Influence of MgO Crystal Surface Orientation on Its Wettability by Molten Al †

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Abstract

The wettability of three different oriented MgO single crystals, (100), (110) and (111), by molten Al was measured by an improved sessile drop method in a purified Ar-3%H₂ atmosphere at temperatures between 1073 and 1473K in order to determine the effect of the MgO substrate crystallographic orientation. Although the reaction products at the Al-MgO interfaces consist of somewhat different forms of Al₂O₃ phases, the wettability of all these substrates by liquid Al is similar. As a consequence, this system displays almost no anisotropy. Some plausible explanations based on several hypotheses are provided to account for this result.

KEY WORDS: (Wettability) (Surface and Interface) (Substrate orientation) (Aluminum) (Magnesia)

1. Introduction

A comprehensive understanding of the wettability of ceramics by liquid metals as well as the influencing factors is not only of scientific interest but also of significant technological importance. It has been realized that the wettability can be affected by the substrate crystallographic orientation[1], such as in the Al-Al$_2$O$_3$ system, however, there are not many systematic investigations on this subject in other metal-ceramic systems. In this study, we investigated the wettability of three different oriented MgO substrates by molten Al with an emphasis on the effect of the MgO crystal orientation.

2. Experimental Procedure

Pure Al (>99.99wt.%) and pure MgO single crystals (Nakazumi Crystal Laboratory Co. Ltd., Japan) were used as the raw materials. Small Al segments weighing about 0.1-0.15g were cut from a 3mm-diameter Al wire. The MgO single crystal wafers with dimensions of 20mm×20mm×0.5mm were cut along (100), (110) and (111) crystallographic planes with an orientation error of ±0.5°. One side of these surfaces was polished to an average roughness of 200Å (20nm).

An improved sessile drop method was employed in this experiment. Details about the experimental apparatus and procedure have been explained elsewhere[2]. After the MgO wafer and the Al segment were ultrasonically cleaned in acetone, the MgO wafer was set in a horizontal position on an Al$_2$O$_3$ supporter inside the chamber and the Al segment was placed in a glass tube with a spring connector on the top of the dropping device

outside the chamber. The chamber was then evacuated to about 5×10^{-4} Pa and subsequently heated to the desired temperature in vacuum at a heating rate of 20°C/min. For the experiments performed at temperatures lower than 1373K, the temperature was first raised to 1373K, maintained for 10min and then cooled to the desired experimental temperature. Such a procedure was to remove substrate surface contaminants as well as to obtain a higher vacuum. The chamber was then purged with a premixed Ar-3%H$_2$ gas purified using platinum asbestos and magnesium perchlorate and the pressure was controlled to about 120kPa (approx.1.2atm). After the temperature and the atmosphere had stabilized, the Al segment was inserted into the bottom of the alumina tube and kept for 1min in order for it to melt and reach the experimental temperature. The molten Al was then forced out from a small hole (φ=1mm) in the bottom of the alumina tube (99.6% purity) and dropped onto the MgO substrate by a gradual decrease in the pressure inside the chamber to about 110kPa (approx. 1.1atm). At the same time, the initial oxide on the Al surface was mechanically removed as the liquid passed through the hole.

The captured drop profiles were analyzed by an axisymmetric-drop-shape-analysis (ADSA) program, by which the contact angle, surface tension and density could be simultaneously calculated while the operator's subjectivity was removed. The reaction phases at the Al-MgO interface were identified by EDAX and X-ray diffraction (XRD) after removal of the solidified Al droplet in a 15wt.%NaOH distilled-water solution.
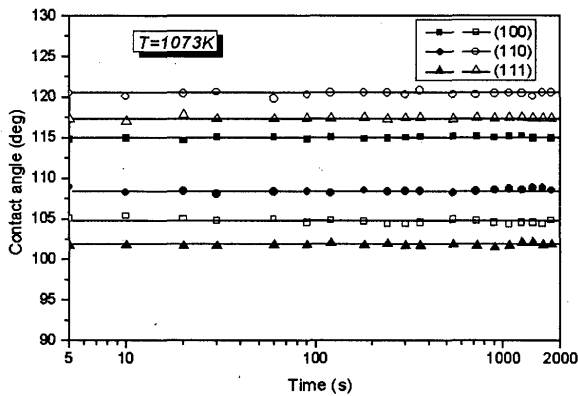
3. Results

