

Title	Wetting of $\alpha$ -Al <sub>2</sub> O <sub>3</sub> Single Crystals by Molten Al (Materials, Metallurgy & Weldability, INTERNATIONAL SYMPOSIUM OF JWRI 30TH ANNIVERSARY)
Author(s)	Shen, Ping; Fujii, Hidetoshi; Matsumoto, Taihei et al.
Citation	Transactions of JWRI. 2003, 32(1), p. 155-158
Version Type	VoR
URL	<a href="https://doi.org/10.18910/12890">https://doi.org/10.18910/12890</a>
rights	
Note	

*Osaka University Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

Osaka University

# Wetting of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Single Crystals by Molten Al †

SHEN Ping\*, FUJII Hidetoshi\*\*, MATSUMOTO Taihei\*\*\* and NOGI Kiyoshi\*\*\*\*

## Abstract

The wettability of three different oriented  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals, R (01 $\bar{1}2$ ), A (11 $\bar{2}0$ ) and C (0001), by molten Al was studied over a wide temperature range (800°C~1500°C) in order to determine the effect of the substrate crystallographic orientation (anisotropy). The results show that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate orientation has a significant effect on the wettability, especially at relatively low temperatures. The wettability is in the order of  $R \geq A > C$  ( $1 \times 1$ )  $> C$  ( $\sqrt{31} \times \sqrt{31}$ )  $R \pm 9^\circ$ . The dependence of the wettability on the substrate orientation is discussed according to the nature of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface atomic termination structures.

**KEY WORDS:** (Wetting) (adhesion) (Surface) (Substrate orientation) (Aluminum) (Alumina)

## 1. Introduction

Alumina is one of the most thoroughly studied oxide ceramics with a wide range of applications, and the wetting of alumina by molten Al has been investigated by many researchers<sup>1-10</sup>. 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<sup>10</sup> characterized by the continuous oxidation of Al at relatively low temperatures<sup>5-9</sup> and the reaction between Al and Al<sub>2</sub>O<sub>3</sub> to form a gas phase (Al<sub>2</sub>O) and reaction rings at the triple junction at relatively high temperatures<sup>1-5</sup>, which lead to a large scatter in the reported contact angles.

Despite extensive research on this material, the effect of the anisotropy of the alumina single crystal as well as its surface structural change on the wetting behavior has never been systematically studied, even though it is an important question, especially in crystal/film epitaxial growth and adhesion. Therefore, in our recent study, the wettability of different oriented  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals by molten Al has been thoroughly investigated and part of the results is presented in Ref. 11).

## 2. Experimental Procedure

An improved sessile drop method was used in our experiment. Details about it can be found in Ref. 11). The materials are high-purity (99.99%) R (01 $\bar{1}2$ ), A (11 $\bar{2}0$ ) and C (0001)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals

(Hereafter designated only by the letters R, A and C, respectively.) and high-purity (99.99%) Al wire segments. The single crystals were from Kyocera Co., Ltd., Japan, with an average surface roughness (Ra) of less than 1Å and a plane orientation error of  $\pm 0.3^\circ$ .

## 3. Results and Discussion

Fig.1 (a-c) show the variations in the contact angles of R, A, and C by molten Al with time at temperatures from 800°C to 1500°C. It is clear that R and A show a similar behavior of the contact angle versus time over the entire temperature range, while C exhibits a different behavior at temperatures lower than 1200°C. The contact angles of the C single crystals first increase with time and then reach a constant value. The time needed to reach a constant angle decreases with the temperature increase. The increase in the contact angle is due to a surface structural transformation from a (1 $\times$ 1) to a final ( $\sqrt{31} \times \sqrt{31}$ )  $R \pm 9^\circ$  structure<sup>11</sup>, (Here  $R \pm 9^\circ$  denotes rotation by  $\pm 9^\circ$ ), which is extremely stable at temperatures higher than 1200°C. However, in the presence of Al, the transformation temperature shifts to a much lower value<sup>12</sup>.

