Dynamics Investigation of Prenucleation at Liquid–Metal/Oxide Interfaces

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Oxide particles, including magnesia, spinel, and alumina, are inevitably formed in the liquid during liquid–metal handling and casting. They may act as nucleation sites for potential grain refinement. Knowledge about atomic ordering (prenucleation) at liquid–metal/oxide (M(l)/oxide) interfaces is important for an understanding of heterogeneous nucleation during casting.

liquid–metal/oxide interfaces prenucleation ab initio molecular dynamics modeling heterogeneous nucleation

1. Introduction

The light metals, Mg and Al have close-packed structures [1][2]. Their densities are about one-fifth and one-third of that of iron, respectively. Moreover, Mg and Al metals have unique properties, such as high specific strengths and excellent castability. Thus, Mg and Al alloys have been widely used in a variety of engineering fields, particularly in the automotive and aerospace industries [3][4]. The current regulations on environmental protection demand further improvements in the chemical and mechanical properties of light alloys. One important approach is to achieve solidified products of fine and uniform microstructures by controlling the solidification processes [5][6][7].

The conventional way to obtain a fine and uniform microstructure of cast alloys is via the addition of grain refiners during casting [4][7]. The added chemicals remain in the cast parts, which may hinder the recycling of the products. Recently, Fan and co-workers developed a new approach to grain refinement using native oxide particles as nucleation sites [6]. This approach is helpful not only for obtaining cast parts of increased integrity, improved mechanical properties, and reduced casting costs but also for facilitating metal recycling. Meanwhile, the application of this approach for casting alloys of desirable microstructure and properties demands knowledge about the atomic ordering at the interfaces between the liquid metals and the oxide substrates.

There have been both experimental and theoretical efforts to obtain insight into the formation, polymorphs, and morphologies of oxide particles and atomic arrangements at liquid–metal/oxide (noted as M(*l*)/oxide) interfaces. Here, researchers provide an overview of the recent advances in the understanding of prenucleation at the M(*l*)/oxide interfaces using ab initio molecular dynamics (AIMD) techniques.

2. AIMD Investigations of Prenucleation at the M(*l*)/Oxide Interfaces

2.1. Supercells and Details of AIMD Simulations

High-resolution transmission electron microscopy (HR-TEM) investigations revealed that the native oxide particles have dominant MgO{1 1 1}, γ-Al_2O_3{1 1 1}, $MgAl_2O_4${1 1 1}, and α-Al_2O_3{0 0 01} facets in liquid metals and their alloys. Based on the experimental results, the researchers built supercells for the M(*l*)/oxide interfaces for the AIMD simulations. The built supercells are hexagonal. The dimension of the *a*-axis is a = (5√2/2) a_0 for MgO{1 1 1}, a = 3 a_0 for α-Al_2O_3{0 0 0 1} and a = (3√2/2) a_0 for $MgAl_2O_4$ and γ-Al_2O_3 spinel (a_0 is the lengths of the *a*-axis of the oxides with consideration of the thermal expansion at the simulation temperature). The dimension of the *c*-axis is determined by the oxide slab and the number of metal atoms with the atomic volume at the simulation temperature [2].

A pseudo-potential plane-wave approach based on the density-functional theory (DFT) was used for the present study. This approach was implanted into the first-principles code VASP (Vienna ab initio simulation package) [8]. VASP permits variable fractional occupation numbers, which works well for insulating/metallic interfaces [8][9]. The molecular dynamics simulation uses the finite-temperature density functional theory of one-electron states, the exact energy minimization and calculation of the exact Hellmann-Feynman forces after each MD step using the preconditioned conjugate techniques, and the Nosé dynamics for generating a canonical NVT ensemble. The Gaussian smearing was employed with the width of smearing (0.1 eV). The code also utilizes the projector augmented-wave (PAW) method [10] within the generalized gradient approximation [11].

For electronic structure calculations, researchers used cut-off energies of 400.0 eV for the wave functions and 550.0 eV for the augmentation functions. Reasonably dense *k*-meshes were used for sampling the electronic wave functions, e.g., a 2 × 2 × 1 (8 *k*-points) in the Brillouin zone (BZ) of the supercell of the interfaces, based on the Monkhorst-Pack scheme [12]. For the AIMD simulations of the interfaces, researchers employed cut-off energy of 320 eV and the Γ-point in the BZ, considering the lack of periodicity of the whole system in molecule/solid-substrate and liquid/solid interfaces [9][13][14][15][16]. Test simulations using different cut-off energies demonstrated that the settings are reasonable.

