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Influence of substrate crystallographic orientation on the wettability and adhesion of α-Al_2O_3 single crystals by liquid Al and Cu

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The wettability and adhesion of α-Al_2O_3 single crystals with different crystallographic orientations by liquid Al and Cu were investigated using an improved sessile drop method. It was demonstrated that the α-Al_2O_3 surface orientation has a noticeable effect on the wettability and adhesion of the Al/α-Al_2O_3 system, but a negligible effect for the Cu/α-Al_2O_3 system. The results were explained by the interfacial atomic bonding mechanism with consideration of the alumina surface atomic configurations.

1. Introduction

Alumina is a technologically important oxide crystal because of its wide applications in catalysts, electronic packaging and other fields where ceramic-metal bonding is used [1]. A precise knowledge of its surface structure and its wettability and adhesion by molten metals is a prerequisite for understanding and controlling the physical and chemical processes involved in many of its applications. With respect to this, numerous studies have been performed on these issues. However, to our knowledge, only a rather limited number of studies have been concerned with the effect of the alumina surface anisotropy on the wetting [2–8] and related the alumina surface structure to its wettability and adhesion by molten metals [2, 7]. On the other hand, almost all the models developed up to now, except for those in some recent initiative *ab-initio* (or *first principles*) computations [9–12], do not explicitly take into account the possible dependence of the wettability and adhesion on the substrate surface structure and crystallographic orientation. In fact, despite the aforementioned studies, due to the experimental findings of the negligible substrate orientation dependence of the wettability and adhesion of α-Al_2O_3 by molten Al [2, 3], Cu [4, 5], Ni and Au [8], this important influence was generally disregarded and the nature involved in it was not revealed and well understood.

Recently, a systematic experimental investigation on the influence of the surface anisotropy of the oxide crystals (such as α-Al_2O_3, MgO and TiO_2) on their wettability and adhesion by molten metals (such as Al and Cu) has been carried out in our laboratory. In this article, we present the experimental results for the α-Al_2O_3 substrates with an effort to reveal the nature behind the apparent influence.

2. Experimental procedure

The materials used in the experiments were high-purity (99.99 wt%) α-Al_2O_3 single crystal wafers (Kyocera Co., Ltd., Japan), and high purity Al (99.99 wt%) and Cu (99.99 wt%) wire segments. The single crystals, with dimensions of ϕ 20 mm × 1 mm, had three faces, R$(01\bar{1}2)$, A$(11\bar{2}0)$ and C(0001) (hereafter represented by letters "R", "A" and "C", respectively). The surfaces were cut along their crystallographic planes with an error of $\pm 0.3^\circ$ and one side was polished to an average roughness (Ra) of 3 nm as measured by a surface profilometer (DEKTAK 3, Veeco Instruments, NY, USA).

The wetting experiments were performed using an improved sessile drop method previously described in detail [13, 14]. Before the experiment, the materials were ultrasonically cleaned in acetone. The chamber was first heated in vacuum to the testing temperature, at which the vacuum level was about $(5–1) \times 10^{-4}$ Pa. A purified Ar-3%H_2 gas with an oxygen partial pressure on the order of 10^{-18} Pa (measured at 1073 K) was then introduced. The atmospheric pressure in the chamber was controlled in the range of 0.11–0.12 MPa. After the temperature and the atmosphere had stabilized, the Al or Cu sample located outside the chamber was immediately inserted into the bottom of the alumina dropping tube (in 99.6 wt% purity) and held for 60s in order for it to melt and reach the testing temperature. The molten metal was then forced out from a small hole ($\phi = 1$ mm) at the bottom of the alumina tube and dropped onto the alumina substrate. At the same time, a photograph was taken and defined as the drop profile at zero time. Subsequent photographs were taken at certain intervals.

After the experiment, all the captured drop profiles were analyzed by an axisymmetric-drop-shape analysis

(ADSA) program to determine the density, surface tension and contact angle simultaneously by comparing the observed shape with that of the solution to the Laplace equation. This program offers a high degree of accuracy and removes the operator's subjectivity.

3. Results

3.1. Al/α-Al_2O_3 system

Details about the wetting results in the Al/α-Al_2O_3 system have been published elsewhere [14–16]. Here, in order to clearly show the effect of the alumina surface crystallographic orientation on the wettability and adhesion, we summarize the results in Figs 1–2, which respectively show the variations in the possible intrinsic contact angles, θ, and work of adhesion, W_{ad}, for molten Al on the three faces of the α-Al_2O_3 single crystals as a function of temperature. The legends, C-(1×1) and C-$(\sqrt{31} \times \sqrt{31})$, represent the unreconstructed basal (1×1) and the reconstructed $(\sqrt{31} \times \sqrt{31})R \pm 9°$ surfaces, respectively. The latter is extremely stable at temperatures higher than 1500 K, however, Al or Si vapors shift the transformation temperature towards 1200 K or less [17], which leads to a change (increase) in the contact angle as a function of time during the isothermal dwells [15].

