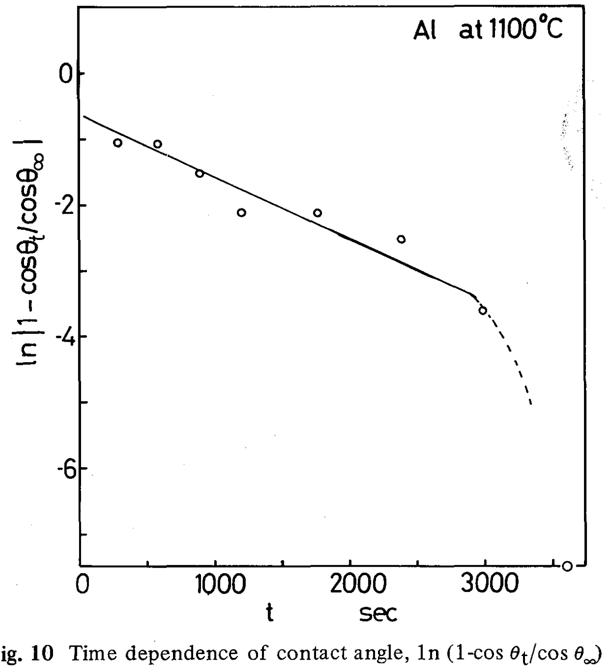

Fig. 10 Time dependence of contact angle, ln (1-cos θ_t/cos θ_∞) vs t, for pure aluminum at 1100°C.

$$\frac{d(\cos\theta_t)}{dt} = b(\cos\theta_\infty - \cos\theta_t) \tag{2}$$

which gives the first order kinetics of wetting. However, b is the apparent rate constant of wetting during a primary spreading process because the quantity of wetting is given as the product of the surface tension of liquid and the equilibrium contact angle. Suciu et al.[6] stated that the wetting process of equation (1) is dominated by the mass, the surface or interface tension and the viscosity coefficient of liquid drop etc. except for the interface reaction between solid and liquid.

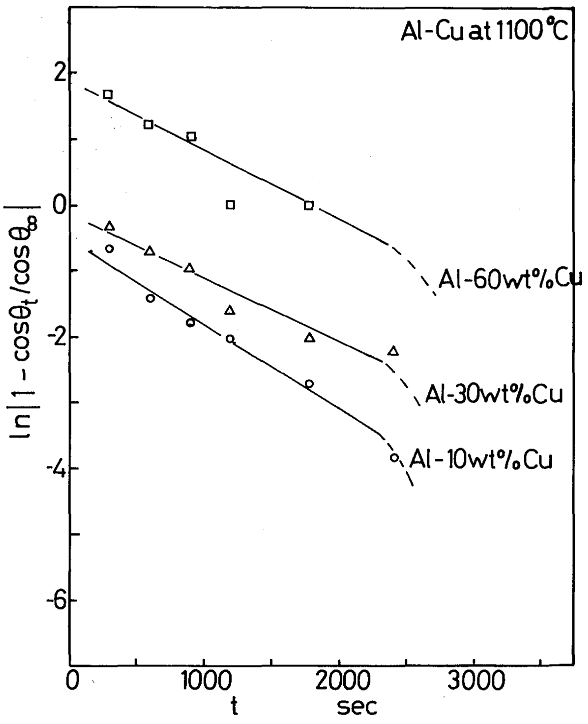

Fig. 11 Time dependence of contact angle, ln (1-cos θ_t/cos θ_∞) vs t, for aluminum-copper alloys at 1100°C.

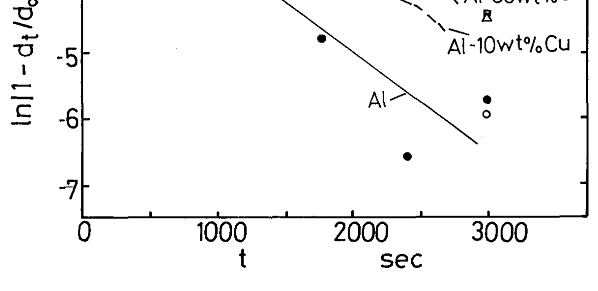

Fig. 12 Time dependence of base diameter of drop, ln (1-d_t/d_∞) vs t, for aluminum-copper alloys at 1100°C.

