Reactive wetting of molten Al on different oriented $\alpha$-Al$_2$O$_3$ single crystals at high temperatures

Ping Shen *, Hidetoshi Fujii, Taihei Matsumoto, Kiyoshi Nogi

Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Received 7 February 2003; received in revised form 28 May 2003; accepted 5 June 2003

Abstract

The reactive wetting of molten Al on three different oriented $\alpha$-Al$_2$O$_3$ single crystals, $R(01\overline{1}2)$, $A(11\overline{2}0)$ and $C(0001)$, was investigated by an improved sessile drop method at temperatures between 1350 and 1500 °C in a reduced Ar–3%H$_2$ atmosphere. The wettability is in the order of $R > A > C$. The spreading is reaction-limited and the rate is dominated by the change in the solid–liquid interfacial free energy per unit time.

© 2003 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Wetting; Al; Kinetics; Substrate orientation

1. Introduction

The wetting/spreading of a metal droplet on a smooth solid surface is important for many diverse technologies such as brazing, lubrication and composite infiltration [1]. A fundamental understanding of the wetting/spreading kinetics is essential for process control in related industrial applications. In non-reactive systems, the wetting is controlled by the viscous flow and the equilibrium can be rapidly achieved in times on the order of $10^{-4}$–$10^{-1}$ s. In reactive systems, however, the wetting is interactively coupled with the reaction and the time needed to reach a steady contact angle is usually in the range of $10^{-1}$–$10^{-4}$ s [2,3].

Two limiting cases in reactive wetting, depending on the rate of the chemical reaction at the triple line compared to the rate of the reactive solute diffusion from the drop bulk to the triple line, have been identified by Eustathopoulos, Mortensen and their co-workers [2–10]. For systems exhibiting relatively sluggish reaction kinetics, the diffusion of the solute to the triple line is comparatively rapid (or non-existent when the droplet is made of a pure reactive metal). In this case, if the reaction does not significantly change the droplet composition and if a steady configuration is established at the triple junction, the spreading is reaction-limited and the triple line velocity is constant with time [2,4],

$$R_t - R_0 = Kt$$

(1)

where $R_t$ and $R_0$ are the droplet base radii at times $t$ and 0, respectively, and $K$ is a system constant, independent of the droplet volume $V_d$. For systems exhibiting a rapid reaction rate, the solute diffusion is rate-limiting as the contact angle continuously decreases, leading to a reduction in the
diffusion field. As a result, the spreading is diffusion-limited and can be characterized by [2,8]

\[ R_4^t - R_0^t = K^t V dt \]  

(2)

Among the metal–ceramic systems, Al/Al₂O₃ is an intriguing system and the wettability of α-Al₂O₃ by molten Al has been extensively studied [11–19]. However, few specific investigations exist about the wetting/spreading kinetics even though a continuous decrease in the contact angle with time has been observed [14–19]. On the other hand, little information is provided on the effect of substrate anisotropy. In this context, this article represents just such a study.

2. Experimental procedure

Wetting experiments were performed using an improved sessile drop method described in more detail in Ref. [20]. The substrates were high-purity (99.99%) α-Al₂O₃ single crystals, R(0112), A(1120) and C(0001) (hereafter designated only by the letters R, A and C, respectively) with a surface roughness of less than 1 Å and a crystallographic orientation error of ±0.3°. The Al specimens were in the form of a wire segment with a purity of 99.99%.

Before the experiments, the samples were ultrasonically cleaned in acetone. The α-Al₂O₃ substrates were placed horizontally in the chamber while the Al segments were placed in the dropping device outside the chamber. The chamber was first evacuated to about 5 × 10⁻⁴ Pa at room temperature and then heated to the desired experimental temperature. After the temperature was reached, the chamber was purged with a purified Ar–3%H₂ gas to a pressure of about 0.11 MPa. The Al segment was inserted into the bottom of the alumina tube after the temperature and the atmosphere had stabilized. Molten Al was then forced from a small hole at the bottom of the alumina tube and dropped onto the α-Al₂O₃ substrate by a gradual decrease in the pressure inside the chamber, which creates a small pressure difference between the chamber and the alumina tube. At the same time, the initial surface oxide, if still present, was mechanically removed.

As soon as the molten Al came into contact with the α-Al₂O₃ substrate, a photo was taken and defined as the drop profile at zero time. The captured photographs were analyzed in a computer with automatic image processing programs, in which the contact angle, surface tension and density could be calculated all at once. The drop base diameter/radius, which is a common parameter for the assessment of the movement of the triple line, was directly measured from the drop profiles at a magnification of about 30 times.