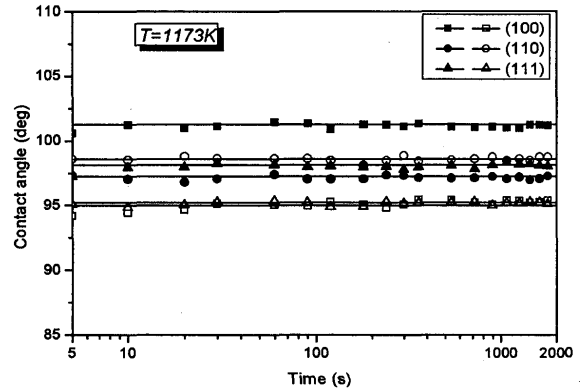Fig. 1 Variations in the contact angles with time at 1073K

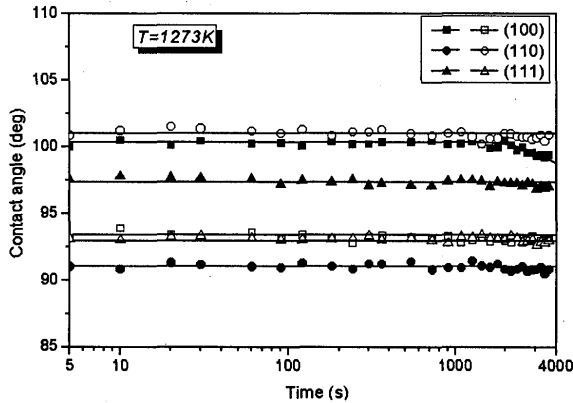Fig. 2 Variations in the contact angles with time at 1173K

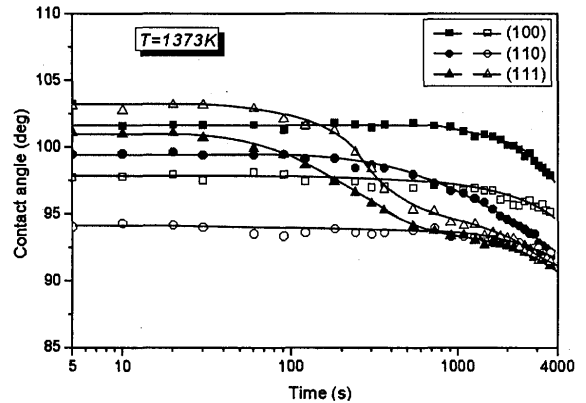Fig. 3 Variations in the contact angles with time at 1273K

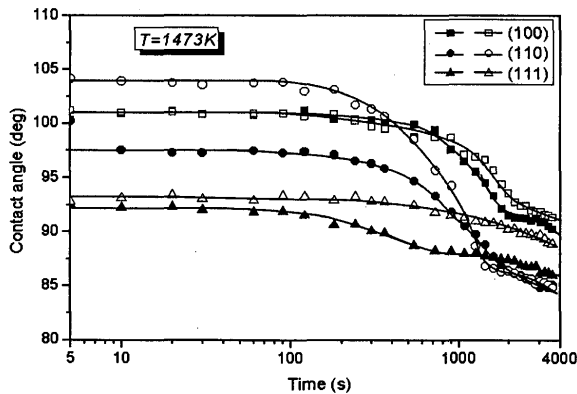Fig. 4 Variations in the contact angles with time at 1373K

Fig. 5 Variations in the contact angles with time at 1473K

Figs.1-5 show the variations in contact angles of the molten Al on the three faces of MgO single crystals at temperatures between 1073 and 1473K as plotted on a logarithmic time scale. As can be seen, at low temperatures (T≤1273K), the contact angle does not considerably vary with time during the isothermal dwellings. However, at high temperatures (T>1273K), a noticeable decrease in the contact angle with time is observed. The initial contact angles, typically at times less than 60s, do not show a significant difference in the above temperature range and are generally between 90 and 105°, except for those at 1073K, which are much higher and possibly affected by the molten Al surface

oxidation. More importantly, the initial contact angles, on the whole, do not show a remarkable and constant dependence on the MgO substrate orientation. On the other hand, they exhibit a relatively larger scatter in the different runs of the experiments as compared to other systems such as Al/α-Al$_2$O$_3$ under the same experimental conditions[2], which may mask this weak dependence if it is really present.