Further, in order to make clear the physical meaning of b in eq.(1) we tried to apply Newman's equation to the spreading of each tested melt as shown in **Fig. 12.** (d_t/d_∞) was used instead of $(\cos\theta_t/\cos\theta_\infty)$ in equation (1), where d_∞ is the equilibrium base diameter of drop and d_t is the diameter at time t as shown in Fig. 1. The values at 60 min were used as d_∞. The slopes in Fig. 12 are the rate constants of spreading. From the Figures 10 and 11 the apparent rate constants of wetting are $(0.95 \sim 1.8) \times 10^{-3}$ $\sec^{-1}$ for aluminum-copper alloys on alumina at 1100°C and from the Figure 12 the rate constants of spreading are $(0.71 \sim 1.6) \times 10^{-3}$ $\sec^{-1}$ for the alloys at 1100°C. Both values are almost same. This means that b is also dominated by the interface reaction between liquid and solid, because the spreading occurs by the interaction between liquid and solid. The structure of interface of Al_2O_3/Al drop melted at 1100°C for 60 min is given in **Fig. 13.** The intermediary layer of between Al and Al_2O_3 is very thin because it can not be obviously seen by the SEM observation.

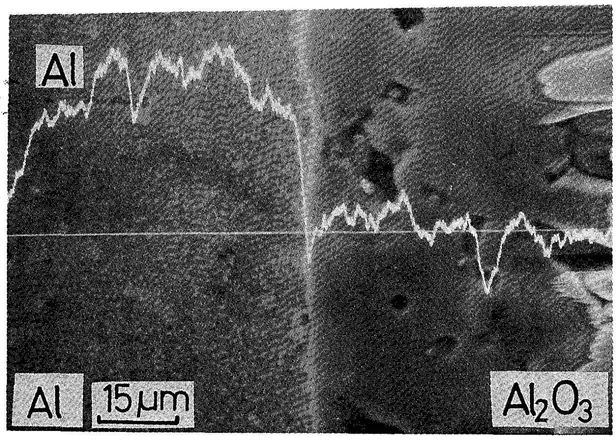

Fig. 13 Microphotograph and line analysis of Al at interface between aluminum and alumina. (A sessile drop of pure aluminum on alumina was melted at 1100°C for 60 min.)

The solid-liquid contact angle is determined by equilibrium of the thermodynamic surface energies as shown in Fig. 1. The vectorial addition of these surface energies gives Young's equation.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta_\infty \qquad (3)$$

where γ_{SG} is the solid-vapor surface energy, γ_{SL} is the interfacial (liquid-solid) energy, and γ_{LG} is the liquid-vapor surface energy.

Further, the work of adhesion, W_{ad}, is defined by the Durpè equation as

$$W_{ad} = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \qquad (4)$$

The work of adhesion is the work required to separate a unit area of solid-liquid interface into two surfaces. Eqs.(3) and (4) give Young-Duprè equation of W_{ad} as follows,

$$W_{ad} = \gamma_{LG}(1 + \cos\theta_\infty) \qquad (5)$$

Limited data by Semechenko⁷⁾ reported that γ_{LG} of aluminum-copper alloys decreases from 820 ergs/cm² for pure aluminum to 467 ergs/cm² for Al-5wt%Cu alloy and 452 ergs/cm² for Al-33wt%Cu alloy at 700°C. On the other hand, a comprehensive study by Eremenko et al.⁸⁾ has indicated that γ_{LG} of aluminum-copper alloys increases with an increase in copper content at 1100°C. From the present results of equilibrium contact angles of molten aluminum-copper alloys and γ_{LG} of Eremenko's work we estimated the work of adhesion W_{ad} of molten aluminum-copper alloys at 1100°C as shown in **Fig. 14.** The work of adhesion of the molten alloy slightly increases from 1297 ergs/cm² for pure aluminum to 1331 ergs/cm² for Al-10wt%Cu alloy, and markedly decreases to 517 ergs/cm² at 1100°C.

