Reactive Wetting of Ceramics by Liquid Metals

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In order to establish a method for estimation of the wetting of ceramics accompanied by interfacial reaction, the authors' previous work has been rearranged. The wetting was estimated using meniscography and an improved sessile drop method both of which were devised to measure the wetting from the initial contact. Using a logarithmic time scale, in all the systems (Cu/Hg, Graphite/Al and Al-Si alloys, MgO/Al and AlN/Al), similar wetting curves were obtained as a function of time. The wetting progresses through the following four phases, I: dynamic non-equilibrium phase, II: quasi-equilibrium phase, III: chemical non-equilibrium phase, and IV: equilibrium phase. During each phase the values of, the original wetting speed, the original wettability, the interfacial reaction wetting speed and the equilibrium wettability can be obtained respectively. The condition of wetting increase was also defined, and it was confirmed that phase III can be further separated into two stages, one of which is in the condition of wetting increase and the other which is not. The transient minimum contact angle shown by Aksay *et al.* was not observed throughout the experiments.

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I. Introduction

The wetting of ceramics by liquid metals is one of the most important processes in fabricating metal matrix composites and also in melting and casting metals, bonding ceramics to metals, etc. Most of the wetting systems between ceramics and metals are accompanied by interfacial reactions. These interfacial reactions make the wetting phenomena so complicated that the nature of the wetting process has been sometimes misinterpreted.

Wettability has been examined from several points of view⁽¹⁾⁽²⁾ since it was expressed with contact angle θ by Young⁽³⁾. The degree of wetting of a solid by a liquid, or wettability, is characterized by the conditions of thermodynamic equilibrium⁽⁴⁾. For example, Aksay *et al.*⁽²⁾ discussed the phenomena theoretically based on interfacial reactions and showed the transient minimum of contact angle, is caused by the free energy of reaction $\Delta G^{\alpha\beta}$.

There are many papers which are concerned with wetting. Nevertheless, only a few papers have discussed the variation of θ with time for the case of contact between a sessile drop and a substrate⁽⁵⁾⁽⁶⁾.

The object of the work described in this paper was an explanation of the wetting phenomena mainly on the basis of the authors' experimental work⁽⁷⁾⁻⁽¹¹⁾ of the nature, but in particular, of its time dependency.

II. Measurement of Wetting with Meniscograph and Sessile Drop Method

Young⁽³⁾ proposed treating the contact angle of a liquid as the dynamical equilibrium of a drop resting on a plane solid surface under the balance of three interfacial energies, which is known as the Sessile Drop Method [Fig. 1-a)]. Our measuring system consists of a sealed chamber provided with viewing windows and an Al dropping device⁽⁸⁾⁽⁹⁾ which enables the elapsed time to be accurately determined after the placement of a drop on a solid. Usually, the contact angle, θ , is calculated using Bashforth and Adams' table⁽¹²⁾.

Similarly, the Wilhelmy Method⁽¹³⁾ or Meniscograph⁽¹⁴⁾⁽¹⁵⁾ is used for the measurement of wetting and wettability [Fig. 1-b)]. The equations for the force acting on the specimen are as follows;

$$F = P\gamma_{lv} \cos \theta - g\rho dS \quad (1)$$

$$\sin \theta = 1 - \rho gh^2 / 2\gamma_{lv} \quad (2)$$

where F is the total force on the specimen, P is the

Fig. 1 Relationship between contact angle and three interfacial energies. a) Principle of sessile drop method. b) Principle of Meniscograph.

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perimeter of the specimen, γ_{lv} is the surface tension of the liquid, g is the acceleration due to gravity, ρ is the density of the liquid, d is the depth of immersion, S is the cross sectional area of the specimen, and h is the height of the meniscus. In principle, the contact angle, θ , is estimated simply from a wetting curve when F is set to $g\rho dS$ in air, so that when

$$\begin{aligned}\gamma_{lv} \cos \theta &= \gamma_{lv}, & \theta &= 0^\circ; \\ \gamma_{lv} \cos \theta &= 0, & \theta &= 90^\circ; \\ \gamma_{lv} \cos \theta &= -\gamma_{lv}, & \theta &= 180^\circ;\end{aligned}\quad (3)$$

Generally, the adhesion tension, $\gamma_{lv} \cos \theta$, is calculated from the detection of the total force, F , which is monitored at 0.02 s intervals using a microcomputer. The wetting change over a short time interval is then easily obtained from the continuous measurement of F . This is the main reason for adopting the Meniscograph for the assessment of the wetting in this investigation.