The variations in the true contact angles with temperature are shown in Fig.2 (a-c) for the R, A and C single crystals, respectively. The true contact angle is based on the following assumptions: the values at 30s are the true contact angles for all the single crystals, however,

† Received on January 31, 2003

\* Foreign Research Fellow

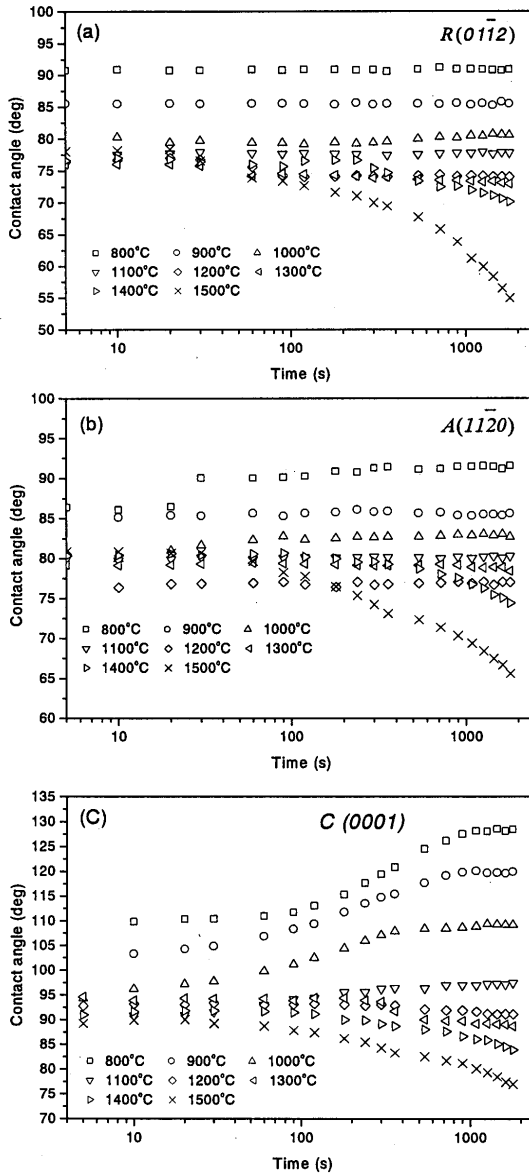
\*\* Associate Professor

\*\*\* Research Associate

\*\*\*\* Professor

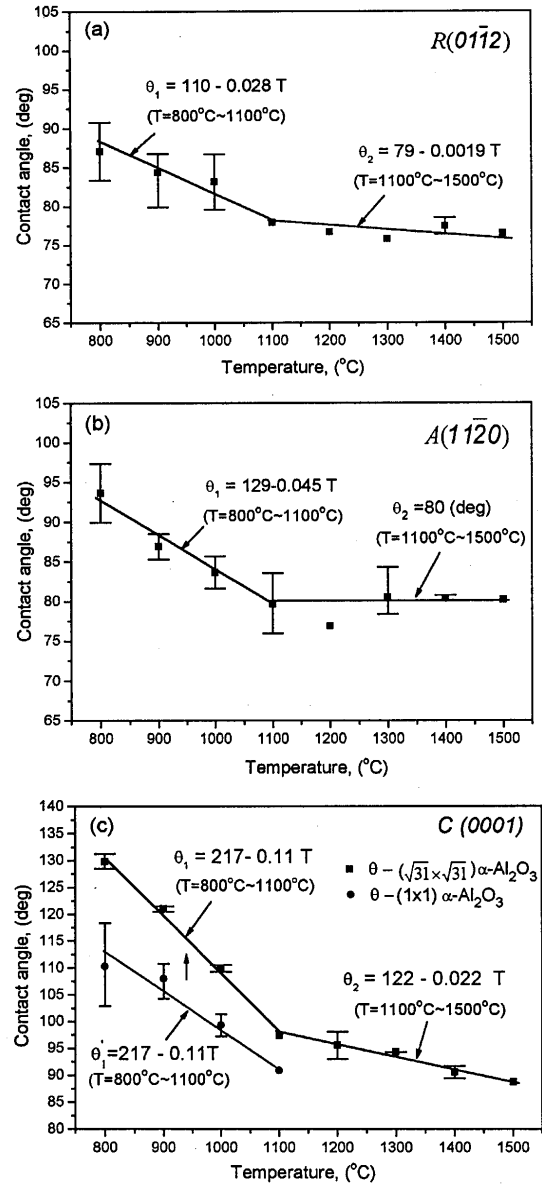
Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567-0047, Japan

## Wetting of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Single Crystals by Molten Al



**Fig. 1** Variations in the contact angles of the R (a), A (b), and C (c) single crystals by molten Al with time at temperatures from 800°C to 1500°C

for the C face, the values at 30min in the temperature range of 800-1100°C are also employed since they may represent the final reconstructed ( $\sqrt{31} \times \sqrt{31}$ ) $R \pm 9^\circ$  structure while the values at 30s in the same temperature range may represent the relaxed yet unreconstructed (1 $\times$ 1) surface structure. Such assumptions are because the initial values before 30s may not be very accurate due to drop vibration after its breakaway from the alumina tube even if the dropping distance is very short, whereas the values at a long time may be affected by surface oxidation of the molten Al at low temperatures and the interfacial reaction between Al and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at high temperatures. As indicated in Fig.2 (a-c), the influence of