The researchers prepared liquid Al or Mg samples by equilibrating at 3000 K for 2000 steps (1.5 fs per step). Then the obtained liquid was cooled to the desired temperature. researchers used the obtained liquid Al or Mg samples together with the oxide substrates for building the M(*l*)/oxide simulation systems. researchers employed two different approaches in the AIMD simulation depending on the systems. Full relaxation of atoms is used all the time. The other adopted a two-step approach: researchers first performed AIMD simulations with the substrate O atoms pinned for about 2 ps (1.5 ps per step). Then, researchers equilibrated the systems further with full relaxation of the substrate atoms for another 4000 to 7000 steps. The time-averaged method was used to sample the interfaces over 3.0 to 4.5 ps to ensure statistically meaningful results [9][13].

2.2. Prenucleation at the Al(l)/Al_2O_3 Interfaces

The researchers first discuss the atomic evolutions at the M(*l*)/oxide interfaces using the Al(*l*)/Al_2O_3 interfaces at 1000 K as an example. During simulations, researchers observed that the liquid Al atoms move quickly to the oxide substrates, forming a terminating layer. The number of atoms in this newly formed metal layer becomes gradually stabilized, forming a new substrate surface within 2 ps. Then, the atoms/ions in the oxide substrates vibrate around their equilibrium positions, while the liquid metal atoms away from the interfaces move around freely. The simulations revealed that the behavior of liquid atoms near the substrates varies depending on the nature of the substrate surfaces.

The rate for reaching equilibration of the M(*l*)/oxide interfaces can also be observed from the variations of total valence-electrons free energies with the simulation time, for the Al(*l*)/Al_2O_3 interfaces [17][18]. The energy reduction is fast in the first 0.5ps and then levels off with time. The time required for reaching a constant energy value varies for the different interfaces.

The terminating Al layers at the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ interface are flat and contain vacancies. The terminating Al layers at the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$ and Al(*l*)/α-$Al_2O_3\{0\ 0\ 0\ 1\}$ interfaces contain both vacancies and displacements along the direction perpendicular to the substrates. Analysis showed that there is moderate atomic ordering in the first Al layer but little in the second Al layer in the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ interface. At the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$ and Al(*l*)/α-$Al_2O_3\{0\ 0\ 0\ 1\}$ interfaces even the first Al layer has little atomic ordering.

The epitaxial nucleation model indicates that the substrate surface atoms template ordering in the nearby liquid to nucleate [19]. The terminating Al atoms at the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}$ interfaces show stronger localization than those at the Al(*l*)/α-$Al_2O_3\{0\ 0\ 0\ 1\}$. At the first layer of the Al(*l*)/α-$Al_2O_3\{0\ 0\ 0\ 1\}$ and Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$ interfaces, Al atoms are more liquid-like as compared with those at the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ interface. Thus, prenucleation at the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ interface is more pronounced than at the other interfaces.

There are apparent holes at the termination layers of the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}$ systems. The occupation of the octahedral sites in the terminating layers was analyzed using the time-averaged atomic positions over 3 ps: The occupation rate at the terminating layer by Al is 54.0% in the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$ system and 58.1% in the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ system. These values are lower than that in the bulk alumina (66.7%), but they are comparable with that for the Al(*l*)/α-$Al_2O_3\{1\ 1\ 1\}$ system (55.9%). These occupation rates of the terminating Al layers are notably lower than those in the Al(*l*)/$MgAl_2O_4\{1\ 1\ 1\}$ system (70.4 to 75.0%) [20]. This reflects the role of the crystal chemistry of the substrates. The simulations also revealed structural coupling of the terminating Al layer to the γ-$Al_2O_3\{1\ 1\ 1\}$ substrate: In the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$ system, the multiple-peaked terminating Al layer is coupled to the single peak in the subsurface Al layer, whereas in the Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ system the single-peaked Al terminating layer is accompanied by the multiple-peaked subsurface Al layer in the substrate.

In summary, researchers have the following conclusions:

(i). The Al and O atoms/ions in the substrates form layers of atomic ordering;

(ii).The substrates are terminated by a layer of Al atoms. The terminating Al atoms form a single peak at the Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_2}$ interface, whereas they form multiple peaks (three sublayers) at the Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_1}$ interface;

(iii).The Al-O interatomic distances between the terminating Al atoms and the outmost O ions are close to those in the bulk substrate. This indicates that the terminating Al atoms are chemically bonded to the substrates, becoming an integrated part of the substrates;

(iv).Both layering and in-plane ordering at the Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_2}$ interface are more pronounced than that at Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_1}$ and Al(*l*)/α-Al_2O_3{0 0 0 1}.