III. Aksay's Model of the Wetting⁽²⁾ Accompanied by Chemical Reactions

Aksay *et al.* showed four types of models for the wetting associated with chemical reactions as follows: a) only the solid is not saturated with some or all of the components of the liquid, b) only the liquid is not saturated with some or all of the components of the solid, c) both phases are unsaturated with respect to the other, and d) a compound forms at the interface. Several dynamic wetting phases associated with the cases of a) and b) are schematically shown in Fig. 2. At the time $t=t_0$, Fig. 2-a) and b) show an instantaneous quasichemical equilibrium involving no interfacial reaction between the liquid and the solid. As the reaction proceeds the interfacial free energy and the surface free energy of the liquid will change by Δg^{sl} or Δg^{lv} , respectively, at $t=t_1$ due to the free energy of the reaction. According to the change of $\Delta g^{\alpha\beta}$ (where $\alpha\beta$ are the solid, liquid or vapor phases), a transient minimum will be observed as shown in Fig. 3.

IV. Wetting of Cu by Hg with Meniscograph⁽⁷⁾

According to the phase diagram of the Cu/Hg system by Hansen⁽¹⁶⁾, there is a peritectic at a temperature of 369 K. The extent of wetting would expectedly change at temperatures above or below the peritectic temperature due to the formation of intermetallic compounds or the dissolution of Cu into Hg at the interface. The main experimental conditions are as follows: depth of immersion: 5 mm, speed of immersion; 30 mm/s.

The results are shown in Fig. 4-a) and b) on a normal and a logarithmic time scale. From Fig. 4-a), it is very difficult to recognize the dissolution of Cu at 381 K and the formation of intermetallic compounds at the interface at 355 K. On the other hand, when the logarithmic time scale is adopted, those phenomena can be recognized more easily than when using the normal time scale.

Fig. 2 Aksay's models of a sessile drop⁽²⁾. a) When the initial solid is not saturated with some or all of the components of liquid. b) When the initial liquid is not saturated with some or all of the components of solid.

Three phases are evident in the wetting curves when plotted on the logarithmic scale. The first phase represents the period of wetting and the second phase is a period for quasi-equilibrium for Cu/Hg. The third phase corresponds to the period of the chemical reaction between Cu and Hg at 355 K or the dissolution of Cu into Hg at 381 K. The reaction products were confirmed with X-ray diffraction patterns and were found to be CuHg and $\text{Cu}_{15}\text{Hg}_{11}$. The shift from the second phase to the third phase depends on the nucleation and growth of the compound or the dissolution of Cu at the interface.

Now, it is necessary to consider how to quantitatively describe the wetting speed in the first phase from a wetting curve. Suppose that the solid is dipped completely into the liquid to a fixed depth and is not wet at $t=0$. This means that the contact angle θ is equal to 180° and $\gamma_{lv} \cos \theta = -\gamma_{lv}$ at $t=0$. The value of $\gamma_{lv} \cos \theta = -\gamma_{lv}$, 456 mN/m⁽¹⁷⁾, in this case, was used for the calculation of the wetting speed. In addition, suppose that wetting starts at $t=0$, $\gamma_{lv} \cos \theta$ changes exponentially with time from the initial wetting phase to the equilibrium of the wetting

Fig. 3 Variation in dynamic interfacial tension with time during a chemical reaction between two phases shown by Aksay⁽²⁾. The initial pure dynamic interfacial tension is indicated by $\gamma_{\alpha\beta}^0$. The degree of minimization of the interfacial tension at t_m is proportional to $\Delta g^{\alpha\beta}$.

