

A first-principles study of the formation of atomically rough {111} MgO surface and its effect on prenucleation of Mg

C. M. FANG^{1,a} and Z. FAN^{1,b}

¹BCAST, Brunel University London, Kingston, Uxbridge, UB8 3PH, UK

^a Changming.fang@brunel.ac.uk ^b zhongyun.fan@brunel.ac.uk

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Abstract. Based on the recent studies of the effects of lattice misfit and substrate chemistry on prenucleation, we investigate the interface between liquid Mg and MgO{111} using an *ab initio* molecular dynamics simulation (*A/MD*) technique. Our study reveals the formation of an atomically rough Mg layer on the {111}MgO surface when MgO is in contact with Mg melt. This atomically rough substrate surface deteriorates significantly the atomic ordering in the liquid adjacent to the liquid/substrate interface. Consequently, it reduces the potency of MgO as a substrate for heterogeneous nucleation.

Introduction

Grain refiners have been widely used in casting of light metals to improve the mechanical properties of the products. Traditionally, grain refinement is achieved by enhancing heterogeneous nucleation through addition of potent solid particles [1,2]. Recently, it has been suggested that the most effective grain refinement can be achieved by the least potent particles if no other more potent particles of significance exist in the melt [3]. The role of MgO in nucleation of Mg is a good model system to demonstrate this theory [3]. Magnesia (MgO) exists in Mg melts due to the high affinity between O and Mg. Experiments showed that oxidation of the Mg alloys occurs at high temperature and MgO is the major products [4-6]. The naturally occurring MgO particles behave as nucleation sites and attribute to refinement of Mg alloys [5]. The misfit between MgO{111} and Mg{0001} is large (8.1%), which makes the L-Mg/MgO{111} a good case to study the structural effect on prenucleation.

Prenucleation refers to the atomic ordering in the liquid adjacent to the substrate at temperatures above the nucleation point. Men and Fan performed atomistic MD simulations of the structural effect (lattice misfit between the substrate and metal) on the prenucleation. A substrate of a smaller misfit provides better structural templating for prenucleation [7], in agreement with the epitaxial nucleation model [6]. Recently we explored the chemical effect of substrates on the prenucleation of light metal adjacent to potent substrates and revealed that a chemical affinitive substrate promotes prenucleation, whereas a chemical repulsive substrate reduces it [8]. Based on these studies, here we investigate the prenucleation in the liquid Mg adjacent to the MgO{111} substrate using a parameter-free *ab initio* MD technique. Both Mg-terminated and O-terminated MgO{111} surfaces were used as starting configurations. Our simulations show a general trend of prenucleation phenomena in Mg liquid induced by the MgO{111} substrates. The obtained information is not only helpful to understand the prenucleation of Mg alloys, but also to get some insight into solidification processes in general.

Details of Computations

The simulation technique uses the periodic boundary conditions (PBC). Sizable supercells were built for producing meaningful results of *ab initio* MD simulations. A hexagonal supercell with $a = 5a_h$, here $a_h = (\sqrt{2}/2)a_o$ and a_o is the lattice parameter of MgO was built for the L-Mg/MgO{111} systems. The substrate is composed of four O layers and three Mg layers (O-terminated) or five Mg layers (Mg-terminated). The length of c -axis is set according to the density of liquid Mg.

We employed the first-principles code VASP (Vienna *Ab initio* Simulation Package) [9] which uses the *ab initio* density functional theory (DFT) within the projector augmented-wave (PAW) framework [10]. The exchange and correlation terms were described using the generalized gradient

approximation (GGA) [11]. For *ab initio* MD simulations, we employed a cut-of energy of 320 eV and the Γ -point in the Brillouin zone.

Mg melt was generated by equilibrating for 6000 to 8000 steps (1.5 fs/step), or 10 picoseconds (ps) at 3000 K. Then the liquid was cooled to the designed temperature. The obtained liquid Mg was used to build the Mg(liquid)/substrate systems, which were heated at the designated temperature for about 7000 steps or ~ 10 ps to ensure equilibrium by checking the configurations and the total energies of the systems. In order to obtain results of meaningful statistics [8,12], we used several different starting configurations and employed the time-averaged atomic position method, using sampling for 2000 to 3000 steps (4 to 6 ps). All substrate/liquid atoms were fully relaxed during the simulations.