**Fig. 2** Variations in the true contact angles of the R (a), A (b) and C (c) single crystals by molten Al with temperature and their linear fit results.

temperature on the wetting behavior for all the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals can be divided into two regions with  $T=1100^\circ\text{C}$  as the boundary. When  $T \leq 1100^\circ\text{C}$ , the true contact angle decreases relatively rapidly with temperature, and when  $T \geq 1100^\circ\text{C}$ , it decreases slowly or remains almost constant.

Fig.3 shows the work of adhesion ( $W_{ad}$ ) of molten Al on the R, A, C (including the (1 $\times$ 1) and ( $\sqrt{31} \times \sqrt{31}$ ) $R \pm 9^\circ$  structures)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals at different temperatures. The  $W_{ad}$  is calculated from the following equation:

$$W_{ad} = \sigma_{lg} (1 + \cos \theta) \quad (1)$$

where  $\sigma_{lg}$  is the surface free energy of liquid Al and  $\theta$

is the true contact angle. Both parameters can be determined from our wetting experiments.

Based on the above results, we can see that the crystallographic orientation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates has a significant effect on the wettability and adhesion of the Al/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system, especially at temperatures lower than 1100°C. The wettability and adhesion are in the sequence of  $R \geq A > C(1 \times 1) > C(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ .

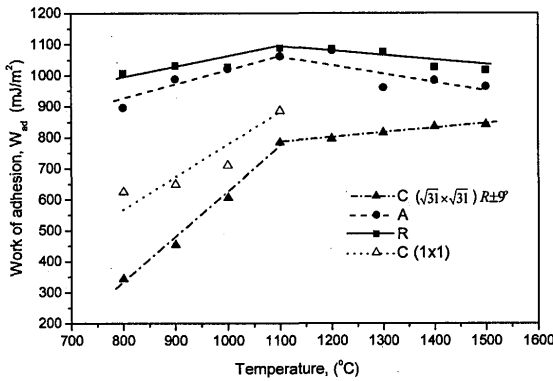


Fig. 3 The work of adhesion,  $W_{ad}$ , of molten Al on three faces of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals

4. Discussion

Explanations concerning the different wettability and adhesion of molten Al on the different oriented  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are based on the consideration of the Madelung energies,  $E_M$ , which involve the sum of the elementary coulomb interactions between pairs of ions ( $i, j$ ) bearing charges  $Q_i$  and  $Q_j$  at a distance  $R_{ij}$ :

$$E_M = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{R_{ij}} \quad (2)$$

The primary interaction at the Al/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interface is the Al-O bond, i.e., the interaction between molten Al atoms and oxygen atoms at the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface<sup>13</sup>. For the simplest consideration, we assume that the oxygen at the interface is in the form of O<sup>2-</sup>, while the neighboring molten Al is in the form of Al<sup>3+</sup> due to the Al-O bond, therefore, the work of adhesion can be written as

$$W_{ad} = k_1 E_M = \frac{N_1 O_{(s)}^{2-} Al_{(l)}^{3+}}{R_{Al(l)-O(s)}} \quad (3)$$

where  $k_1$  is a proportionality constant,  $N_1$  is the number of O<sub>(s)</sub>-Al<sub>(l)</sub> bond pairs, depending on the quantity (or more exactly, the density) of O<sup>2-</sup> on the top layer of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface, and  $R_{Al(l)-O(s)}$  is the distance between O<sup>2-</sup> and Al<sup>3+</sup> at the interface (subscript  $l$  represents the liquid state and  $s$  represents the solid state). As a result,  $W_{ad}$  is essentially dependent on the number of O<sub>(s)</sub>-Al<sub>(l)</sub> bonds, i.e., the quantity/density of O<sup>2-</sup> on the top layer of the  $\alpha$ -

Al<sub>2</sub>O<sub>3</sub> surface if the distance,  $R_{Al(l)-O(s)}$ , is assumed to be the same for all the interfaces.