3. Results

Fig. 1 shows the variations in contact angle with time for molten Al on the R, A and C α-Al₂O₃ single crystals. The contact angles continuously decreased during the isothermal dwells. The rate of the decrease significantly increases with temperature. However, the angles in the first several tens of seconds, typically no more than 30 s, (see small figures with a logarithmic time scale) do not have a remarkable change with both the temperature and time. On the other hand, they differ rather significantly with the substrate orientation, especially for the C face compared with the R and A faces. Such results are completely different from those reported by Ownby et al. [19], in which the contact angle was concluded to be essentially independent of the crystallographic orientation of the α-Al₂O₃ substrates while the initial angles considerably varied with the temperature. The distinct wettability dependency on the α-Al₂O₃ substrate orientation is possibly related to the different furnace atmosphere, mainly the percent of hydrogen, used in our experiments (Ar–3%H₂) as compared to that in Ownby et al.’s. In the latter, a highly reducing H₂(–He) atmosphere was employed. According to some recently published reports [21–24], H₂ and/or water vapor may change an aluminum-terminated C-face α-Al₂O₃ surface to an oxygen-terminated structure, which can lead to a significant improvement on wettability [25] and hence a finally negligible difference in comparison to that of the R and A faces.

Corresponding to Fig. 1, Fig. 2 shows the variations in the relative base radius, \( R_t/R_0 \) with time \( t \).
The $R_0$ is the drop base radius at 30 s. The results show a well-developed linear relationship between $R_t/R_0$ and $t$ during the isothermal dwells except for the initial short periods for molten Al on all the R, A and C $\alpha$-Al$_2$O$_3$ single crystals at all the experimental temperatures

$$R_t/R_0 = C_1 + k_1 t$$

(3)

The values of the coefficients, $C_1$ and $k_1$, are listed in Table 1. Since the values of $C_1$ are close to 1, it yields an expression similar to Eq. (1), indicating that the spreading in the Al/$\alpha$-Al$_2$O$_3$ system at high temperatures is reaction-limited.

Note that the coefficient $k_1$ in Eq. (3) represents the spreading rate, hence the data in Table 1 show that the spreading rate depends not only on the temperature but also on the substrate orientation. An increase in the temperature of about 150 °C will lead to an increase in the spreading rate of more than one order. On the other hand, at relatively low temperatures ($T \leq 1400$ °C), the spreading of the molten Al on the C face is the fastest, whereas at high temperatures ($T > 1400$ °C), the

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$C_1$</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$C_1$</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$C_1$</th>
<th>$k_1$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350</td>
<td>1.00</td>
<td>5.47E-6</td>
<td>1.00</td>
<td>6.22E-6</td>
<td>1.02</td>
<td>9.09E-6</td>
</tr>
<tr>
<td>1400</td>
<td>1.00</td>
<td>1.55E-5</td>
<td>1.00</td>
<td>1.60E-5</td>
<td>1.00</td>
<td>2.14E-5</td>
</tr>
<tr>
<td>1450</td>
<td>1.01</td>
<td>2.61E-5</td>
<td>1.00</td>
<td>4.17E-5</td>
<td>1.00</td>
<td>3.34E-5</td>
</tr>
<tr>
<td>1500</td>
<td>1.00</td>
<td>8.18E-5</td>
<td>1.00</td>
<td>1.30E-4</td>
<td>1.01</td>
<td>9.84E-5</td>
</tr>
</tbody>
</table>
spreading on the A face tends to be the fastest. The
magnitude of the increase for the A face is much
more significant than that for the R and C faces.
The different spreading rates on the different faces
of the \( \alpha \)-Al\(_2\)O\(_3\) crystals indicate that the substrate
orientation affects not only the wettability but also
the wetting progress.

