



PERGAMON

Scripta Materialia 48 (2003) 779–784



www.actamat-journals.com

Wetting of (0001) α -Al₂O₃ single crystals by molten Al

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

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

Received 29 August 2002; received in revised form 17 October 2002; accepted 22 October 2002

Abstract

The wetting behavior of (0001) α -Al₂O₃ by molten Al was studied over a wide temperature range between 700 and 1500 °C. The increase in the contact angle with time at temperatures lower than 1200 °C is attributed to the surface structural reconstruction of the (0001) α -Al₂O₃. High-temperature annealing of the substrate does not have a significant influence on the wettability.

© 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Wetting; Al; Surface structural reconstruction; Interface

1. Introduction

Alumina is one of the most thoroughly studied oxide ceramics with a wide range of applications, and wetting of alumina by molten Al has been investigated by many researchers [1–10]. The system seems to be a very simple if not trivial binary Al–O system, however, it turns out that the wetting is a non-equilibrium phenomenon [10] characterized by the continuous oxidation of Al at relatively low temperatures [5–9] and the reaction between Al and Al₂O₃ to form a gas phase (Al₂O) and reaction rings at the triple junction line at relatively high temperatures [1–5], which lead to a large scatter in the reported contact angles.

Despite extensive research on this material, the effect of anisotropy of the alumina single crystal as well as its surface structural change on the wetting

behavior has never been systematically studied. Brennan and Pask [2], and Ownby et al. [4] reported the effect of the alumina crystallographic orientation and concluded that the contact angle is essentially independent of this parameter. Vikner [11] also studied the Cu–Al₂O₃ system with a random, *C*(0001) and *R*(1 $\bar{1}$ 02) α -Al₂O₃ and found that the contact angle difference between the different orientated surfaces was less than 10°. In an earlier paper on the wettability of MgO single crystals by liquid Pb, Sn and Bi, Nogi et al. [12] showed that the wettability was apparently dependent on the crystallographic orientation and heat treatment of the MgO substrate. Furthermore, they also observed the surface arrangement of MgO using atomic force microscopy and suggested that the wettability could be affected by the surface arrangement. Except for these facts, few other experimental studies have been carried out on the relationship between wettability and surface structure or crystallographic orientation, even though this is an important question, especially in

* Corresponding author. Tel./fax: +81-6-6879-8663.

E-mail address: shenping@jwri.osaka-u.ac.jp (P. Shen).

crystal/film epitaxial growth and adhesion. Thus, in our recent studies, the wettability of different oriented α -Al₂O₃ single crystals by molten Al has been thoroughly investigated. In this paper, the results for the (0001) α -Al₂O₃ face are presented.

2. Experimental procedure

The high-purity (99.99%) α -Al₂O₃ single crystals used in this study were from Kyocera Co. Ltd., Japan, with a 20 mm diameter size and 1 mm thickness. The (0001) face, designated by the letter C, is the basal plane, cut at a 90° (with an error of $\pm 0.3^\circ$) orientation from the *c* axis. The surface was polished to an average roughness (Ra) of less than 1 Å. The Al samples were in the form of a wire segment with a diameter of 3 mm and a purity of 99.99%. To avoid drop distortion, the weight of the Al segment in every experiment was controlled to be about 0.2 g.

An improved sessile drop method [13,14] was adopted for this experiment. Fig. 1 shows a schematic of the experimental apparatus. It consists of a vacuum chamber with a tantalum cylindrical heater and a Mo reflector, an evacuating system with a rotary pump and a turbo molecular pump, a dropping device, a temperature program controller with a W–5%Ra/W–26%Rh thermocouple, a 10 mW He–Ne laser, a band-pass filter and a high-resolution digital camera with 2000 × 1312 pixels. The band-pass filter can cut all other wavelengths except the laser beam (632 nm); therefore, a high definition drop profile can be obtained in our experiments.

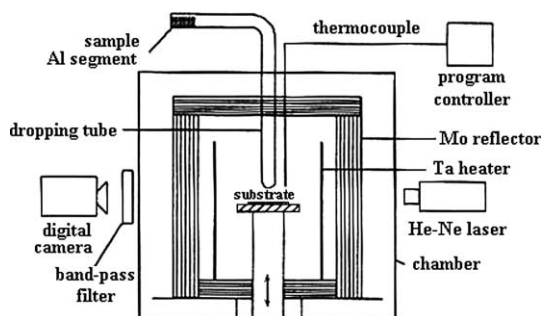


Fig. 1. Schematic of experimental apparatus.

