Wetting of α-Al₂O₃ Single Crystals by Molten Al †

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Abstract

The wettability of three different oriented α-Al₂O₃ single crystals, R (01$\bar{1}$2), A(11$\bar{2}$0) and C (0001), by molten Al was studied over a wide temperature range (800°C~1500°C) in order to determine the effect of the substrate crystallographic orientation (anisotropy). The results show that the α-Al₂O₃ substrate orientation has a significant effect on the wettability, especially at relatively low temperatures. The wettability is in the order of R≥A>C (1×1) >C ($\sqrt{31} \times \sqrt{31}$)R±9° . The dependence of the wettability on the substrate orientation is discussed according to the nature of the α-Al₂O₃ 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[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 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 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 α-Al₂O₃ 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) α-Al₂O₃ 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 ± 0.3°.

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 (1×1) to a final $(\sqrt{31} \times \sqrt{31})R \pm 9°$ structure[11], (Here $R \pm 9°$ denotes rotation by ±9°), 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[12].

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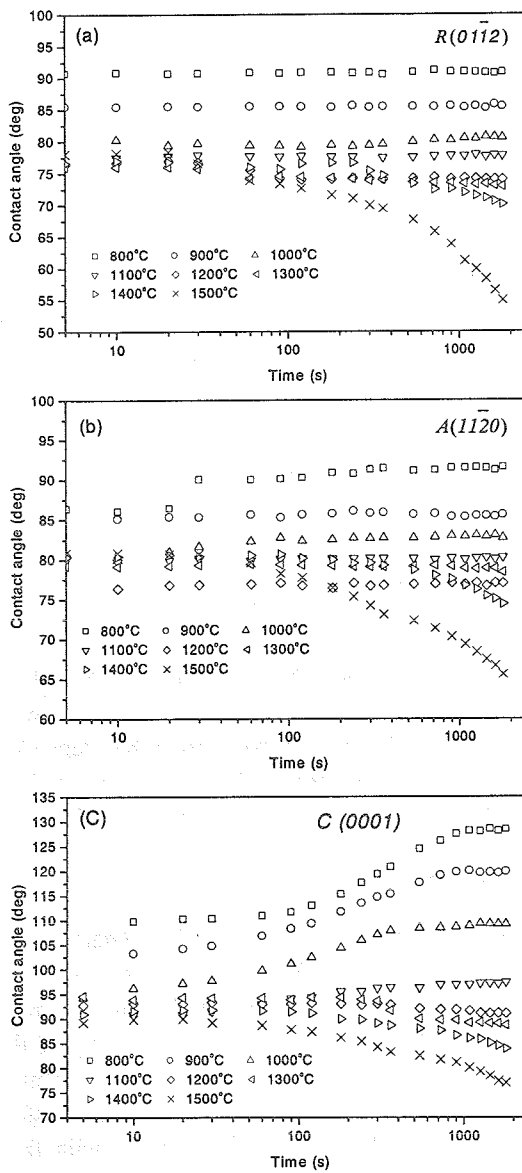
Fig. 1 Variations in the contact angles of the R (a), A (b), and C (c) single crystals by molten Al with time at temperatures from 800°C to 1500°C
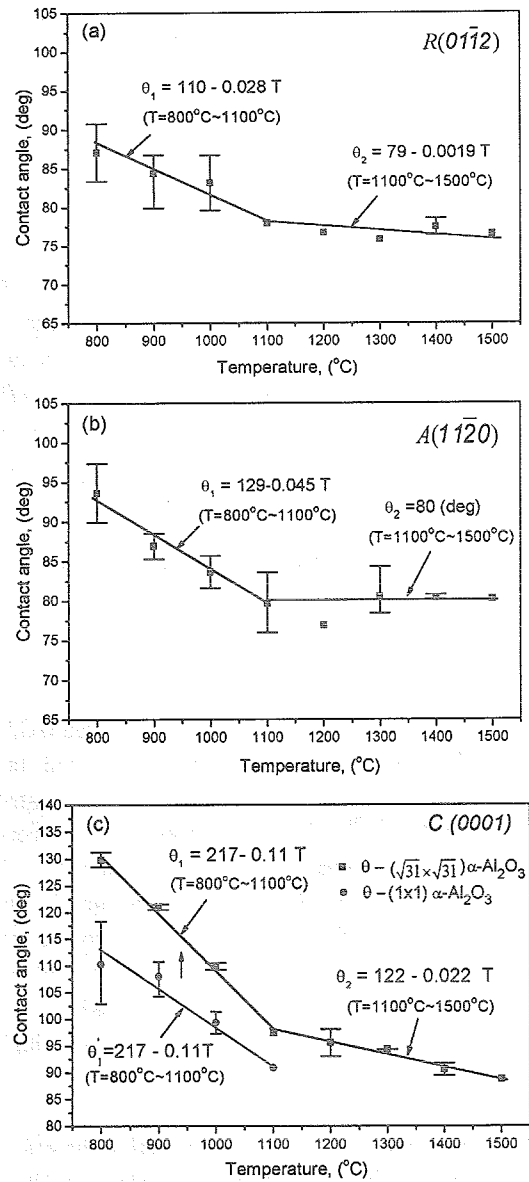

Fig. 2 Variations in the true contact angles of the R (a), A (b) and C (c) single crystals by molten Al with temperature and their linear fit results.