Microstructural observations indicate that the interfacial reaction occurred in all the Al-MgO samples examined at temperatures higher than 1073K. The reaction products, as identified by EDAX and XRD analyses, are mainly Al$_2$O$_3$ phases, without a pronounced spinel (MgAl$_2$O$_4$) phase. The Mg and Al species at the MgO-Al$_2$O$_3$ interface, both in a vertical depth profile (see Fig.6a) and a horizontal surface profile (see Fig.6b), vary rather sharply. The sharp elemental alteration at the MgO-Al$_2$O$_3$ interface is thought to be a result of rapid Mg evaporation, either directly from the reacted surface/interface, or through the liquid Al after it was displaced from the MgO substrate. In fact, fine Mg powders were found deposited on the chamber wall after every high-temperature experiment.

On the other hand, the XRD results further reveal that the Al$_2$O$_3$ products formed are sensitive to the substrate orientation. Figs.7-9, respectively, show the XRD spectra of the Al-(100), (110) and (111)MgO interfacial (and surface) phases after removal of the solidified Al droplet as compared to those of the as-received and annealed
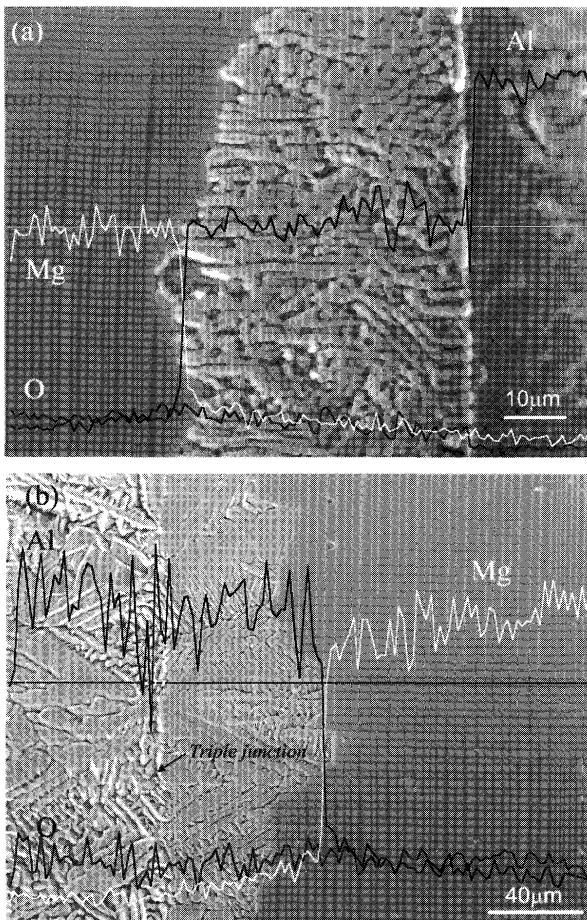
Fig.6 Mcrostructures and elemental composition alternations at a vertical-section interface (a) and a horizontal triple-junction interface (b) (after removal of the Al droplet) in an Al-(111)MgO sample after dwelling at 1273K for 3600s.

MgO surfaces. Clearly, the primary reaction product at the Al-(100)MgO interface is α-Al_2O_3 while that at the Al-(110)MgO and Al-(111)MgO interfaces is κ'-, κ-, and δ-Al_2O_3 phases. The latter phases are usually obtained during the dehydration of the hydrated α-Al_2O_3 phase[3-4], therefore, it was first conjectured that the H_2 atmosphere employed in the experiments was responsible for their formation. However, our later experiments under purified Ar atmosphere (>99.999% purity) demonstrate that the same reaction products were produced at the Al-(110) and (111)MgO interfaces. As a result, the H_2 atmosphere should not be the decisive factor. The true reasons for their formation remain unclear at the present time.