Note that in Fig.3,  $W_{ad}(R) \geq W_{ad}(A) > W_{ad}(C(1 \times 1)) > W_{ad}(C(\sqrt{31} \times \sqrt{31}))$ . This is most favorable for the C plane to be Al-terminated while the R and A planes are O-terminated. (Here, we do not consider the combined termination). Otherwise, if the C plane is also O-terminated, as seen from the surface structure of these planes<sup>14-15</sup>, one may draw the conclusion that  $W_{ad}(C)$  should be larger than both  $W_{ad}(R)$  and  $W_{ad}(A)$  because the quantity/density of O<sup>2-</sup> on the top layers ranks  $N_1(C) > N_1(R) > N_1(A)$ , which obviously contradicts our experimental results. Conversely, if the C plane is terminated with Al, it is natural for  $W_{ad}(C)$  to be the smallest since the Al-Al bond is much weaker than the Al-O bond. Also, it is reasonable that there is only a minor difference between  $W_{ad}(R)$  and  $W_{ad}(A)$  because of the additional contribution of oxygen in the second layer of the A-plane surface with a relatively large distance<sup>15-16</sup>,  $R_{O(s)-Al(l)}$ , providing that they are both terminated with oxygen on the top layers. Furthermore, based on the stronger adhesion on the relaxed, yet unreconstructed, C-(1x1) surface than that on the reconstructed C-( $\sqrt{31} \times \sqrt{31}$ ) $R \pm 9^\circ$  surface, we deduce that the latter must be an oxygen-deficient structure in comparison to the former. This deduction is consistent with the results obtained from other surface analysis techniques<sup>12,17</sup>.

5. Conclusions

The effect of the substrate crystallographic orientation on the wettability of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals by molten Al was determined in this study. Our results show that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate orientation has a significant effect on the wettability, especially at relatively low temperatures. The wettability is in the sequence of  $R \geq A > C(1 \times 1) > C(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ . The dependence of the wettability on the substrate orientation is essentially determined by the nature of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface atomic terminations. The R and A faces are most likely to be oxygen-terminated while the C face is Al-terminated.

Acknowledgement

This work is supported by the NEDO International Joint Research Grant and by "Priority Assistance of the Formation of Worldwide Renowned Centers of Research - The 21st Century COE Program" from the Ministry of Education, Sports, Culture, Science and Technology of Japan.

## Wetting of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Single Crystals by Molten Al

### References

- 1) R.D. Carnahan, T.L. Johnston and C.H. Li: *J. Am. Ceram. Soc.*, 41(1958), 343.
- 2) J.J. Brennan and J.A. Pask: *J. Am. Ceram. Soc.*, 51(1968), 569.
- 3) J.A. Champion, B.J. Keen and J.M. Sillwood: *J. Mater. Sci.*, 4(1969), 39.
- 4) P.D. Ownby, Ke Wen K. Li and D.A. Weirauch Jr.: *J. Am. Ceram. Soc.*, 74(1991), 1275.
- 5) W. Jung, H. Song, S.W. Pask and D.-Y. Kim: *Metall. Mater. Trans.*, B, 27B (1996), 51.
- 6) V. Laurent, D. Chatain, C. Chatillon, N. Eustathopoulos: *Acta Metall.*, 36(1988), 1797.
- 7) H. John and H. Hansner: *J. Mater. Sci. Lett.*, 5(1986), 549.
- 8) D.-J. Wang and S.-T. Wu: *Acta Metall. Mater.*, 42(1994), 4029.
- 9) H.-N. Ho and S.-T. Wu: *Jpn. J. Appl. Phys.*, 37(1998), 274.
- 10) G. Levi and W.D. Kaplan: *Acta Mater.*, 50(2002), 75.
- 11) P. Shen, H. Fujii, T. Matsumoto and K. Nogi: *Scripta Mater.*, 48(2003), 779.
- 12) T.M. French and G.A. Somorjai: *J. Phys. Chem.*, 74(1970), 2489.
- 13) D.J. Siegel, L.G. Hector Jr. and J.B. Adams: *Phys. Rev.*, B, 65 (2002), 085415.
- 14) V.E. Henrich and P.A. Cox: *"The Surface Science of Metal Oxides"*, Cambridge Univ. Press, Cambridge, (1994).
- 15) P.W. Tasker: *"Structure and Properties of MgO and Al<sub>2</sub>O<sub>3</sub> Ceramics"*, edited by W. D. Kingry, The American Ceramic Society, (1984), 176.
- 16) I. Manassidis and M.J. Gillan: *J. Am. Ceram. Soc.*, 77 (1994), 335.
- 17) G. Renaud, B. Villette, I. Vilfan and A. Bourret: *Phys. Rev. Lett.*, 73(1994), 1825.