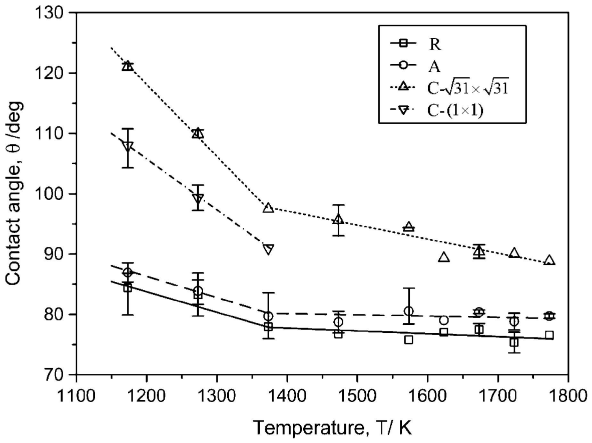

Figure 1 Variation in the possible intrinsic contact angles, θ, for molten Al on the different faces of the α-Al_2O_3 single crystals as a function of temperature.

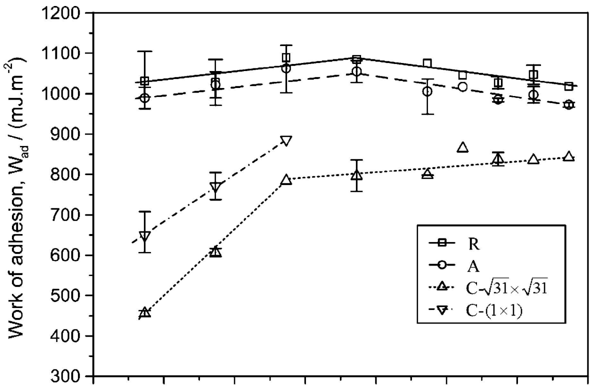

Figure 2 Variation in the work of adhesion, W_{ad}, for molten Al on the different faces of the α-Al_2O_3 single crystals as a function of temperature.

The values of W_{ad} were calculated from the Young-Dupré equation,

$$W_{ad} = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} = \sigma_{lv}(1 + \cos\theta) \qquad (1)$$

where σ_{sv}, σ_{sl} and σ_{lv} are the solid-vapor, solid-liquid and liquid-vapor interfacial free energies, respectively, and θ is the intrinsic contact angle. The values of the molten Al surface free energy (surface tension), $\sigma_{lv(Al)}$, at various temperatures are given by the following equation

$$\sigma_{lv(Al)} = 985 - 0.19(T/K - 933) \quad \text{mJ/m}^2 \qquad (2)$$

It is clear that the wettability and adhesion of α-Al_2O_3 by molten Al are sensitive to the alumina surface crystallographic orientation, which are in the order of $R \geq A > C - (1 \times 1) > C - (\sqrt{31} \times \sqrt{31})$, particularly at relatively low temperatures. The dependence of the wettability and adhesion on the temperature is more significant for the C face than that for the R and A faces.

3.2. Cu/α-Al_2O_3 system

Tables I–II show the possible intrinsic contact angles and work of adhesion for molten Cu on the R, A and C faces of the α-Al_2O_3 single crystals at temperatures between 1423 and 1673 K. The temperature dependence of the molten Cu surface tension was determined to be the following,

$$\sigma_{lv(Cu)} = 1304 - 0.25(T/K - 1356) \quad (\text{mJ/m}^2) \qquad (3)$$

As can be seen, the wettability and adhesion in the Cu/α-Al_2O_3 system do not show a noticeable dependence on the crystallographic orientation of the alumina substrates. Also, they do not show a significant dependence on the temperature.

TABLE I Possible intrinsic contact angles, θ, for Cu on the R, A and C α-Al_2O_3 single crystals at temperatures between 1423 and 1673 K

	θ (deg.)		
Temperature T (K)	R	A	C
1423	113	113	114
1473	115	113	113
1573	115	115	115
1673	115	115	114

TABLE II Work of adhesion, W_{ad}, for Cu on the R, A and C α-Al_2O_3 single crystals at temperatures between 1423 and 1673 K

	Work of adhesion, W_{ad} (mJ·m^{-2})		
Temperature T (K)	R	A	C
1423	784	784	764
1473	736	777	777
1573	722	722	722
1673	707	707	727

4. Discussion

The different alumina surface orientation dependences of the wettability and adhesion in the Al/α-Al_2O_3 and Cu/α-Al_2O_3 systems indicate that, on the one hand, the alumina surface crystallographic orientation can indeed play a significant role in determining the wettability and adhesion, and on the other hand, the dependence is related to the detailed system, i.e., to the liquid metal.