4. Discussion

The weak dependence of the wettability of the Al-MgO system on the MgO substrate orientation seems somewhat unexpected. In a previous comparative study on the wettability in non-reactive Me(Me=Pb, Sn and Bi)/MgO systems at 873K in a purified H_2 atmosphere[5], the wettability was found essentially dependent on the MgO substrate orientation in the order of (100)>(111)>(110). On the other hand, theoretical studies
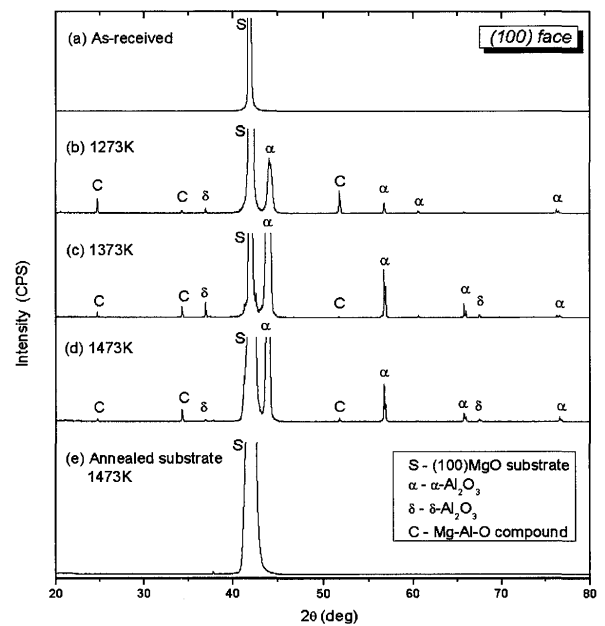

Fig.7 XRD spectra of the interfacial (and surface) phases in the Al-(100)MgO samples after removal of the solidified Al droplet as compared to the as-received (unheated) and annealed (100)MgO specimens. (Some strong peaks of the major phases are cut in order to show all the minor phases.)
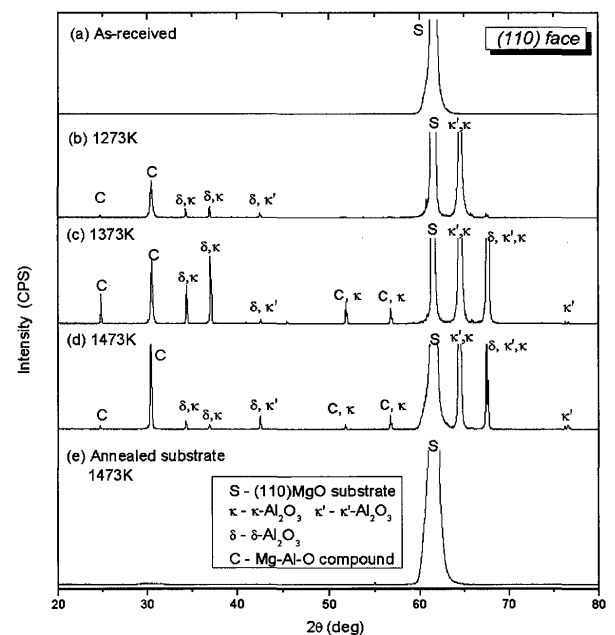
Fig.8 RD spectra of the interfacial (and surface) phases in the Al-(110)MgO samples after removal of the solidified Al droplet as compared to the as-received (unheated) and annealed (110)MgO specimens. (Some strong peaks of the major phases are cut in order to show all the minor phases.)

of the transition metals, such as Pd, Cu and Ag, deposition on the MgO substrates[6-9] indicated that the work of adhesion on the (110) and (111) surfaces was much stronger than that on the neutral (001)MgO surface, i.e., the wettability of the former two was better than that of the latter as deduced from the Young-Dupré equation

Fig.9 XRD spectra of the interfacial (and surface) phases in the Al-(111)MgO samples after removal of the solidified Al droplet as compared to the as-received (unheated) and annealed (111)MgO specimens. (Some strong peaks of the major phases are cut in order to show all the minor phases.)
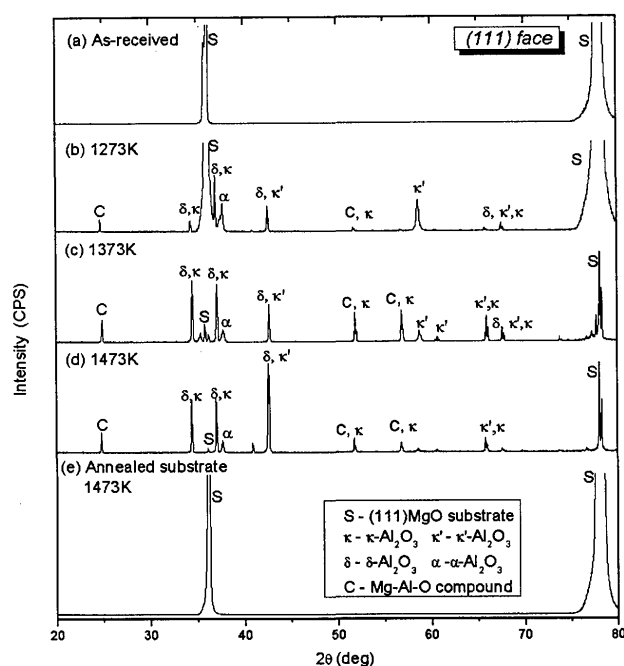