Fig. 4 Wetting curves of Cu by Hg. a) Normal (linear) time scale. b) Logarithmic time scale.

phase, and equilibrates at $t = \infty$. Thus $\gamma_{lv} \cos \theta$ is described as follows:

$$\gamma_{lv} \cos \theta = K \exp(kt) + C \quad (4)$$

Fig. 5 Calculation of original wetting speed based on a wetting curve.

where K is $-(\gamma_{lv} + C)$; C is the equilibrium adhesion tension, $\gamma_{lv} \cos \theta_{eq}$; k is a constant for wetting speed, s^{-1} ; and t is the time after dipping, s .

The constant k can be obtained by substituting the mean values of $(t, \gamma_{lv} \cos \theta)$ into the equation. An example of the calculation by regression analysis is shown in Fig. 5. As a result, it is revealed that the error between the measured value and the calculated value in the period of $t \geq 5$ s falls within 1 mN/m. Therefore, we can call the constant k the original wetting speed. The original wetting speed is the most important value for soldering, joining, casting, plating, fabricating of MMC, etc. because the initial several seconds are the most important period for these operations.

V. Wetting of Graphite (Abbreviated as Gr) by Al and Al-Si⁽¹⁰⁾

These experiments were carried out with the Meniscograph apparatus⁽⁷⁾ previously described. The experimental conditions were as follows: atmosphere, purified He + 3 volume% H₂ (1.05 atm); depth of immersion, 10 mm and speed of immersion, 30 mm/s. The experiments were conducted using 99.99 mass% Al, 99.999 mass% Si and Gr ≥ 99.7 mass% C.

Figure 6 shows the wetting curves of Gr by 99.99 mass% Al on a normal time scale and a logarithmic time scale. As can be seen from Fig. 6-b), the result clearly indicates that there are three phases identical to those in Fig. 4-b), namely the wetting phase, the quasi-equilibrium phase and the interfacial reaction phase. The reaction product was analyzed with EPMA and microdiffractometry and the formation of Al₄C₃ was confirmed. In this figure, the value of $\gamma_{lv} \cos \theta$ during the first ten seconds is nearly equal to γ_{lv} of the liquid Al, which is indicating that $\theta \approx 180^\circ$.

The result of the same experiment carried out with the sessile drop method⁽⁸⁾⁽⁹⁾ is shown in Fig. 7. This figure indicates clearly that there are also three phases of wetting but that the initial phase can not be clearly distinguished. From high speed 8 mm film recordings, it was established that the liquid metal drop vibrates for several seconds

Fig. 6 Wetting curves of graphite by Al (1273 K). a) Linear time scale. b) Logarithmic time scale.

Fig. 7 Contact angle curve of Al on graphite measured with the improved sessile drop method (1273 K).

after contact with the substrate⁽⁸⁾. These vibrations gradually diminished and the contact angle became constant by the time 5 s had elapsed.

A smooth mirrored aluminum liquid surface can be maintained during most of the measurements by removing the oxide film with a surface skimmer of pure Al_2O_3 before the measurement. In every measurement, powdered Al which had evaporated from the liquid, adhered to the inner surface of the chamber. Nevertheless, occasionally there were numerous small scattered oxide islands on the melt. It was suggested that these

Fig. 8 Effect of a oxide film on the wetting curves in graphite/Al system.

Fig. 9 Wetting curves of graphite by Al and Al-Si alloys (1273 K).

islands must be trapped on a thin oxide film. If the surface was covered with a thin oxide film, the beginning of interfacial reaction at the interface was delayed, as can be seen in Fig. 8. Since it appeared that the existence of the oxide film at the interface is a factor impeding the onset of the interfacial reaction, any dip cycle in which the surface was covered with a thin oxide film, was disregarded.

The Si contents of aluminum alloys were varied in the experiments (Fig. 9). Figure 9 revealed that the speed of wetting in the interfacial reaction phase (interfacial reaction wetting speed) is influenced with the Si content, and that a critical content must exist between 10 and 20 mass%.

The reaction products were mainly Al_4C_3 which was confirmed with EPMA and X-ray diffraction, and SiC was observed only in case of 20 mass% Si. These phenomena must be dependent on the activity of Si in the liquid aluminum. The stability of the two reaction products is considered to be represented by the following:

It was confirmed by the thermochemical calculation⁽¹⁰⁾ that SiC will be stable in aluminum alloys containing more than 13 mass% of Si at 1273 K. These results show that the speed of wetting within the third phase depends on the nature of the chemical reactions.