Before the experiment, both the Al₂O₃ substrate and the Al wire segment were immersed in acetone and ultrasonically cleaned for 3 min three times, then the Al₂O₃ substrate was placed horizontally in the chamber while the Al specimen was placed in a glass tube with a spring connector on the top of the dropping device outside the chamber. The chamber was first evacuated to a vacuum of about 5×10^{-4} Pa and then heated to the desired temperature at the heating rate of 20 °C/min. After the experimental temperature was reached, the chamber was purged with a premixed high-purity Ar + 3% H₂ gas purified using platinum asbestos and magnesium perchlorate. The Al segment was inserted into the bottom of the alumina tube after the temperature and atmosphere were 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 small pressure difference between the chamber and the alumina tube. At the same time, the initial surface oxide 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. Subsequent photos were taken at time intervals of 10 s, 30 s, 1 min and 3 min. 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 which removed the operator's subjectivity.

3. Results and discussion

Fig. 2 shows the variation in contact angle with time for a series of temperatures. It is interesting to note that at temperatures lower than 1200 °C, the contact angle increases with time to different extents, while at temperatures higher than 1200 °C, the contact angle decreases with time. At 1200 °C, it remains nearly constant. Such a result has never been reported by other researchers. Levi et al. [10] and Wu et al. [8,9] also measured the contact angle of Al on (0001) α -Al₂O₃ single crystals at low temperatures, but their results indicate that the contact angle does not show any increase with time. Others either only gave the relationship of

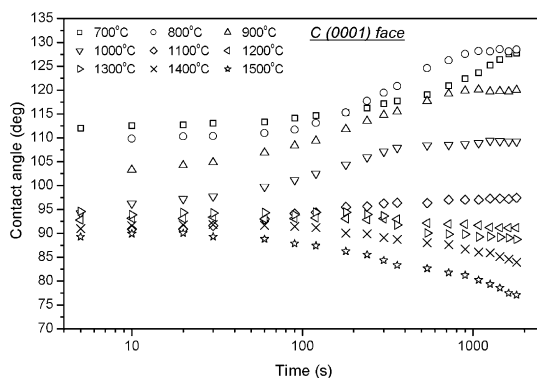


Fig. 2. Variation in contact angle with time.

the contact angle with time at high-temperatures [1,3,4] or did not indicate the crystallographic plane of the single crystals they used [6].

It should be pointed out that our results at low temperatures ($800\text{ }^{\circ}\text{C} \leq T \leq 1100\text{ }^{\circ}\text{C}$) are obviously not due to the oxidation of the molten Al drop because the increasing phenomenon was reproduced in all the low-temperature experiments, while the alternate experiments performed on the $R(01\bar{1}2)$ and $A(11\bar{2}0)$ planes show contact angles not increasing with time but remaining constant. Moreover, the contact angle values on these faces are much lower than those of the C face, which demonstrates that the wettability of $\alpha\text{-Al}_2\text{O}_3$ by molten Al is sensitive to the crystallographic orientation of the $\alpha\text{-Al}_2\text{O}_3$ substrate, as will be presented in another paper.

The complex wetting behavior of $C(0001)$ $\alpha\text{-Al}_2\text{O}_3$ over a wide temperature range is summarized in Fig. 3. From Fig. 2, it is clear that the contact angle changes with time except at the temperature of $1200\text{ }^{\circ}\text{C}$, thus, it may be difficult to ascertain the true contact angle. Here, we assume that when the temperature is in the range of $700\text{--}1100\text{ }^{\circ}\text{C}$, the final values at 30 min are the true contact angles, whereas in the range of $1200\text{--}1500\text{ }^{\circ}\text{C}$, the values at 30 s are adopted. This is reasonable because in the former, the contact angles at 30 min change very slightly with time; while in the latter, the contact angles progressively decrease resulting from an interfacial reaction between Al and Al_2O_3 , and they may never reach a truly constant value as observed from the experiment at