(v).There are atomic vacancies in the terminating Al layers.

Charge and charge transfer provide direct evidence about chemical interactions in a compound or at an interface. researchers performed electronic structure calculations of the equilibrated Al(*l*)/Al_2O_3 interfaces.

The O and Al ions in the substrates are charged with −1.3e and +2.0e, respectively. The Al away from the substrates is electronically neutral. The terminating Al atoms are positively charged with electrons transferred to the outmost O ions. Thus, chemically the terminating Al ions/atoms are bonded to the substrates, being the integrated part of the substrates.

In summary, the AIMD simulations revealed an Al layer terminating the Al(*l*)/Al_2O_3 substrate. The terminating Al atoms are positively charged, chemically bonded to the outmost O ions, thus being an integral part of the substrates. The terminating Al layers contain vacancies and displacements vertical to the substrate surface, resulting in atomic roughness. Consequently, the prenucleation at the Al(*l*)/Al_2O_3 interfaces is overall weakened, and they are impotent substrates for heterogeneous nucleation of solid Al.

2.3. Prenucleation at the M(l)/MgO{1 1 1} (M = Mg, Al) Interfaces

The Mg and O layers in the MgO{1 1 1} substrates are well-ordered and solid-like. This corresponds to the strong chemical bonding in MgO. Although the liquid metal atoms away from the substrates display disordering and behave liquid-like, those near the interfaces exhibit layering. There is a metal layer terminating the MgO{1 1 1} substrates. The terminating Mg atoms at the M(*l*)/MgO{1 1 1}$_{Mg}$ form a single peak, whereas the terminating Al atoms at Al(*l*)/MgO{1 1 1}$_{Al}$ form a peak and a shoulder at 0.8Å away from the artificial dividing interface. There is an isolated Al layer (the first metal layer) at the Al(*l*)/MgO{1 1 1}$_{Mg}$ interface, whereas the first Al layer at the Al(*l*)/MgO{1 1 1}$_{Al}$ interface is admixed with the second Al layers.

researchers also analyzed the time-averaged atomic arrangements for the liquid atoms adjacent to the substrates at the M(*l*)/MgO{1 1 1} interfaces.

In the Al(*l*)/MgO{1 1 1}$_{Mg}$ system, the terminating Mg layer at the Al(*l*)/MgO{1 1 1}$_{Mg}$ interface has a sharp peak in the atomic density profile, and the Al atoms in the first layer display significant ordering. Similarly, the terminating Mg atoms at the Mg(*l*)/MgO{1 1 1} interface form a sharp peak in the density profile and display strong localization. Meanwhile, there are some unoccupied sites at the terminating layer. Statistics provided the site occupation of 92% [21]. Comparatively, the terminating Al atoms at the Al(*l*)/MgO{1 1 1}$_{Al}$ interface are less localized and contain some disordering. This is reflected in the in-plane ordering coefficients. The in-plane ordering coefficients of the terminating Mg layers at both Mg(*l*)/MgO{1 1 1} and Al(*l*)/MgO{1 1 1}$_{Mg}$ interfaces are close to around 0.6, being significantly larger than that (about 0.2) at the Al(*l*)/MgO{1 1 1}Al interface.

The present study reveals that the atomic structure and the interfacial interactions are crucial in the determination of the prenucleation at a liquid/solid interface. This also indicates possibilities to control the prenucleation or nucleation potency of the substrates via, e.g., segregating impurity atoms at the interfaces.

2.4. General Features of the M(l)/Oxide Interfaces

The investigation revealed a wide variety of atomic arrangements at the M(*l*)/oxide interfaces, as exampled in the previous sections. The systematic study revealed the common features of the M(*l*)/oxide interfaces.

As mentioned previously, Mg and Al have different valence electrons. To keep charge balance, the different valences of Al (3+ in ionic model) and Mg (2+) cause different occupation ration (N_{metal}/N_O) in the bulk substrate: 100.0% for MgO, 66.7% (2/3) for Al_2O_3 and 75.0% (3/4) for $MgAl_2O_4$. Such charge balance influences the composition and structure of the terminating metal layer at the M(*l*)/oxide interfaces. This normalization has been applied to calculate the atomic roughness [18].

Table 1. Summary of the characteristics of the terminating metal layer in different M(*l*)/oxide interfaces.