VI. Wetting of MgO by Al⁽⁸⁾⁽⁹⁾ and AlN by Al⁽¹¹⁾ (Influence of Impurities and Grain-Boundaries)

Experiments were carried out using the sessile drop method with 99.99 mass% Al pellets, two types of sintered MgO plates (A and B) and single crystal MgO plates (type C) (Table 1) and two AlN samples which differed in chemical composition (Table 2). In the case of the MgO single crystal the (100) cleavage surface was used in the investigation. An atmosphere identical to that used with the Meniscograph⁽¹⁰⁾ was employed in these experiments.

Figure 10 shows contact angle curves for MgO-A at three different experimental temperatures as plotted on a normal and a logarithmic time scale. The contact angle curves plotted on a linear time scale suggest that it seems reasonable that the value of the contact angle when it is apparently steady should be adopted to evaluate the wetting. However, the contact angle curves plotted on a logarithmic time scale clearly indicate that there are three phases, the same as already mentioned.

Judging from Fig. 10-b), it becomes apparent that in order not to overestimate wettability for the original system (original wettability), the contact angle obtained during the second phase should be adopted. For example, at 1333 K the apparently steady contact angle is about 90° as shown in Fig. 10-a), whereas the contact angle of the second phase is about 110° as shown in Fig. 10-b).

Figure 11 shows a secondary electron image of a polished cross section of a 1333 K drop cycle MgO-A sample. The shape is identical to that in one of the Aksay's models in Fig. 2-a). The reaction zone is produced only in the MgO sample and extends beyond the interface to form a ring enclosing the aluminum drop, and the spinel (MgO·Al₂O₃) was confirmed as has been reported by Mcevoy *et al.*⁽¹⁸⁾. By EPMA analysis of the reaction zone/MgO region, grain boundary diffusion of Al in the non-reacted MgO was found. At the same time, EPMA analysis of the Al/reaction zone region revealed the presence of Ca in the solidified Al and at the interface. Ca in the solidified Al is particularly important since Ca has a pronounced effect of decreasing the surface tension of liquid Al⁽¹⁹⁾.

Table 1 Chemical composition of MgO (mass%).

Sample	MgO	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃
A	96.85	1.71	0.83	0.05	0.03
B	99.7	0.05	tr.	tr.	0.03
C	99.9	tr.	tr.	tr.	tr.

Table 2 Yttrium and oxygen contents in each AlN (mass%).

Sample	Y	O
AlN-A	0.11	0.30
AlN-B	4.1	2.0

Fig. 10 Contact angle curves of Al on 96.85 mass% MgO (A).
a) Linear time scale. b) Logarithmic time scale.

Fig. 11 Appearance of a polished cross section of a 1333 K drop cycle MgO-A sample (10.8 ks).

It appeared that there was no interfacial reaction wetting phase in the case of the wetting curve at 1173 K in Fig. 10. However, an analysis of its cross section indicates the existence of the reaction zone⁽⁸⁾. This result suggests that the beginning of the chemical reaction at the interface can not be certified from the wetting curve alone.

Figure 12 plots the changes of the interfacial area (as indicated by the diameter $2x$) and the changes in the contact angle on a logarithmic time scale for each of the three temperatures. As can be seen from this figure at 1333 K, there are two distinct stages in the third phase by

Fig. 12 Relationship between interfacial diameter and contact angle.

the volume change of the droplet with interfacial reaction and evaporation, viz:

- ① contact angle decrease with increase in interfacial area: advancing contact angle,
- ② contact angle decrease without increase in interfacial area: receding contact angle.

In any system it is therefore essential to take into account changes in both contact angle and interfacial diameter. In order for wetting to be evaluated as increasing, the following two conditions must be satisfied:

$$d\theta/dt < 0 \quad \text{and} \quad d(2x)/dt > 0 \quad (6)$$

where $d\theta/dt$ = rate of change of contact angle and $d(2x)/dt$ = rate of change of diameter.