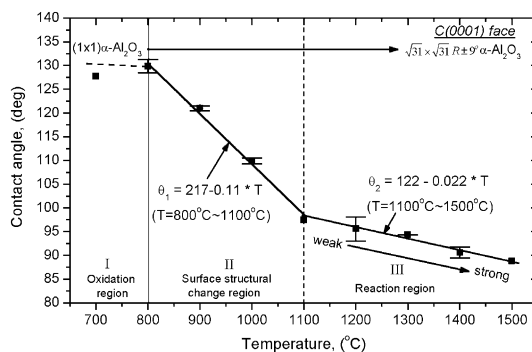
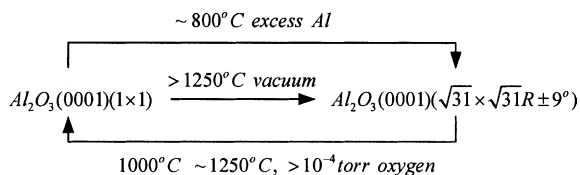


Fig. 3. Variation in contact angle with temperature.

$1500\text{ }^{\circ}\text{C}$ with a long time of 160 min. On the other hand, the initial values before 30 s may not be very accurate due to drop vibration after its breakaway from the alumina tube. Furthermore, it should be noted that the scatter in the values taken from 2–3 runs of the experiments is also shown in Fig. 3 and the maximum is no more than $\pm 3^{\circ}$. However, at a temperature of $700\text{ }^{\circ}\text{C}$, the value determined at 30 min is not very accurate due to oxidation; therefore, a dashed line was adopted to roughly show its tendency. Under our experimental conditions, the oxidation of the Al drop is not very serious at temperatures higher than $800\text{ }^{\circ}\text{C}$ as confirmed from the wetting behavior of all the $C(0001)$, $R(01\bar{1}2)$, and $A(11\bar{2}0)$ $\alpha\text{-Al}_2\text{O}_3$ single crystals as well as the sample appearance after the experiments.

As shown in Fig. 3, the wetting of Al on $C(0001)$ $\alpha\text{-Al}_2\text{O}_3$ can be roughly divided into three regions: (I) *oxidation region* (when $T < 800\text{ }^{\circ}\text{C}$); (II) *surface structural change region* (when $800\text{ }^{\circ}\text{C} \leq T \leq 1100\text{ }^{\circ}\text{C}$); (III) *reaction region* (when $1100\text{ }^{\circ}\text{C} \leq T \leq 1500\text{ }^{\circ}\text{C}$). The increase in the contact angle with time at $800\text{--}1100\text{ }^{\circ}\text{C}$ can be interpreted by the surface structural change in the $C(0001)$ $\alpha\text{-Al}_2\text{O}_3$ substrate. The surface structural change in $C(0001)$ $\alpha\text{-Al}_2\text{O}_3$, which has been studied and confirmed by many researchers [15–21], can be simply summarized as follows [17]:



The temperatures shown in the above scheme may have an error of less than ± 100 °C, as pointed out by French and Somorjai [17]. Importantly, the surface of (0001) α -Al₂O₃ is generally regarded to be an aluminum-terminated structure [17–25], although different opinions of a single oxygen-layer termination [26] or aluminum–oxygen combined termination [27] also exist. For the reconstructed ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) α -Al₂O₃, both experiments and theoretical calculations demonstrate that in a vacuum it is a surface oxygen-deficient structure [17,18,22,24], which is extremely stable at high temperatures, while the presence of excess Al or Si can shift the transformation temperature towards lower temperatures. Furthermore, such a structural transformation can also be made reversible by changing the various experimental conditions or the surface chemical composition using oxygen or aluminum [17].

According to the above illustration and in association with our experimental results, it is clear that in the presence of Al, when the temperature is lower than about 1100 °C, the (1 × 1) surface structure will transform to the ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) reconstructed structure; the higher the temperature, the faster the transformation rate. Because from the viewpoint of thermodynamics, any change in surface structure leads to minimization of surface/interface free energy, the solid–gas interface free energy, σ_{sg} , will decrease after surface structural reconstruction. On the other hand, if the solid–liquid free interface energy, σ_{sl} , also decreases, its extent is sure to be weaker than that of the σ_{sg} because the reconstructed ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) surface is an oxygen-deficient structure and the σ_{sl} is mainly related to the interaction of molten aluminum atoms with oxygen atoms in the α -Al₂O₃ substrate. Therefore, according to Young's equation, $\sigma_{sg} = \sigma_{sl} + \sigma_{lg} \cos \theta$, the decrease in $\sigma_{sg} - \sigma_{sl}$ will lead to an increase in the contact angle. Also, it is easy to understand that the time needed to reach a constant contact angle decreases with temperature, as shown in Fig. 2, if the structural reconstruction kinetics is taken into account.