(a) Surface structure   (b) Bulk structure

Fig.10 Schematic diagrams of the (100), (110), (111) MgO surface structures (a) and bulk structures (b) [25].

Table 1. Number of oxygen atoms at the MgO surfaces and in the bulk crystals

Crystal	Number of oxygen atom ($\times 10^{-5}$ mol.m^{-2})	
	Surface	Bulk
(100)	3.15	1.85
(110)	3.85	1.32
(111)	3.87	2.13

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

where W_{ad} is the work of adhesion and σ_{lv} is the liquid-vapor interfacial free energy.

The exact reasons for the different results in the aforementioned metal-MgO systems are unclear, however, as far as the Al-MgO system is concerned, the following factors are noteworthy, and may account for the results obtained in this study:

Firstly, although the (111)MgO surface is polar and known as energetically unstable as compared to the (100) surface[10], and the surface free energies of the three faces at ambient temperature are in the order of (111)>(110)>(100) [11-14], a number of experimental and theoretical studies support the main idea that the (110) and (111)MgO surfaces spontaneously facet into the (100) (or other low-energy) face(s) in a microscopic size[15-17], and/or reconstruct[18-19] in order to lower their relatively high surface free energies during annealing. The surface faceting, as observed by Henrich[15] and Chern et al.[16], can occur even after annealing the substrate at 900K. At higher temperatures, the faceted scale is greater than a few micrometers[15-16] and the surface reconstruction is distinguishable[17,19]. The reconstruction, on the other hand, can also be driven by desorbed hydroxyl groups after annealing the substrates at low temperatures as observed on a polar (111) NiO surface[20], which is similar to MgO in its crystal structure.

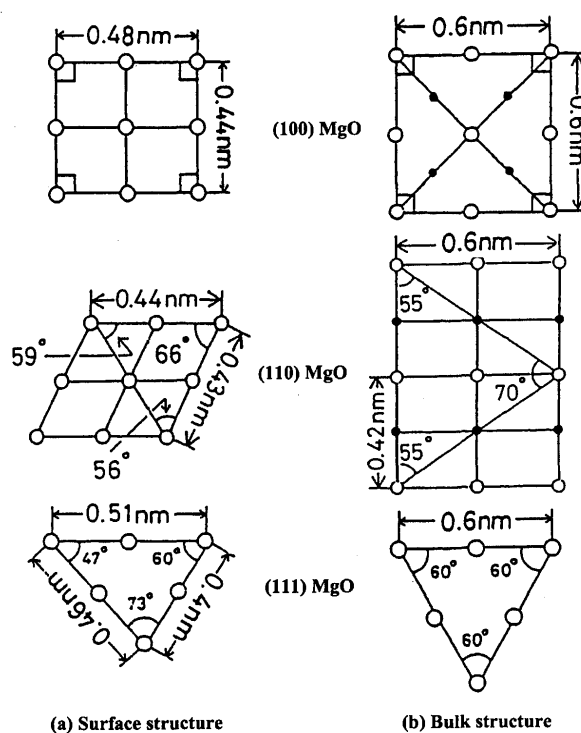Secondly, as demonstrated by theoretical density functional calculations[21], the bonds at the Al/oxygen-terminated (100)MgO interface are much stronger than those at the Al/magnesium-terminated (100)MgO interface. Therefore, the adhesion and the wettability are primarily determined by the quantity, or more exactly, the density of the oxygen atoms at the top-layer of the MgO surfaces, which is very similar to that found in the Al/α-Al$_2$O$_3$ system as we have described in detail in Ref. 22). In addition, theoretical calculations and experimental observations both favor that the geometry of the MgO surfaces can be characterized by surface rumples with the Mg atoms moving inwards and the oxygen atoms moving outwards[23-24]. Atomic force microscope (AFM) observations on the MgO surfaces further provide the images of the MgO surface structures, which are quite different from the bulk ones[25]. **Fig.10** shows schematic diagrams of the different oriented MgO surface and bulk structures, from which the number of the oxygen atoms both at the surface and in the bulk can be calculated and the results are presented in **Table 1**. Apparently, the densities of the oxygen atoms at the three surfaces are not very different, implying similar Al-O bonds at the Al-MgO interfaces and hence similar adhesion and wettability of the different oriented MgO substrates by molten Al.
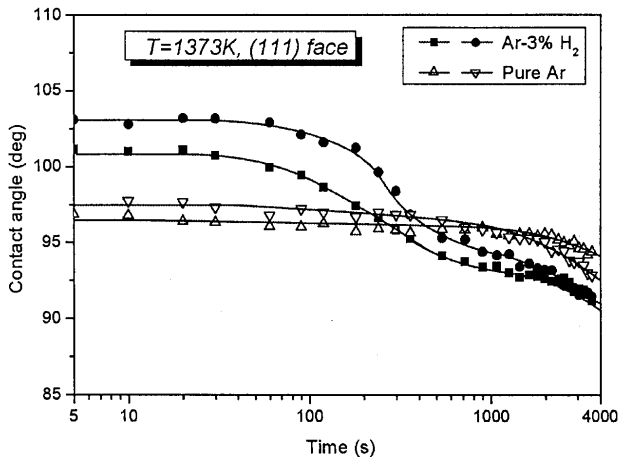
Fig.11 Comparison of the contact angles in the Al-(111)MgO samples at 1373K under the Ar-3%H$_2$ and pure Ar atmospheres.

