Effects of lattice mismatch on interfacial structures of liquid and solidified Al in contact with hetero-phase substrates: MD simulations

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H Men[1] **and Z Fan**

The EPSRC Centre-LiME, BCAST, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

E-mail: Hua.Men@brunel.ac.uk

Abstract. In this study, the effects of the misfit on in-plane structures of liquid Al and interfacial structure of solidified Al in contact with the heterophase substrates have been investigated, using molecular dynamics (MD) simulations. The MD simulations were conducted for Al/fcc (111) substrates with varied misfits. The order parameter and atomic arrangement indicated that the in-plane ordering of the liquid at the interface decreases significantly with an increase of the misfit, i.e., solid-like for small misfit and liquid-like for large misfit. Further, our MD simulation results revealed that a perfect orientation relationship forms at the interface between the substrate and the solidified Al for a misfit of less than -3% and the boundary is coherent. With an increase in the misfit, Shockley partial and extended dislocations form at the interface, and the boundary becomes a semi-coherent or low-angle twist boundary.

1. Introduction

The structural properties of heterogeneous liquid-solid interfaces have been the subject of many nucleation and wetting studies [1]. Theoretical studies [2-6] have suggested that the liquid atoms adjacent to the solid substrate exhibit a density oscillation at the interface or free surface. Experimental observations [7-9] and MD simulations [10-13] have demonstrated that the liquid atoms can order for a few atomic layers at the interface or free surface, but that the in-plane structure within these layers could be liquid-like or solid-like. The effect of the substrate on the in-plane ordering has not been made clear.

X-ray diffraction experiments and MD simulations have indicated that the in-plane structure of liquid Ga at its free surface is similar to the bulk liquid without any obvious positional order [14, 15], and direct high-resolution transmission electron microscopy (HRTEM) observations [16, 17] have provided evidence for the layering and in-plane ordering of liquid Al adjacent to the interface with sapphire. High-energy x-ray reflection has revealed that the layering at a liquid Hg/sapphire interface is less pronounced than at a liquid Hg/vapor interface [18]. With MD simulation, Hashibon et al. [11, 12] studied a model metallic liquid/substrate interface to investigate the structural correlations between the liquid metal and the substrate. An exponential decay of the density profile within the liquid metal was found at the interface [12], and this was independent of the orientations of the substrates [11]. There is a far greater in-plane ordering of the liquid atoms in contact with a bcc (100) substrate than a (110) substrate [11]. These findings suggest that substrate orientation has a strong influence on in-plane atomic ordering.

The present industrial practices of grain refinement have shown that a very potent nucleating particle requires a good atomic match between the substrate and the solidified phase, typically with less than 10% misfit [19], suggesting that misfit has an important effect on the heterogeneous nucleation in the melts. For example, TiB_2 is very potent nucleating particles for α-Al [20]. HRTEM observations [20, 21] found that the TiB_2 particles in some Al amorphous alloys appear to be coated with a thin layer Al_3Ti, which has a small misfit of 0.09% with α-Al at 933 K and is essential for the TiB_2 to be potent nucleates.

In this paper, we have used MD simulations to investigate the effects of lattice misfit on the in-plane ordering of liquid atoms at the liquid/substrate interface and the structures of the solidified Al at the interface. Misfit has significant effects on the in-plane ordering at the liquid/substrate interface, as well as the boundary between the substrate and the solidified phase at the very earliest stage of the nucleation.

2. Simulation method

The MD simulations were conducted for Al atoms and an fcc substrate with the [111] surface orientation. The DL_POLY_2.20 MD package [22] was used in the simulations. Ercolessi and Adams's embedded atom method (EAM) potential for Al [23] was adopted to calculate the inter-atomic force, with a cut-off distance of R_{cut}=5.558 Å.