In order to understand the dominating factor for these different dependence behaviors, let us first take into account the surface structures of the R, A and C faces of the α-Al_2O_3 crystal. Although the nature of the atomic termination at the different α-Al_2O_3 surfaces, so far, is still an open question due to lack of definitive experimental evidence to demonstrate that the real termination is aluminum (Al) or oxygen (O) at the top layer of the surfaces [1], most researchers favor that the clean C face is Al-terminated and the clean R and A faces are oxygen-terminated [14]. A schematic representation of the possible surface structures of the R, A and C faces of α-Al_2O_3 was presented in Fig. 8 of Ref. [14].

Next, let us consider the anisotropy of the α-Al_2O_3 surface free energy. As indicated in Table III, theoretical calculations [18, 19] demonstrate that the surface energies of the different faces of α-Al_2O_3 are very different for the unrelaxed surfaces but tend to be much closer for the relaxed surfaces. Taking the temperature influence into account, Levi *et al.* [20] demonstrated that the value of the C face calculated by Manassidis and Gillan [19] using first principles fits well with the experimental result. Ownby and Liu [5] also suggested that the sapphire surface energy varies with the surface crystallographic orientation only below the temperature where the sapphire surface undergoes reconstruction (they gave a value of about 1200 K). Above this temperature, σ_{SV} becomes increasingly less a function of the crystallographic orientation until a critical temperature (below the alumina melting temperature) is reached where it is no longer a function of the crystallographic orientation at all. Recently, Choi *et al.* [21] and Kitayama and Glaeser [22] have experimentally determined the relative surface energies of the alumina crystals with some low-index planes at temperatures up to 2073 K by measurement of the equilibrium (Wulff) shape of internal cavities in sapphire substrates. Their results (see Table IV) show that the sapphire surfaces have some extent of anisotropy at high temperatures. The relative energy difference among the R, A and C faces is between 3 and 15% but generally decreases with increasing temperature. On the other hand, it is obvious that the surface free energy of liquid metal, σ_{lv}, is independent of the alumina surface crystallographic orientation. Accordingly, we assume here that the strong dependence of the wettability and adhesion on the α-Al_2O_3 surface orientation at high temperatures (e.g., $T > 1200$ K) is mainly dominated by the anisotropy of the solid-liquid interfacial free energy, σ_{sl}.

TABLE III Theoretically calculated surface energies for the unrelaxed and relaxed R, A and C faces of α-Al_2O_3 at absolute 0 K

	Surface energy ($J.m^{-2}$)					
	First Principles ([a][18], [b][19])				Interaction model [19]	
Surface	Unrelaxed		Relaxed		Unrelaxed	Relaxed
R	3.55[a]	2.51[b]	2.57[a]	1.97[b]	3.63	2.29
A	5.17[a]	2.49[b]	2.65[a]	1.86[b]	4.37	2.50
C	6.53[a]	3.77[b]	2.97[a]	1.76[b]	5.95	2.03

TABLE IV Relative surface energies of the C, R and A α-Al_2O_3 faces determined by Wulff shape measurement method [21, 22]

	Relative σ_{sv} ($J.m^{-2}$)		
Surface	1873 K [21]	1873 K [22]	2073 K [22]
C(0001)	1.00	1.00	1.00
R(01$\bar{1}$2)	1.05	0.855	0.95
A(11$\bar{2}$0)	1.12	0.974	1.08

Furthermore, assuming that the cohesion and adhesion result from atomic interactions between nearest neighbours, Eustathopoulos and Drevet [23] derived the following expression for the work of adhesion, W_{ad}, in the frame of a simple, broken-bond, atomistic model

$$W_{ad} = Z\varepsilon_{AO-M}/\varpi \tag{4}$$

where Z is the number of broken bonds of AO (oxide crystal), ε_{AO-M} is the average bond energy (here, defined as a positive quantity) taking into account both interactions of M(metal)-O and M-A through the M-AO interface, and ϖ is the average surface area in AO. Considering the atomic configurations at the AO (here, it is α-Al_2O_3) surface, Equation 4 might be further written as

$$W_{ad} = (Z_{O-M}\varepsilon_{O-M} + Z_{Al-M}\varepsilon_{Al-M})/\varpi \tag{5}$$

where Z_{O-M} and Z_{Al-M} are the numbers of O—M and Al—M bonds at the metal(M)/alumina interface, and ε_{O-M} and ε_{Al-M} are the bond energies of O—M and Al—M, respectively.