4. Discussion

As indicated in Fig. 1, the wetting/spreading
process in the Al/\( \alpha \)-Al\(_2\)O\(_3\) system, from a simple
point of view, might be divided into two stages.
The first stage is very short, typically no more than
30 s and can be characterized by the very rapid
wetting (for the R and A faces) or near wetting (for
the C face) under the driving force of balancing the
interfacial tensions. A transient static equilibrium
may exist in this stage since the contact angles
remain almost constant [26]. These angles are also
the true contact angles because the contact surface
is smooth; while after a relatively long dwell time,
the surface, especially at the triple junction, is no
longer smooth due to the \( \alpha \)-Al\(_2\)O\(_3\) dissolution and
reaction with the molten Al, therefore, the angles
measured in the later periods, in a strict sense, are
no longer the true contact angles as described by
Young’s equation but the apparent ones. The
second stage is a long and progressive spreading
stage, mainly characterized by a constant spreading
rate with a continuous decrease in the contact
angle and increase in the drop base diameter/radius
as the \( \alpha \)-Al\(_2\)O\(_3\) substrate progressively reacts
with the molten Al. The linear spreading in the Al/
\( \alpha \)-Al\(_2\)O\(_3\) system seems similar to that in other re-
action-limited systems such as Al/C [4,5], CuSi/SiC
[6] and CuSi/C\(_x\) [7]. However, a major difference is
that the reaction product at the Al/\( \alpha \)-Al\(_2\)O\(_3\) inter-
facing is a gas phase (Al\(_2\)O) which can easily run
away either directly from the triple line or through
the liquid bulk. As a consequence, the contact
phases at the liquid–solid interface are perma-
nently the molten Al and solid \( \alpha \)-Al\(_2\)O\(_3\) and the
reaction between them will never end as long as the
partial pressure of the Al\(_2\)O gas in the atmosphere
does not reach its equilibrium value, leading to an
inaccessible steady equilibrium angle even after
isothermal dwells for 8 h as demonstrated in
Ownby et al.’s experiments [19]. Whereas, in most
reactive wetting systems, the substrate dissolves in
the liquid and usually forms novel compounds
different from the substrate phase), initially as
discrete crystals nucleating on the preferred sites at
the solid–liquid interface and later growing into a
continuous layer of the reaction product(s). Such
reactions yield one or more interfaces rather than a
single one as in the Al/\( \alpha \)-Al\(_2\)O\(_3\) system, and the
final static wetting equilibrium is established at the
newly formed liquid–solid interface after either a
short or long wetting period. As a result, the
equilibrium contact angles in these systems are
usually represented by the final static wetting an-
gles.

Here, we assume the first stage in the Al/\( \alpha \)-Al\(_2\)O\(_3\) system as a transient static equilibrium stage and
the contact angles in this stage, or more definitely,
at the time of about 30 s as the equilibrium angles
(\( \theta_0 \)). Table 2 gives their values (they may have
some errors in comparison to the true equilibrium
contact angles). Note that they vary only slightly
with the temperature but relatively significantly
with the substrate orientation. The reasons for the
dependence of the wettability on the substrate
orientation have been presented elsewhere [27].

The static equilibrium is broken and the triple
line starts to move when the chemical reaction
between the molten Al and \( \alpha \)-Al\(_2\)O\(_3\) substrate oc-
curs and causes a reduction in the solid–liquid
interfacial free energy, \( \sigma_{sl} \),

\[
\sigma_{sl} = \sigma_{sl}^0 + \Delta \sigma(t)
\]

where \( \sigma_{sl}^0 \) is the initial equilibrium solid–liquid inter-
facial free energy and \( \Delta \sigma(t) \) is the change in the solid–liquid interfacial free energy. At this time, a

Table 2
Assumed equilibrium contact angles for the molten Al on the R, A and C \( \alpha \)-Al\(_2\)O\(_3\) crystals at temperatures ranging from 1350 to
1500 °C

| \( \alpha \)-Al\(_2\)O\(_3\) face | Equilibrium contact angles, \( \theta_0 (\degree) \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | 1350 °C | 1400 °C | 1450 °C | 1500 °C |
| R               | 77      | 77      | 77      | 77      |
| A               | 79      | 80      | 80      | 81      |
| C               | 89      | 90      | 90      | 89      |
driving force for the initiation of the spreading is produced. Assuming that the solid–vapor and liquid–vapor interfacial free energies, $\sigma_{sv}$ and $\sigma_{lv}$, do not change with time, the substrate surface is flat and the viscous resistance can be neglected, the driving force can be expressed by

$$F(t) = \sigma_{sv} - (\sigma_{sa}^0 + \Delta \sigma(t)) - \sigma_{lv} \cos \theta_i$$  \hspace{1cm} (5a)$$

or

$$F(t) = -\Delta \sigma(t) + \sigma_{lv}(\cos \theta_0 - \cos \theta_i)$$  \hspace{1cm} (5b)$$

As the reaction progresses, the spreading goes into a dynamic equilibrium stage \cite{26,28} since the spreading rate is constant as reflected in Fig. 2, which also means that the driving force decreases again to zero, otherwise, the spreading rate will not be constant but further increase. It is conceivable that from the static equilibrium stage to the dynamic equilibrium stage, a non-equilibrium transition stage must be experienced, in which the spreading rate is accelerated to the constant value under the action of the driving force. In this sense, the entire wetting/spreading process may consist of three stages rather than two, i.e., (i) a transient static equilibrium stage, (ii) a non-equilibrium transition stage, and (iii) a dynamic equilibrium spreading stage. However, a detailed analysis on the non-equilibrium transition stage is not presented in this article.