The setup of a representative simulation cell is shown in figure 1. The dark balls represent the substrate atoms, while the light balls represent the Al atoms. The initial configuration of Al has an fcc lattice, with a lattice parameter of 4.12 Å. The material of the substrate is also Al, with a negative mismatch of 0~-10%. The mismatch is defined as

$$f = \frac{d_m - d_{sb}}{d_m}$$

where d_m and d_{sb} are the corresponding inter-planar spacing of the metal and the substrate, respectively. Al atoms were allowed to move freely under the effect of the interatomic potential. The substrate atoms were frozen to a perfect fcc lattice configuration, which in this way can be considered as a dissimilar material with a much higher melting temperature. The dimensions of the substrate are $5d_{[111]} \times 18d_{[110]} \times 36d_{[211]}$, and the initial dimensions of Al are $18d_{[111]} \times 18d_{[110]} \times 36d_{[211]}$. Periodic boundary conditions were imposed in the $x([11\bar{2}])$- and $y([\bar{1}10])$-dimensions to prevent edge effects. The z-dimension ([111]) is considered as a dynamic variable, and above Al sample a vacuum region was inserted with periodic boundary conditions in all directions.
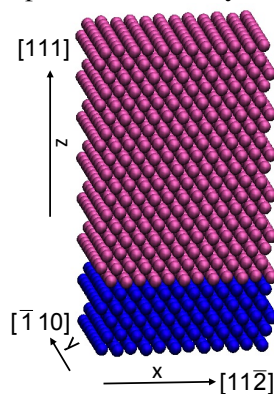

Figure 1. The illustration of a representative simulation cell. The dark balls represent the fcc substrate atoms, and the light balls represent the Al atoms.

Figure 2. The order parameter $S(z)$ of liquid Al in the MD simulation cells with f=0~-10%. It can be seen that the in-plane ordering at the interface decreases dramatically with an increase of f.

The velocity-Verlet algorithm was used to integrate the equations of motion, and the Berendsen NVT ensemble was used for the temperature control. The time step of the MD simulation was 0.001
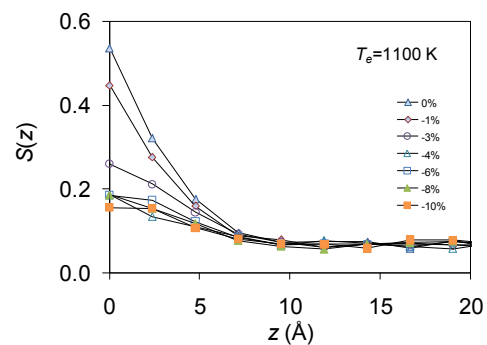
ps. The simulation was first performed at 1 K for 40,000 steps. The system temperature was then increased by a step of 50 K, and the simulation runs for 40,000 steps at each step temperature. After the system temperature was increased to 1400 K, it was cooled to the desired temperature or 0.001 K in a step of 50 K. Once the desired temperature was reached, the system was allowed to run at this temperature for a few tens of thousands of steps before taking the data. During this run, the total energy was monitored to verify the approach to equilibrium.

3. Results

3.1. Effect of misfit on in-plane ordering

To investigate the effect of lattice misfit on the in-plane ordering of liquid atoms at the interface, MD simulations were conducted for the simulation cells with different lattice misfits at a fixed temperature of 1100 K. The degree of ordering in the liquid can be measured by the order parameter $S(z)$, which is described elsewhere [24]. Figure 2 shows $S(z)$ of the liquid atoms in the MD simulation cells with f=0~-10%. The magnitude of f has a significant effect on $S(z)$ of the liquid atoms at the interface, and the in-plane ordering dramatically decreases with an increase of f. For f=0~-3%, the in-plane ordering of the liquid can be observed within the first three layers, but the value of $S(z)$ of the corresponding layer decreases significantly with an increase of f. When $|f| \geq 4\%$, the value of $S(z)$ of the liquid is less than 0.2 even at the first layer, just slightly greater than that of the bulk liquid, indicating that the ordering of the liquid atoms adjacent to the interface is considerably lower. This is in contrast to the layering of the liquid at the interface revealed by the density profile, which is independent of the magnitude of f [24].