Results and Discussions

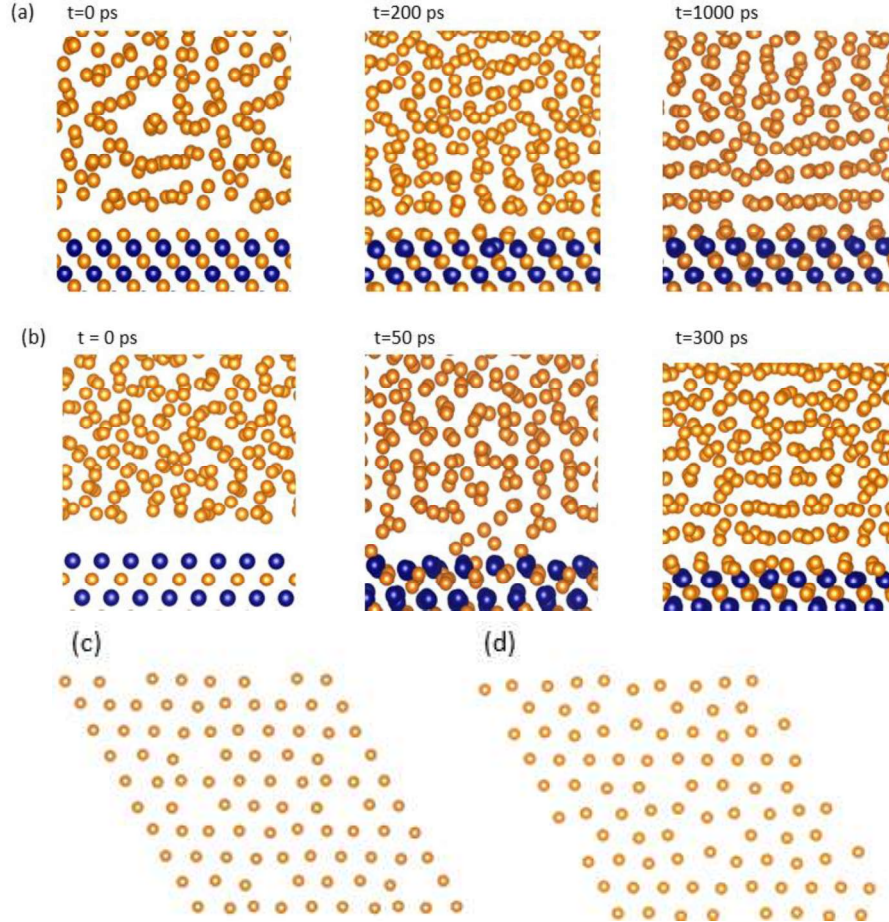


Figure 1. Snapshots showing the formation processes (a, b) and the resultant atomic arrangements of the newly formed Mg layer on the MgO{111} substrates with Mg- (a, d) and O-termination (b, c). The orange spheres represent Mg, dark blue for O.

First we address formation processes of the MgO{111} surface in liquid Mg by means of *ab initio* MD simulations using the O- and Mg-terminated MgO{111} substrates. The simulations showed that on the O-terminated substrate the liquid Mg atoms adjacent to the substrate were moving quickly and approaching to terminating O layer, as shown in Fig. 1b. Then a new Mg layer was formed on the substrate. This movement is accompanied by the movements of other adjacent Mg atoms, gradually forming layers of Mg on the substrate. This process happens in a rather short time (0.1 to 0.3 ps). Careful analysis shows that there are vacancies at the newly formed Mg layer (Fig. 1c). For the liquid Mg on the Mg-terminated MgO{111} substrate, during the MD simulations some of the terminating Mg atoms/ions were gradually moving into the liquid, leaving vacancies at the terminating Mg layer (Figs. 1a and 1d). Analysis showed no notable difference for the simulated systems from the O-

termination or Mg-termination $\text{MgO}\{111\}$ in liquid Mg with the resultant atomic arrangements of the metal layer (Fig. 1).