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 $(\sqrt{31}\times\sqrt{31})R\pm9°$ structure while the values at 30s in the same temperature range may represent the relaxed yet unreconstructed (1×1) 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 α-Al₂O₃ at high temperatures. As indicated in Fig.2 (a-c), the influence of

temperature on the wetting behavior for all the α-Al₂O₃ single crystals can be divided into two regions with T=1100°C as the boundary. When T ≤ 1100°C, the true contact angle decreases relatively rapidly with temperature, and when T ≥ 1100°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 (1×1) and $(\sqrt{31}\times\sqrt{31})R\pm9°$ structures) α-Al₂O₃ single crystals at different temperatures. The W_{ad} is calculated from the following equation:

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

where σ_{lg} is the surface free energy of liquid Al and θ

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 α-Al_2O_3 substrates has a significant effect on the wettability and adhesion of the Al/α-Al_2O_3 system, especially at temperatures lower than 1100°C. The wettability and adhesion are in the sequence of R$\geq$A>C(1×1)>C($\sqrt{31}\times\sqrt{31}$)$R\pm9°$.
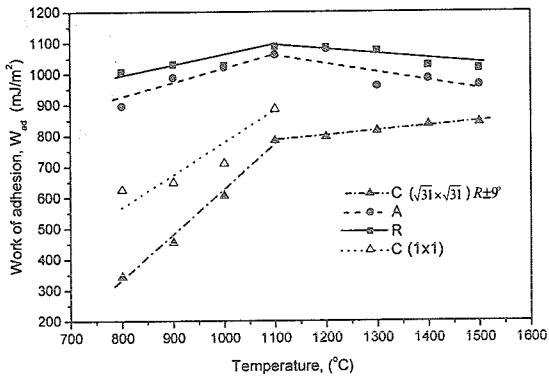

Fig. 3 The work of adhesion, W_{ad}, of molten Al on three faces of α-Al_2O_3 single crystals

4. Discussion

Explanations concerning the different wettability and adhesion of molten Al on the different oriented α-Al_2O_3 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}:

$$E_M = \frac{1}{2}\sum_{i\neq j}\frac{Q_iQ_j}{R_{ij}} \qquad (2)$$

The primary interaction at the Al/α-Al_2O_3 interface is the Al-O bond, *i.e.*, the interaction between molten Al atoms and oxygen atoms at the α-Al_2O_3 surface[13]. For the simplest consideration, we assume that the oxygen at the interface is in the form of O^{2-}, while the neighboring molten Al is in the form of Al^{3+} due to the Al-O bond, therefore, the work of adhesion can be written as

$$W_{ad} = k_1E_M = \frac{N_1O^{2-}_{(s)}Al^{3+}_{(l)}}{R_{Al(l)-O(s)}} \qquad (3)$$

where k_1 is a proportionality constant, N_1 is the number of $O_{(s)}$-$Al_{(l)}$ bond pairs, depending on the quantity (or more exactly, the density) of O^{2-} on the top layer of the α-Al_2O_3 surface, and $R_{Al(l)-O(s)}$ is the distance between O^{2-} and Al^{3+} 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 $O_{(s)}$-$Al_{(l)}$ bonds, *i.e.*, the quantity/density of O^{2-} on the top layer of the α-

Al_2O_3 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(1×1))>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[14-15], 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^{2-} 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[15-16], $R_{O(s)-Al(l)}$, providing that they are both terminated with oxygen on the top layers. Furthermore, based on the stronger adhesion on the relaxed, yet unreconstructed, C$-$(1×1) surface than that on the reconstructed C$-$($\sqrt{31}\times\sqrt{31}$)$R\pm9°$ 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[12,17].

5. Conclusions

The effect of the substrate crystallographic orientation on the wettability of the α-Al_2O_3 single crystals by molten Al was determined in this study. Our results show that the α-Al_2O_3 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(1×1)>C($\sqrt{31}\times\sqrt{31}$)$R\pm9°$. The dependence of the wettability on the substrate orientation is essentially determined by the nature of the α-Al_2O_3 surface atomic terminations. The R and A faces are most likely to be oxygen-terminated while the C face is Al-terminated.

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