Figure 3 shows the atomic arrangement in the first three layers of the liquid atoms in the simulation cell with f=-2% at T_e=1100 K. The dark balls represent the relaxed positions of the Al atoms at 0 K, and the light balls denote the instantaneous positions of Al atoms equilibrated for 40 ps at T_e=1100 K. The deviation of the instantaneous position from the relaxed position indicates the degree of disordering for the in-plane structure. It can be seen that the first and second layers of liquid atoms exhibit a solid-like structure, with much less ordering in the third layer.
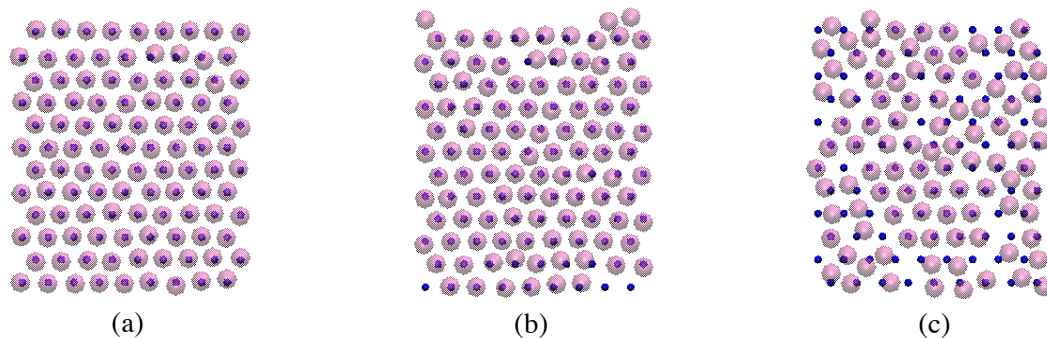

| (a) | (b) | (c) |

Figure 3. Snapshots of atomic arrangement in the (a) first, (b) second and (c) third layers of liquid atoms in the MD simulation cell with f=-2% at 1100 K. The dark balls represent the relaxed positions of Al atoms at 0 K, and the light balls represent the instantaneous positions of liquid atoms equilibrated for 40 ps at 1100 K. The first and second atomic layers exhibit a solid-like structure, and the third layer becomes less ordered.

3.2. Effect of misfit on interfacial structures of solidified Al

The magnitude of f also has a significant effect on the interfacial structures between the substrate and the solidified Al. Figure 4 shows the $[1\bar{1}0]$ projection of the configuration for (a) f=-2% and (b) -4%. A perfect lattice match can be observed at the interface between the substrate and the solidified Al for f=-2%, suggesting that a coherent boundary exists. For f=-4%, it can be seen that one part of the (111) plane of Al at the interface is displaced relative to the substrate atoms along $1/6[\bar{1}\bar{1}2]$, and an intrinsic

stacking fault (ISF) and a Shockley partial dislocation associated with the ISF form. Thus, the interface becomes semi-coherent. The partial is denoted by the symbol ⊥, and the short arrow represents its Burgers vector b=1/6$[1\bar{1}2]$ along the (111) slip plane. The ISF is marked by the dashed line. The regular stacking sequence is ABCABC for the (111) plane in the fcc metals (left), and is changed to ABC/BCA (right).
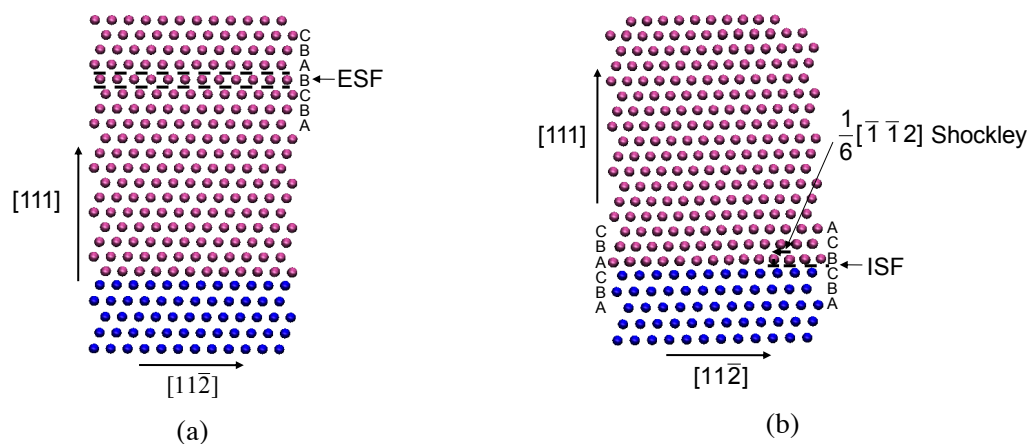