Interface	*f*(%)	M Oc.(%)	*R*(%)	*q*(e/M)	n_{Layers}	$S_M(z)$ 1st L_M	Prenucl.
Al(*l*)/Al{111}$_{Al}$ [22]	0.0	SP 100.0	0.0	0.0	6	0.50	Strong
Mg(*l*)/MgO{111}$_{Mg}$ [21]	+7.9	SP, vac. 92.0	4.0	+0.60	3–4	0.01	researchersak
Al(*l*)/MgO{111}$_{Mg}$ [17][23]	−2.2	SP 100	0.0	+0.69	4	0.30	Moderate-strong
Al(*l*)/MgO{111}$_{Al}$ [17][23]	−2.2	MP, vac. 73.3	8.2	+0.94	3–4	0.01	researchersak
Al(*l*)/α-Al_2O_3{0001}$_{Al}$ [17][23]	+5.6	MP, vac. 55.9	30.8	+0.95	3	0.01	researchersak
Al(*l*)/$MgAl_2O_4${111}$_{Al\_2}$ [20]	+1.4	SP, vac.	5.3	+1.07	3–4	0.18	Moderate

Interface	*f*(%)	M Oc.(%)	*R*(%)	*q*(e/M)	n_{Layers}	S_M(z) 1st L_M	Prenucl.
		70.4					
Al(*l*)/MgAl$_2$O$_4${111}$_{AlAlAl}$ [20]	+1.4	MP, vac. 71.8	18.7	+0.40 to +1.42	3	0.01	researchersak
Al(*l*)/MgAl$_2$O$_4${111}$_{MgAlAl}$ [20]	+1.4	MP, vac. 75.0	14.7	+0.44 to +1.17	3	0.05	researchersak
Al(*l*)/MgAl$_2$O$_4${111}$_{MgAlMg}$ [20]	+1.4	MP, vac. 75.0	11.2	+0.21 to +1.11	3	0.02	researchersak
Al(*l*)/γ-Al$_2$O$_3${111}$_{Al\_2}$ [18]	+3.3	SP, vac. 58.1	11.1	+0.80 to +1.20	3–4	0.03	researchersak
Al(*l*)/γ-Al$_2$O$_3${111}$_{Al\_1}$ [18]	+3.3	MP, vac. 54.0	31.1	+0.40 to +1.50	3	0.01	researchersak

rium are

- Crystallographically, there is a range of lattice misfit, from moderate (1.4%) to high (7.9%);
- Geometrically, although the terminating M layer may have a single peak in the atomic density profiles, it contains atomic vacancies and/or vertical atomic displacements and, therefore, is atomically rough.
- Chemically, atoms in the terminating M layer are positively charged and are bonded to the substrates, becoming an integral part of the substrates;
- The terminating metal atoms exhibit structural coupling with the metal atoms at the substrate subsurface layer, which influences the prenucleation at the interfaces.

In addition, **Table 1** shows that layering at the M(*l*)/oxide interfaces ($n_{Layer} \leq 4$) is notably weaker than that of the M(*l*)/M(*s*) interface [22][24]. For instance, there is a flat and charged Mg terminating layer at the Al(*l*)/MgO{1 1 1}$_{Mg}$ interface. It has four recognizable layers, and the in-plane ordering coefficient of the first layer is 0.18 [17][23]. This suggests that the positive charging of the terminating metal atoms influences the ordering of the nearby metal atoms and thus hinders prenucleation at the interfaces.

Lattice misfit between a substrate and a solid metal has been a crucial factor affecting mainly atomic ordering at the liquid–metal/solid interfaces. **Table 1** shows that the lattice misfit between MgO{1 1 1} and Mg{0 0 0 1} is significant (7.9%). At the Mg(*l*)/MgO{1 1 1}$_{Mg}$ interface with a flat Mg terminating layer, there are three to four recognizable layers and 8% vacancies in the terminating layer, likely due to the lattice misfit [21]. Therefore, the weak prenucleation at Mg(*l*)/MgO{1 1 1} originates from the combined effects of pronounced lattice misfit, charging, and roughness of the terminating Mg layer.

Clearly, the atomic roughness of the terminating metal layer reduces the in-plane ordering in a more or less linear way with R < 10%. When R > 10%, the in-plane ordering coefficients at the M(*l*)/oxide interfaces are small.

2.5. Potency of the Oxide Substrates and Its Role in Heterogeneous Nucleation

According to the heterogeneous nucleation theory, potency represents the intrinsic capability of a substrate to nucleate a solid phase in the liquid [6][7][25]. The prenucleation at a liquid/solid interface also relates to the intrinsic capability of the substrate to atomic template ordering in the liquid adjacent to the interface and, therefore, corresponds to the potency of the substrate for nucleation of the solid [22][24][26]. From **Table 1**, researchers can rank the M(*l*)/oxide interfaces in terms of their capability for prenucleation (nucleation potency from high to low): Al(*l*)/MgO$\{1\ 1\ 1\}_{Mg}$ > Al(*l*)/$MgAl_2O_4\{1\ 1\ 1\}_{Al\_2}$ > Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ > Mg(*l*)/MgO{1 1 1}~Al(*l*)/α-Al_2O_3\{0 0 0 1\}~Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_1}$.