When the temperature is higher than 1100 °C, the ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) structure would be stable even in the absence of Al, thus the contact angle

does not further increase. On the contrary, an interfacial reaction between Al and Al₂O₃ occurs and becomes more and more pronounced as the temperature increases. Actually, from surface profile measurements and microstructural observations of the α -Al₂O₃ substrates after the Al drop was etched away in a 10 wt.% NaOH solution, no reaction rings could be detected outside or beneath the Al drop when the temperature is lower than 1100 °C. In contrast, when the temperature is higher than 1100 °C, reaction rings, whose depths from less than 1 μm for samples at 1100 °C for 30 min to about 6 μm at 1400 °C for 30 min and further to more than 50 μm at 1500 °C for 160 min, were found beneath or outside the Al drop. As has been pointed out, the decrease in contact angle may not end with a constant value, and the observed continuously changing angles are not the true contact angles because the interface close to the triple junction line is no longer straight and smooth due to the Al attack and reaction with the substrate. Thus, the values at 30 s were used as the true contact angles.

In the latter two regions, a linear relationship between the determined true contact angle and temperature was also indicated in Fig. 3. When $800 \text{ }^\circ\text{C} \leq T \leq 1100 \text{ }^\circ\text{C}$, $\theta_1 = 217 - 0.11T$; and when $1100 \text{ }^\circ\text{C} \leq T \leq 1500 \text{ }^\circ\text{C}$, $\theta_2 = 122 - 0.022T$. Obviously, the decrease in the true contact angle with temperature is much more significant in the low-temperature region than that in the high-temperature region. However, at a temperature lower than 800 °C, the true contact angle is difficult to estimate due to the presence of oxidation.

In addition, the effect of high-temperature annealing on the wettability of the Al/(0001) α -Al₂O₃ system was also investigated and the results are shown in Fig. 4. It seems that annealing of the (0001) α -Al₂O₃ substrate does not have a significant effect on the true contact angle measured once the surface structure becomes stable. This result implies that the reconstructed ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) structure at 1400 °C can be quickly reversed to the (1 × 1) structure during cooling to 900 °C in a relatively short time. After that, the (1 × 1) structure transformed again to the ($\sqrt{31} \times \sqrt{31}R \pm 9^\circ$) structure in the presence of molten Al. Such a reversible transformation in the (0001) α -Al₂O₃

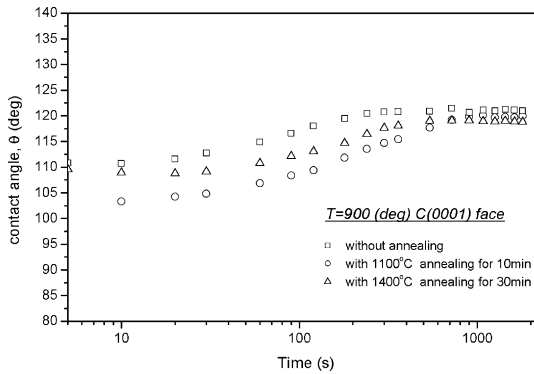


Fig. 4. Effect of annealing on contact angle at 900 °C.

surface was also demonstrated by Charig using low-energy electron diffraction [15].

At the end of this paper, it might be necessary to point out that the H_2 atmosphere may exert an influence on the wettability of molten Al on (0001) α - Al_2O_3 since according to some reports, H_2 can change the aluminum-terminated (0001) α - Al_2O_3 surface to be oxygen-terminated [19,28–30]. If so, the wettability is expected to be improved. This possibility will be examined in our future research.