The influence of impurity and grain boundaries on the wetting of MgO by Al is shown in Figs. 13 and 14. At a constant temperature the polycrystalline samples produced similar contact angles in the second phase, while the single crystal sample showed a slightly higher contact angle. In the third phase, however, contact angles become significantly different. These results mean that the original contact angle of the MgO/Al system⁽⁹⁾ (original wettability) is shown in the second phase, as used in Cassie's equation⁽²⁰⁾ for a composite substrate. The transition from the second phase to the third phase corresponds to the development of interfacial reactions. As the temperature increases, the duration of the second phase becomes short. The faster the interfacial reaction for three types of MgO, the shorter the duration of the second phase.

Figure 15 illustrates the reaction zones of the three types of MgO after holding at 1373 K for 10.8 ks⁽⁹⁾. The presence of Ca in the metal and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ at the interface in the MgO-A/Al system must originate from the impurities in the ceramic sample. However $\alpha\text{-Al}_2\text{O}_3$ is confirmed at the interface in the MgO-C/Al system instead of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ as in the MgO-B/Al system. The activity

Fig. 13 Contact angle curves for 96.85 mass% MgO (A) and 99.7 mass% MgO (B).

Fig. 14 Contact angle curves for single crystal (100) MgO (C) and 99.7 mass% sintered MgO (B).

Fig. 15 Schematic representation of interfacial structures in three kinds of MgO developed during phase III.

of Mg in Al may account for these chemical reactions. The volume of the reaction zone, V_{MgO} , should be directly related to the activity of Mg in Al. However, it is clear that $V_{\text{MgO-B}}$ is much larger than $V_{\text{MgO-C}}$. Thus, the stability of those two is considered to be as follows:

Figure 16 shows wetting curves for two kinds of AlN and a 99.9% Al_2O_3 by Al on a logarithmic time scale. The wetting curves are clearly changed with the Y_2O_3 con-

Fig. 16 Contact angle curves for two kinds of AlN and 99.9 mass% Al_2O_3 at 1373 K.

tent of the substrate: purified AlN (AlN-A) does not vary its contact angle whereas the ordinary one does. By analysis of the reaction zone, the formation of Al_2O_3 at the interface was confirmed in both cases. In case of the high Y_2O_3 content sample, most of the interfacial area was converted to Al_2O_3 and shows the identical contact angle as bulk Al_2O_3 . This situation must represent the chemical equilibrium state (the fourth phase) for the system.

VII. Summary

In all the experimental results, similar wetting curves with time are obtained. Analysis of the overall results indicates the following:

(1) There are four phases in a wetting system accompanied by interfacial reactions at the interface. These are as follows (Tables 3 and 4).

(2) Wetting speed in phase I is the most important value for soldering, joining, casting, plating, fabricating

Table 3 Four wetting phases.

Phase	Wetting situation	Adopted Characteristic value
I	Dynamic non-equilibrium	Wetting speed of S_0/L_0^* (original wetting speed)
II	Quasi-equilibrium	Contact angle of S_0/L_0 (original wettability)
III	Chemical non-equilibrium	Wetting speed accompanied by reaction (interfacial reaction wetting speed)
IV	Equilibrium	Contact angle of S_e/L_e^{**} (equilibrium wettability)

* S_0/L_0 interface of the initial condition (S_0 : solid, L_0 : liquid).

** S_e/L_e interface of the equilibrium condition (S_e : solid, L_e : liquid).

Table 4 Wetting phases and observed contact angles.

Phase	Dynamic state	Chemical state	Time, s	θ observed*
I	non-eq.	—	—5	θ_a
II	eq.	quasi-eq.	5–50	θ_a
III	eq.	non-eq.	50–	θ_a or θ_r
IV	eq.	eq.	$-\infty$	θ_a or θ_r

* θ_a : advancing contact angle. θ_r : receding contact angle only observed with sessile drop method.

of MMC, etc.

(3) The contact angle in phase II should be adopted as a measure of wettability of the original system, S_0/L_0 .

(4) Wetting speed in phase III and the contact angle in phase IV depend on interfacial reaction.

(5) In order to produce an increased degree of wetting the following two conditions must be satisfied:

$$d\theta/dt < 0 \quad \text{and} \quad d(2x)/dt > 0.$$

(6) The transient minimum contact angle shown by Aksay *et al.* was not observed within these experiments.

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