According to Equation 5, the adhesion at the M/α-Al_2O_3 interface can be classified into three typical cases in the light of the magnitude of ε_{O-M} and ε_{Al-M}:

Case 1: If $\varepsilon_{O-M} \gg \varepsilon_{Al-M}$, the contribution from the Al-M bonds can be neglected, i.e., the adhesion is mainly determined by the O—M bonds, which, again, are dependent on the number of the outermost (broken) oxygen atoms at the α-Al_2O_3 surfaces. In this sense, the nature of the atomic termination (Al or O) at the α-Al_2O_3 surfaces can play a significant role in determining the adhesion (as well as the wettability), which is expected to be much stronger for the liquid metal on the O-terminated surface than on the Al-terminated surface, and the interface might be characterized by the formation of a metal oxide crystal.

Case 2: If $\varepsilon_{O-M} \approx \varepsilon_{Al-M}$, the adhesion does not significantly depend on the status of the α-Al_2O_3 surface atomic termination, but on the number of the broken bonds at the alumina surfaces, or alternatively, the number of the interfacial bonds from the interactions between the alumina surface atoms and the neighbouring liquid metal atoms. The interface, on the other hand, may be characterized by the formation of a

TABLE V Bond strengths in diatomic molecules at 298 K [24]

Molecule	Al—Al	Al—O	Cu—Al	Cu—O
Bond strength ($kJ \cdot mol^{-1}$)	133 ± 6	511 ± 3	216.7 ± 10.5	269.0 ± 20.9

spinel-like phase ($M_xAl_yO_z$), if the interfacial bond is strong enough.

Case 3: If $\varepsilon_{O-M} \ll \varepsilon_{Al-M}$, again, the nature of the atomic termination (Al or O) at the α-Al_2O_3 surfaces plays a significant role in determining the adhesion, but in contrast to case 1, the adhesion is expected to be much stronger for the liquid metal on the Al-terminated surface than that on the O-terminated surface, and the interface might be characterized by the formation of an intermetallic compound.

Table V shows the bond strengths in the relevant diatomic molecules at 298 K [24]. Although the real bond strengths at high temperatures may be different from these values, they can be used for a qualitative evaluation. As indicated, for the Al/α-Al_2O_3 system, the strength of the Al—O bond is much higher than that of Al—Al, therefore, according to the above analysis, one may speculate that the much stronger adhesion for molten Al on the *R* and *A* surfaces than that on the *C* surface is likely due to the *R* and *A* surfaces being oxygen (*O*)-terminated (or at least oxygen-rich) while the *C* surface being aluminum (Al)-terminated. This deduction is consistent with most surface science experimental results and theoretical predictions for the clean *R*, *A* and *C* surfaces [14]. In addition, from the results of the stronger adhesion for molten Al on the unreconstructed C-(1 × 1) surface than that on the reconstructed C-($\sqrt{31} \times \sqrt{31}$) surface, one can further deduce that the latter must be a surface oxygen-deficient structure.

For the Cu/α-Al_2O_3 system, the bond strengths of Cu-Al and Cu-O in diatomic molecules do not differ significantly. Although the individual Cu-O bond is slightly stronger than that of Cu-Al, due to the surface reconstruction induced Al rich at the C-($\sqrt{31} \times \sqrt{31}$) surface [1], the total Cu—Al bonds at the Cu/α-$Al_2O_3^C$ interface might be comparable to the Cu—O bonds at the Cu/α-$Al_2O_3^{R,A}$ interfaces, leading to the similar wetting and adhesion results in this system.

Finally, we would like to point out that the alumina surface atomic configuration might be altered by some external factors such as atmosphere and substrate surface preparation methods [25, 26], which, of course, will affect the wettability and adhesion to some extent as we have expounded. Consequently, any conclusion on the alumina surface structure must clearly indicate the specific experimental conditions.

5. Conclusion

The wettability and adhesion of α-Al_2O_3 single crystals with crystallographic orientations of R ($01\bar{1}2$), A($11\bar{2}0$) and *C* (0001) by liquid Al and Cu in an Ar-3%H_2 atmosphere were investigated in this study. The results show that the α-Al_2O_3 surface orientation has a pronounced effect on the wettability and adhesion of the Al/α-Al_2O_3 but a negligible effect for the Cu/α-Al_2O_3 system. They are explained by the interfacial atomic bonding mechanism. That is, the significant substrate orientation dependence of the wettability and adhesion in the Al/α-Al_2O_3 system is mainly determined by the different atomic configurations at the different faces of the α-Al_2O_3 substrates coupled with the Al—O bonds being much stronger than those of Al—Al at the Al/α-Al_2O_3 interface, whereas, the weak dependence in the Cu/α-Al_2O_3 system is attributed to the possibly rather close bond strengths of Cu—Al and Cu—O at the Cu/α-Al_2O_3 interface.

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