Fig. 1c and 1d show that the atoms in the newly formed Mg layer are ordered, forming a 2-dimensional (2D) structure containing vacancies. Analysis showed the concentration of the vacancy is 8 % for both cases (Fig. 1c and 1d). These vacancies cause roughness of the substrate surfaces at atomic level.

Root mean square (RMS) has been widely used to measure the roughness of a solid surface. For the newly formed Mg layer, the surface roughness mainly comes from the Mg vacancies. Therefore, using the RMS relation, $R_{\text{RMS}} = [\sum(\Delta z/d_0)^2/n]^{1/2} \times 100\%$, here Δz is the height difference of one atom with respect to the averaged plane and d_0 the interlayer spacing, n is the number of atoms in the area. $(\Delta z/d_0) = 0$ for an occupied site and $(\Delta z/d_0) = 1$ for an unoccupied site. In this way we obtain $R_{\text{RMS}} = 28\%$ for the newly formed Mg substrate surface.

Next we investigate the impact of the rough substrate surface on atomic ordering in the adjacent liquid Mg. Fig. 2a shows a snapshot of the equilibrated L-Mg/MgO $\{111\}$ interfaces.

The density profile of liquid perpendicular to a substrate, $\rho(z)$ provides a clear statistic description of the atomic layering phenomenon [7,8]. We analysed the density profile for the integrated configurations of the simulated systems for over 3 ps. The density profile, $\rho(z)$ is plotted and shown in Fig. 2b.

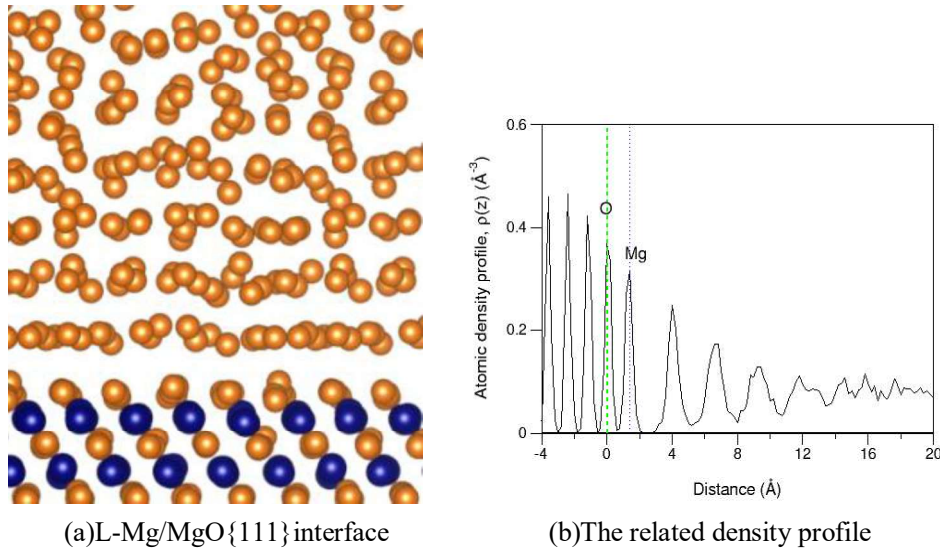


Figure 2. Snapshot for an equilibrated L-Mg/MgO $\{111\}$ interface (a) and the related atomic density profile, $\rho(z)$ (b) simulated at 1000 K. In 2a, the orange spheres represent Mg atoms/ions, the dark blue for O ions. The vertical dotted lines in 2b are used to indicate the important density peaks.

The density profile corresponds well to the related snapshot of the L-Mg/MgO $\{111\}$ interface. The outmost O layer has a sharp peak (the dotted green line). The newly formed Mg layer has also a rather sharp peak (the dotted blue line) though its peak height is lower than that of the outmost O layer. On this Mg layer, there are four recognizable liquid Mg layers. The first liquid Mg layer is well separated from the newly formed Mg layer of the substrate with an interlayer spacing of 2.61 \AA which is close to the interlayer spacing along the $[0001]_{\text{Mg}}$ axis. It is noted that there is a small shoulder at the left side of the first Mg peak. Analysis showed that the atoms at the shoulder of the first Mg peak are mainly positioned at the top of the vacancies of the newly formed Mg layer. This is understandable that the vacancies at the 2D Mg structure produce local potential wells which attract liquid Mg atoms. Fig. 2b also showed that the heights of the peaks decrease with going deeper into liquid.