The prenucleation at Al(*l*)/MgO$\{1\ 1\ 1\}_{Mg}$ and Al(*l*)/$MgAl_2O_4\{1\ 1\ 1\}_{Al\_2}$ is more pronounced than that at the other interfaces. This suggests that the atomic roughness of the terminating metal layer hinders prenucleation. This is confirmed by the weak prenucleation at Al(*l*)/γ-$Al_2O_3\{1\ 1\ 1\}_{Al\_2}$ interface, which has a notable lattice misfit and high atomic roughness caused by vacancies.

Heterogeneous nucleation depends on the nucleation potency of substrates or the prenucleation at the M(*l*)/oxide interfaces. The stronger the prenucleation is, the smaller the driving force it requires.

In order to obtain cast products of fine and uniform microstructures, attention has been paid to the potent particles as potential nucleation sites for grain refinement. The most successful grain-refiners for Al alloys are Al-Ti-B master alloys which contain TiB_2\{0 0 0 1\} substrates [7][27][28][29][30][31][32][33]. Recently, HR-TEM observations revealed that the TiB_2\{0 0 0 1\} substrates are covered by a two-dimension compound (2DC), most likely $TiAl_3$ 2DC [31]. This 2DC enhances the potency of the TiB_2\{0 0 0 1\} substrate for Al nucleation. In this case, the size of the TiB_2 particles plays a crucial role in grain initiation [5][7][34][35]. However, heterogeneous nucleation occurs on the TiB_2 particles of all sizes at the same temperature. When the temperature lowers to the grain initiation temperature, grain initiation starts with the large particles first and gradually occurs at the smaller ones with increasing undercooling. This grain initiation process is considered progressive [5][34], in which only a small number of large-sized particles function as grain-refinement sites.

The oxides are impotent nucleation substrates for Al and Mg alloys. Thus, they require larger nucleation undercooling, which might be lower than that of the corresponding grain initiation temperature if no other more potent particles of significance exist. Under such a situation, when the temperature reaches the nucleation temperature, the nucleation and grain initiation may occur almost simultaneously, in an explosive way [5][6][34]. On most of the substrates, grain initiation occurs. This means large fractions of particles become grain-initiation sites, and thus, the cast products may have fine and uniform microstructures.

3. Modification of the Terminating Metal Layers at the M(*l*)/Oxide Interfaces

Experimental observations revealed the formation of different oxide particles in alloys, e.g., coexisting of MgO and $MgAl_2O_4$ spinel particles in Al-Mg alloys and α- and γ-Al_2O_3 particles in Al-rich alloys. These oxide particles exhibit a wide variety of nucleation potency. Moreover, one type of oxide particle, e.g., γ-Al_2O_3 particles, may have terminating surfaces of different nucleation potency [18]. In liquid, these oxide particles compete for heterogeneous nucleation, and consequently, only some oxide particles of higher potency may participate in the nucleation process [5][34].

Wang et al. investigated the cast samples of Mg-0.5Ca alloy and observed segregation of impurities, including Ca on the MgO{1 1 1} substrates [36]. Ma et al. studied the effects of Cu segregation at the sapphire substrate on the nucleation of Al using an AIMD simulation technique [37]. Recently, Wang et al. observed the segregation of La and Y atoms on Al(*l*)/γ-Al_2O_3{1 1 1} substrates using the HR-TEM techniques [38]. To have a better knowledge of the segregation of the nd^1 elements, Sc, Y, and La atoms at the oxide interfaces, researchers performed systematic AIMD simulations [39].

The AIMD simulations revealed the formation of a 2DC layer of Al_2La at both Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_1}$ and Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_2}$ interfaces. The terminating Al/La layers are composed of multiple peaks and thus become atomically rougher as compared with those Al(*l*)/γ-Al_2O_3{1 1 1} interfaces without segregation. Such surface roughening deteriorates the terminating capability of the Al(*l*)/γ-Al_2O_3{1 1 1}$_{Al\_2}$ interface. Consequently, the nucleation potency of both γ-Al_2O_3{1 1 1}$_{(Al/La)\_1}$ and γ-Al_2O_3{1 1 1}$_{(Al/La)\_2}$ substrates is reduced.

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