4. Conclusions

1. The wetting behavior of (0001) α - Al_2O_3 by molten Al over a wide temperature range between 700 and 1500 °C was studied. The wetting can be divided into three regions: (I) oxidation region; (II) surface structural change region; (III) reaction region. In the latter two regions, the true contact angle linearly decreases with temperature, which can be respectively expressed as

$$\theta_1 = 217 - 0.11T \quad (\text{when } 800 \text{ }^\circ\text{C} \leq T \leq 1100 \text{ }^\circ\text{C})$$

$$\theta_2 = 122 - 0.022T \quad (\text{when } 1100 \text{ }^\circ\text{C} \leq T \leq 1500 \text{ }^\circ\text{C})$$

2. The surface structural reconstruction of (1×1) into $(\sqrt{3}1 \times \sqrt{3}1R \pm 9^\circ)$ exerts a significant influence on the wettability of (0001) α - Al_2O_3 by molten Al. At temperatures lower than 1200 °C, the contact angle increases with time

and then reaches a constant value. The time needed to reach a constant contact angle decreases with temperature. At a temperature of 1200 °C, the contact angle remains nearly constant, implying that the surface structure becomes stable. However, at temperatures higher than 1200 °C, the contact angle progressively decreases with time and never reaches a constant value due to an interfacial reaction between Al and Al_2O_3 .

3. The high-temperature annealing of the (0001) α - Al_2O_3 substrate does not have a significant effect on the wettability of the Al- Al_2O_3 system since the surface structural transformation is reversible.

Acknowledgement

Financial support from the NEDO International Joint Research Grant is gratefully acknowledged.

References

- [1] Carnahan RD, Johnston TL, Li CH. J Am Ceram Soc 1958;41:343.
- [2] Brennan JJ, Pask JA. J Am Ceram Soc 1968;51:569.
- [3] Champion JA, Keen BJ, Sillwood JM. J Mater Sci 1969;4:39.
- [4] Ownby PD, Li Ke Wen K, Weirauch Jr DA. J Am Ceram Soc 1991;74:1275.
- [5] Jung W, Song H, Pask SW, Kim D-Y. Metall Mater Trans B 1996;27B:51.
- [6] Laurent V, Chatain D, Chatillon C, Eustathopoulos N. Acta Metall 1988;36:1797.
- [7] John H, Hansner H. J Mater Sci Lett 1986;5:549.
- [8] Wang D-J, Wu S-T. Acta Metall Mater 1994;42:4029.
- [9] Ho H-N, Wu S-T. Jpn J Appl Phys 1998;37:274.
- [10] Levi G, Kaplan WD. Acta Mater 2002;50:75.
- [11] Vikner P. DEA report, LTPCM, INP Grenoble, France, 1993. Reported in Eustathopoulos N, Nicholas MG, Drevet B, Wettability at High Temperatures, 1999, Elsevier Science, Oxford, UK, p. 205.
- [12] Nogi K, Tsujimoto M, Ogino K, Iwamoto N. Acta Metall Mater 1992;40:1045.
- [13] Nogi K, Ogino K. Can Inst Mine Metall 1983;22:19.
- [14] Fujii H, Nakae H, Okada K. Acta Metall 1993;41:2963.
- [15] Charig JM. Appl Phys Lett 1967;10:139.
- [16] Chang CC. J Appl Phys 1968;39:5570.
- [17] French TM, Somorjai GA. J Phys Chem 1970;74:2489.

- [18] Gautier M, Duraud JP, Van L-P, Guittet MJ. *Surf Sci* 1991;250:71.
- [19] Soares EA, Van Hove MA, Walters CF. *Phys Rev B* 2002;65:195405.
- [20] Ahn J, Rabalais JW. *Surf Sci* 1997;388:121.
- [21] Suzuki T, Hishita S, Oyoshi K, Souda R. *Surf Sci* 1999;437:289.
- [22] Renaud G, Villette B, Vilfan I, Bourret A. *Phys Rev Lett* 1994;73:1825.
- [23] Guo J, Ellis DE, Lam DJ. *Phys Rev B* 1992;45:13647.
- [24] Jarvis EAA, Carter EA. *J Phys Chem B* 2001;105:4045.
- [25] Guénard P, Renaud G, Barbier A. *Surf Rev Lett* 1997;5:321.
- [26] Arbab M, Chottiner GS, Hoffman RW. *Mater Res Soc Symp Proc* 1989;153:63.
- [27] Toofan J, Watson PD. *Surf Sci* 1998;401:162.
- [28] Tepesch PD, Quong AA. *Phys Stat Sol B* 2000;217:377.
- [29] Wang X-G, Chaka A, Scheffler M. *Phys Rev Lett* 2000;84:3650.
- [30] Eng PJ, Trainor TP, Brown Jr GE, Waychunas GA, Neville M, Sutton SR, et al. *Science* 2000;288:1029.