Atomic in-plane ordering of liquid in the layers adjacent to the substrates, or in-plane ordering coefficient is a good indicator for the description of localization of the atoms [7,8]. Here we analyse the in-plane ordering for the newly formed substrate surface layer and the liquid Mg layers adjacent

to the substrates for the integrated configurations from simulations of over 6 ps. The analysis produced that the newly formed Mg layer has a high in-plane ordering coefficient, $S(z)$ being 0.65. $S(z)=0.003$ for the first Mg peak, indicating liquid-like nature of these Mg atoms. $S(z)$ is approaching zero for Mg atoms at the rest Mg layers.

MgO has the NaCl-type structure. The stable surface of MgO at ambient conditions is MgO{001}. A smooth MgO{111} surface is polar and unstable. The situation is different for MgO in a (liquid) metal. The free-electron-see of a metal enhances the occupation of the sites by Mg on the O layer at the MgO{111} substrate. This occupation is also balanced by the interactions between the substrate and the liquid metals. For MgO{111} in liquid Mg, the newly formed Mg surface layer contains vacancies due to the strong chemical interaction between the outmost O layer and the liquid Mg. These vacancies at the terminating Mg layer result in formation of a rough surface of the substrate. This atomically rough surface strongly weakens the templating effect of the substrate.

The epitaxial nucleation theory suggests that heterogeneous nucleation proceeds by a layer-by-layer growth mechanism through structural templating [6]. The lattice misfit has influences on the nucleation undercooling and therefore, can be considered as a direct measure of potency of nucleating particles [7]. This also indicates that heterogeneous nucleation can be controlled by manipulating the lattice misfit between the substrate and the metal. A good example is the recent observation of formation of the 2-dimensional compound (2DC) TiAl₃ on the TiB₂{0001} surface. This newly formed 2DC TiAl₃ decreases the lattice misfit from 4.22% to 0.09 %. This is responsible for the good performance of the Al-5Ti-1B grain refiners [2]. Our recent study also showed chemical factor of substrate on prenucleation phenomenon [8]. A chemical affinitive/repulsive substrate promotes/impedes the prenucleation in the liquid metal adjacent to the substrate. Recent HR-TEM observations revealed formation of a 2DC ZrTi₂ on TiB₂ substrate in Al, the L-Al/TiB₂ (2DC ZrTi₂) interface system [13]. This causes the restoring of the lattice misfit from 0.09 to 4.2 % [13]. *Ab initio* MD simulations discovered that at the L-Al/TiB₂ (2DC ZrTi₂) interface, the surface Zr atoms intrude about 0.45 Å into liquid Al. This causes atomic roughness of the substrate surface. Therefore, the Zr poisoning effect originates from the combination of the lattice mismatch and the surface roughness at atomic level [14]. In the current study we investigated the geometry of MgO{111} surface of thermally equilibrated L-Mg/MgO{111} systems. In liquid Mg, the MgO{111} substrate is terminated by one Mg layer which displays ordering but has vacancies. These vacancies result in atomic roughness of the substrate surface, which reduces the layering and diminishes the in-plane ordering of the liquid Mg adjacent to the substrate. Consequently such atomically rough surface weakens prenucleation at temperatures above nucleation temperature and impedes subsequent heterogeneous nucleation, leading to a larger nucleation undercooling. This study indicates that by manipulation of the atomic roughness of the substrate surface, one may control the nucleation processes of metallic liquid to obtain alloys of desired microstructures.

Summary

AIMD simulations revealed the formation of an Mg layer at the MgO{111} substrate in liquid Mg. This newly formed Mg layer exhibits atomic ordering but contains vacancies. The calculation provided a RMS roughness of 28%. This atomic roughness of the substrate surface weakens layering and diminishes strongly the in-plane ordering of the adjacent liquid Mg, and therefore reduces the templating effect of the substrate. The surface roughness can be considered as the third factor affecting the atomic ordering of liquid metals adjacent to the substrate, beyond the structural [7] and chemical [8] factors. Rough substrate surface may be used as a practical means to manipulate heterogeneous nucleation for more effective grain refinement.

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