Figure 4. A $[1\bar{1}0]$ projection of the configuration of the systems with (a) f=-2% and (b) -4%. For the system of f=-2%, a perfect lattice match exists at the interface between the substrate and the solidified Al. For f=-4%, an ISF and a 1/6$[\bar{1}\bar{1}2]$ Shockley partial dislocation can be observed at the interface, and the boundary becomes semi-coherent.

Figure 5 (a) shows the $[1\bar{1}0]$ projection of the configuration of f=-6%. An ISF and a 1/6$[\bar{1}\bar{1}2]$ Shockley partial dislocation associated with the ISF can also be found at the interface. In the bulk Al, a SF tetrahedron in the 2nd, 3rd and 4th layers from the interface was observed. Figure 5(b) shows the $[\bar{1}\bar{1}2]$ projection of this configuration. It can be seen that an edge dislocation with b=1/2$[1\bar{1}0]$ on the (111) slip plane forms in the bulk Al, which is marked by the long arrow. It is noted that this dislocation is split into two Shockley partial dislocations at the interface (marked by two short arrows). Thus, the interface becomes a low angle twist boundary. The dissociation of a perfect dislocation can reduce the elastic strain energy, and simultaneously an ISF forms between the two Shockley partials. The separation of the extended dislocation is determined by the energy per unit area of the SF. The lower the SF energy is, the wider the split. The energy of the SF is relatively high for Al, 0.135 J m^{-2}, compared to 0.085 J m^{-2} for copper [25]. Therefore, the separation between two partials is relatively small, about $5d_{\{220\}}$ in the present case. Experimental measurements from weak-beam transmission electron microscopy report a value of 8.0 Å for the separation distance in Al [26], and theoretical values range from 5.4 to 16.0 Å determined by MD and first-principle simulations [27-29]. Therefore, the present MD simulation result compares very well with the experimental and theoretical values.

4. Discussion

The present MD simulation has confirmed that the in-plane ordering of the liquid atoms at the interface is strongly dependent on the amplitude of f. The in-plane ordering decreases significantly with an increase of f. For f=0∼-2%, the in-plane structure is solid-like for the first two layers at 1100 K, and less ordered for f=-4% and nearly liquid-like for f=-10% even in the first liquid layer. This is in accordance with the direct experimental observations [16], which revealed that the in-plane structure of liquid Al becomes ordered within 2∼3 atomic layers parallel to the (0006) plane of sapphire (the lattice misfit between α-Al$_2$O$_3$ and solid Al is -0.48% for (0001)$[10\bar{1}0]_{a\text{-}Al_2O_3}$//(100)$[001]_{Al}$