As the dynamic equilibrium is reached, the driving force, $F = 0$. Therefore, from Eq. (5b), we obtain

$$\Delta \sigma(t) = \sigma_{lv}(\cos \theta_0 - \cos \theta_i)$$  \hspace{1cm} (6)$$

Considering that the spreading kinetics can also be reflected from the variations in the contact angle ($\theta$) with time ($t$), Fig. 3 shows the plots of $\ln(\theta_t/\theta_0)$ vs. time ($t$) at various temperatures. It seems that the time-dependent contact angles fit well with the following linear equation

$$\ln(\theta_t/\theta_0) = k_2 t + C_2$$  \hspace{1cm} (7)$$

where $k_2$ and $C_2$ are coefficients and their values are listed in Table 3. Note that the values of $C_2$ are close to zero, thus Eq. (7) can be simplified as

$$\ln(\theta_t/\theta_0) = k_2 t$$  \hspace{1cm} (8)$$

or written as

$$\theta_t = \theta_0 e^{k_2 t}$$  \hspace{1cm} (9)$$

Table 3

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R$</th>
<th>$A$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_2$</td>
<td>$k_2$ (s$^{-1}$)</td>
<td>$C_2$</td>
</tr>
<tr>
<td>1350</td>
<td>-0.03</td>
<td>-1.15E-5</td>
<td>0</td>
</tr>
<tr>
<td>1400</td>
<td>-0.01</td>
<td>-3.02E-5</td>
<td>0</td>
</tr>
<tr>
<td>1450</td>
<td>-0.01</td>
<td>-4.96E-5</td>
<td>-0.01</td>
</tr>
<tr>
<td>1500</td>
<td>0.01</td>
<td>-1.71E-4</td>
<td>0.01</td>
</tr>
</tbody>
</table>

---

Fig. 3. Plots of $\ln(\theta_t/\theta_0)$ vs. $t$ for the molten Al on the $R$ (a), $A$ (b) and $C$ (c) $\alpha$-Al$_2$O$_3$ substrates at various temperatures.
i.e., the time-dependent contact angle exhibits an exponential decay law for the molten Al on all the \( \alpha \)-Al\(_2\)O\(_3\) substrates.

Furthermore, if we only consider a relatively short spreading period, Eq. (9) is approximated to
\[
\theta_t \approx \theta_0 + kt \quad (k = k_2\theta_0)
\]
which shows a linear relationship between the dynamic angle and time.

Since \( \cos \theta_0 - \cos \theta_t \approx -(\theta_0 - \theta_t)/(\text{rad}) \), (as an illustration, Fig. 4 shows the plot of \( \cos \theta_0 - \cos \theta_t \) vs. \( (\theta_0 - \theta_t)/(\text{rad}) \) and the linear fit results), we can further derive from Eq. (6)
\[
\Delta \sigma(t) \approx -\sigma_n(\theta_0 - \theta_t)/(\text{rad}) \approx \sigma_n(k/\text{rad})t
\]
or
\[
\Delta \sigma_t = \Delta \sigma(t)/t \approx k'\sigma_n \quad (k' = k/\text{rad})
\]
i.e., when a dynamic equilibrium of spreading is established, the change in the solid–liquid interfacial free energy per unit time \( (\Delta \sigma_t, \text{N m}^{-1} \text{s}^{-1}) \) is approximately equal to the product of the spreading rate \( (k', \text{ s}^{-1}) \) and the liquid–vapor interfacial free energy \( (\sigma_n, \text{N m}^{-1}) \).

5. Conclusions

The initial equilibrium contact angles of the molten Al on the \( \alpha \)-Al\(_2\)O\(_3\) single crystals do not significantly change with the temperature but vary relatively significantly with the substrate orienta-

Fig. 4. Plot of \( (\cos \theta_0 - \cos \theta_t)/(\text{rad}) \) vs. \( (\theta_0 - \theta_t)/(\text{rad}) \)
\( \theta_t \approx \theta_0 + kt \quad (k = k_2\theta_0) \)
\( \Delta \sigma(t) \approx -\sigma_n(\theta_0 - \theta_t)/(\text{rad}) \approx \sigma_n(k/\text{rad})t \)
\( \Delta \sigma_t = \Delta \sigma(t)/t \approx k'\sigma_n \quad (k' = k/\text{rad}) \)

\[\text{References}\]