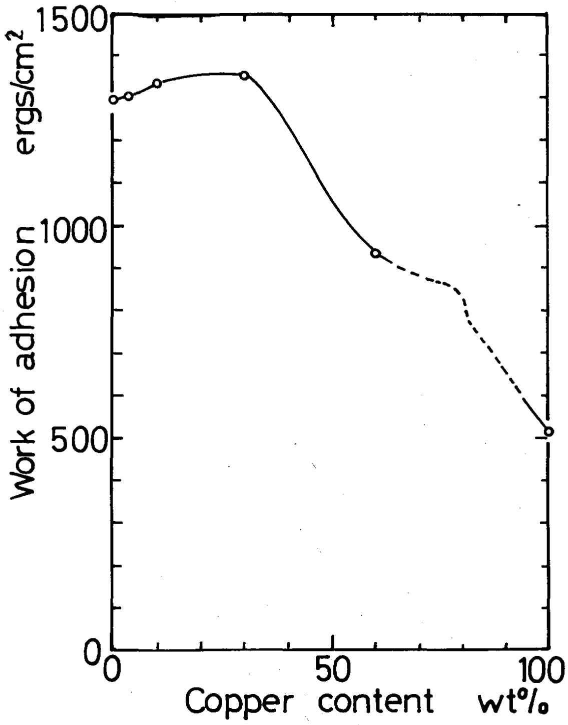

Fig. 14 Work of adhesion of molten aluminum-copper alloys at 1100°C.

5. Conclusions

The sessile drop technique has been used to measure the contact angle of molten aluminum and aluminum-copper alloys with alumina. Time-lapse photography measurements were made in vacuum condition, and as a function of time and temperature over the temperature range 900° to 1250°C. At 900°C the contact angle of aluminum is constant and at temperatures above 1000°C the contact angle decreases with time. The equilibrium contact angle of pure aluminum lowers with increasing temperature. At 1250°C the receding contact angle of drop of aluminum was observed by vaporization of aluminum. The contact angles of molten aluminum-copper alloys decrease with time at 1100°C, and the equilibrium contact angle lowers slightly from 52° for pure aluminum to 51° for 30wt%Cu-Al alloy, and markedly rises to 128° for pure copper at 1100°C.

The process of wetting or spreading of molten drops is interpreted in terms of first order kinetics. The chemical reaction between aluminum and alumina may dominate the apparent wetting or spreading of molten aluminum and aluminum-copper alloys on alumina. The work of adhesion of molten aluminum-copper alloys slightly increases from 1297 ergs/cm² for pure aluminum up to 1360 ergs/cm² for Al-30wt%Cu alloy, and markedly decreases to 517 ergs/cm² for pure copper at 1100°C.

References

1) J.A. Champion, B.J. Keene and J.M. Sillword, J. Mater. Sci., 4 (1969), 39.

2) S.M. Wolf, A.P. Levitt and J. Brown, Chem. Eng. Progress, 62 (1966), 74.

3) N. Mori, H. Sotano, A. Kitahara, K. Ogi and K. Matsuda, J. Japan Inst. Metals, 47 (1983), 1132.

4) I. Okamoto and T. Hashimoto, Diffusion Welding and Brazing, Sanpo Pub. Co., (1976), Japan.

5) S. Newman, J. Colloid and Interface, 26 (1968), 209.

6) D.G. Suciu, O. Smigelschi and E. Ruckenstein, J. Colloid and Interface Science, 33 (1970), 131.

7) V.K. Semechenko, Surface Phenomena in Metals and Alloys, Addison-Wesley Pub. Co., Massachusetts, (1962).

8) V.N. Eremenko, V.I. Nizhenko and Y.V. Naidich, Izv. Akad. Nauk SSSR, Otd, Tekh. Nauk, Met. i Toplivo, (1961), No.3, 150.