crystallographic orientations at 933 K). For the systems with small f, the solid-like layers of the liquid atoms could serve as a template for the growth of the new phase on the substrates, with very small undercooling.
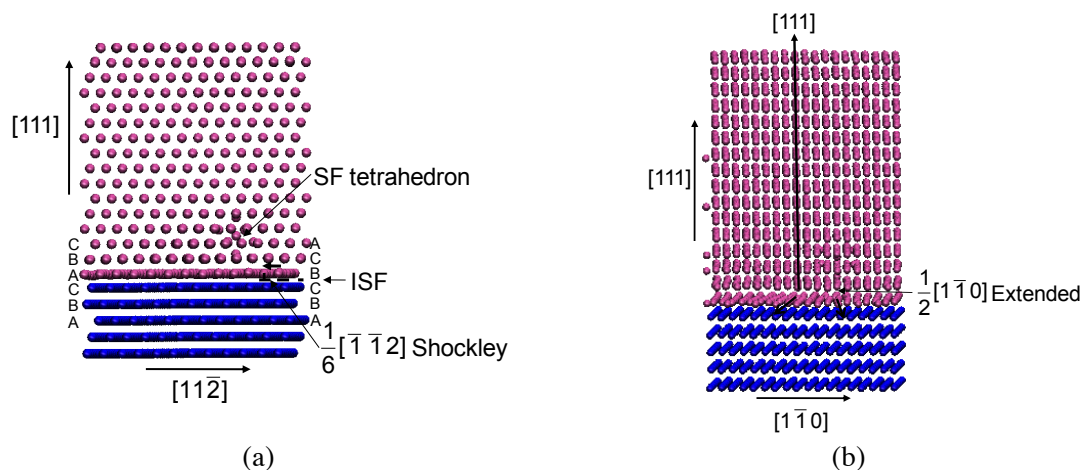

Figure 5. (a) $[1\bar{1}0]$ and (b) $[11\bar{2}]$ projections of the configuration of the system with f=-6%. In the $[1\bar{1}0]$ projection, an ISF and a $1/6[\bar{1}\bar{1}2]$ Shockley partial form at the interface. In the $[11\bar{2}]$ projection, an ½ $[1\bar{1}0]$ edge dislocation dissociates into two Shockley partials at the interface, and an ISF forms between them. The boundary becomes low angle twist boundary.

The magnitude of f has a significant effect on the interfacial structures of the solidified phase. For small misfits (0~-3%), the boundary is coherent, and this is consistent with the solid-like structure of the liquid atoms adjacent to the substrate with small f above the melting temperature. It implied that the epitaxial layers of α-Al phase can form on the substrate during nucleation, and this seems to be in accordance with the HRTEM observation [20, 21], which revealed the copious nucleation of α-Al on TiB$_2$ in some Al amorphous alloys. However, the total elastic strain energy in the epitaxial layers increases with an increase of f. With a further increase in f (-4 and -5%), $1/6[112]$ Shockley partial dislocations form at the interface to release the strain energy in the bulk Al, and the boundary becomes semi-coherent. The interfacial energy will increase due to the contribution from the Shockley partial dislocations and the associated SF. For systems with larger f (-6~-8%), ½ [110] extended dislocations form at the interface and the boundary becomes a low angle twist boundary, leading to a further increase in the interfacial energy. In these cases, the activation energy is necessary for formation of the nuclei from the atoms with liquid-like structure at the interface, and the nucleation barrier has to be overcome for the nucleation of new phase on such substrates.

5. Summary
MD simulations have been conducted to investigate the effect of lattice misfit f on the in-plane ordering of liquid atoms at a liquid/substrate interface, and on the interfacial structure of the solidified phase. It was found that the in-plane ordering decreases with an increase in f. The in-plane structure of the liquid within the two atomic layers is solid-like for f=0~-3%, and less ordered for f=-4% and nearly liquid-like for f=-10% even at the first layer at 1100 K. The misfit also has a significant effect on the interfacial structures of the solidified Al. A perfect lattice match exists between the substrate and the bulk Al for small f (0~-3%). With an increase in f, a Shockley partial dislocation and then an extended dislocation form at the interface, and the boundary becomes a semi-coherent or low angle twist boundary.

Acknowledgments

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