Finally, the H$_2$ atmosphere employed in the experiments might also have an influence on the wettability. **Fig.11** compares the contact angles in the Al-(111)MgO samples at 1373K under the purified Ar-3%H$_2$ and Ar (99.999% purity) atmospheres. As can be seen, the initial contact angles under the Ar atmosphere are a few degrees smaller than those under the Ar-3%H$_2$ atmosphere. Similar results were also obtained in the Al-(110)MgO samples. However, due to the relatively large scatter of the contact angles in the Al-MgO system as well as the relatively minor difference in the results under these two atmospheres, it is difficult for us to draw definite conclusions on the influence of H$_2$. Numerous studies have reported that H$_2$ can adsorb on and further interact with the MgO surfaces[26-30]. *Ab initio* total-energy calculations performed by Refson et al.[31] showed that a chemisorption reaction involving a reconstruction to form a (111) hydroxyl MgO surface was strongly preferred. They even claimed that the protonation stabilized the otherwise unstable (111) surface and that this, not the neutral (100), was the most stable MgO surface under ambient conditions. The hydroxylation is regarded as a particularly efficient mechanism for stabilization of the (110) and (111)MgO surfaces since it decreases their surface free energies. However, considering that dehydroxylation usually occurs at temperatures higher than 1073K, the function of H$_2$ might be rather limited since the gas was introduced only after the experimental temperature was reached. Even so, there are reports that the faceted (111)MgO surface has a higher absorptivity and reactivity[32] and the binding energy of water on an Al-doped (100)MgO surface is much higher that that on the pure (100)MgO surface[33]. As a consequence, if the H$_2$ molecules could indeed adsorb on and further interact with the MgO surfaces at high temperatures, the differences in the MgO surface structures and the surface free energies are expected to be reduced, which also favors the result of the similar wettability among the different MgO substrates by molten Al.

5. Conclusions

The wettability of three different oriented MgO single crystals, (100), (110) and (111), by molten Al was investigated at 1073-1473K mainly in a purified Ar-3%H$_2$ atmosphere using an improved sessile drop method. The results show that the possible intrinsic contact angles of the Al-MgO system are in the range of 90-105°, neither significantly depending on the MgO substrate orientation nor on the temperature. The weak dependence of the wettability on the MgO surface orientation is explained by the similar densities of the oxygen atoms at the three MgO surfaces, the MgO surface faceting and reconstruction during heating and isothermal dwelling processes as well as the H$_2$ molecules possible dissociative chemisorption on the MgO surfaces. The latter two are considered as favoring stabilization of the high energy (110) and (111) surfaces and thus alleviating the difference in the surface free energies among these three surfaces.

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