Heterogeneous nucleation of solid Al from the melt by TiB₂ and Al₃Ti: An *ab initio* molecular dynamics study

Junsheng Wang, ¹ Andrew Horsfield, ¹ Udo Schwingenschlögl, ² and Peter D. Lee ¹ ¹Department of Materials, Imperial College, London SW7 2AZ, United Kingdom ²PSE Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia (Received 23 July 2010; published 16 November 2010)

The nucleation of solid Al from the melt by TiB₂ is well established and is believed to involve the formation of Al₃Ti. Since the atomic-scale mechanisms involved are not fully understood, we look to computer simulation to provide insight. As there is an absence of suitable potentials for all of this complex system we have performed large-scale density-functional-theory molecular dynamics simulations of the nucleation of solid Al from the melt on TiB2 and Al3Ti substrates at undercoolings of around 2 K. Using periodic boundary conditions, we find limited ordering and no signs of incipient growth in the liquid Al close to the B-terminated surface of TiB₂. By contrast, we see fcc-like ordering near the Ti-terminated surface, with growth being frustrated by the lattice mismatch between bulk Al and the TiB2 substrate. The Al interatomic distances at the Ti-terminated surface are similar to distances found in Al₃Ti; we suggest that the layer encasing TiB₂ observed experimentally may be strained Al on a Ti-terminated surface rather than Al₃Ti. For the Al₃Ti substrate, fcc-like structures are observed on both sides which extend rapidly into the melt. Periodic boundaries introduce unphysical stresses which we removed by introducing a vacuum region to separate the liquid from the solid at one of the interfaces. We see ordering in the Al on both the B-terminated (0001) surface of TiB₂, and on Al₃Ti(112), with the ordering able to be stronger on the Al₃Ti substrate. However, we cannot draw strong conclusions as these simulations need more time to allow long-ranged fluctuations in the liquid Al to dampen out. The huge computational cost restricted the range and duration of simulations that was possible.

DOI: 10.1103/PhysRevB.82.184203 PACS number(s): 81.10.Aj, 61.20.Ja, 64.60.Q-, 64.70.D-

I. INTRODUCTION

One procedure to form metal into a useful object is to melt it and pour it into a mold; the metal then cools to form a solid casting. However, the way the solid forms during cooling can have a profound effect on the mechanical properties of the resultant casting. In particular, the size of the grains that form influences the strength: for greater strength we need smaller grains. Left to itself, the growth of solid will mostly nucleate on the walls of the mold, and will grow along one axis producing columnar grains. To produce an even distribution of small grains, a refiner consisting of small solid particles is added to nucleate solid throughout the melt. The refiner also changes the shape of the grains: they have equal size in all three dimensions (3D) (equiaxed grains).

In 1951 Cibula proposed that TiB₂ is an effective nucleant for primary α -Al in the melt, and now the addition of master A1-Ti-B alloys is almost universally practiced in Al alloy castings.² For example, A1-5 wt %Ti-1 wt %B master alloys are commercially available that contain submicron sized TiB₂ particles and a small amount of Ti solute. However, the mechanism by which it operates is still not fully understood because of the difficulties in measuring directly the nucleation kinetics at high temperature. In particular, there has been a long-running debate over the relative importance of Al₃Ti, TiB₂ and excess Ti. A number of studies³⁻⁶ have been carried out to try to identify the mechanism of α -Al nucleation. Mohanty and Gruzleski⁷ designed an experiment to directly add TiB2 refiner using an inert gas stream; this enabled them to study the effect of the refiner on grain size during Al-Si alloy solidification. Using a combination of optical microscopy, scanning electron microscopy and an electron probe microanalyzer, they found that TiB₂ was pushed into the region between α -Al dendrites if no Ti was added, and that Al₃Ti layers were absent, suggesting that TiB_2 alone does not nucleate α -Al. On the other hand, they reported the presence of blocky Al₃Ti crystals in the center of each grain when both TiB2 and solute Ti are present. Schumacher and Greer⁸ performed the first experiment to identify the nucleation agents for α -Al using high-resolution transmission electron microscopy. They added an A1-Ti-B alloy to molten Al₈₅Ni₅Y₈Co₂, which they then rapidly quenched to form a glass, which can be considered an analog of a liquid. The quench stopped the growth of solid Al, preventing it from obscuring the part of the system involved in nucleation. They were then able to observe the absorption of Ti onto TiB₂ to form layers, which they believed to be Al₃Ti, on which Al crystals then grew. Their study provides direct evidence for the existence of layers which they state is Al₃Ti on top of TiB₂ prior to the nucleation of α -Al, and initiated subsequent experimental work⁹ to identify the crystal orientation relationships between those phases. Recently, Ingbal et al. 10-12 carried out in situ x-ray diffraction experiments on pure Al with different volume fractions of TiB2 inoculants and Ti solute concentrations using a synchrotron x-ray source. They successfully identified the formation of a metastable phase prior to the formation of solid α -Al, which they identified as Al₃Ti on the TiB₂. This gives strong support to the observation of Schumacher and Greer⁸ that the nucleation of Al on TiB₂ requires a precursor layer of Al₃Ti.

A full atomistic understanding of the nucleation mechanism is difficult to obtain from experiment, so we have turned to computer simulations to identify the events that occur. Since there is no set of suitable potentials that span Al,

Simulation	System	T (K)	B.C.	No. of planes in Al ₃ Ti or TiB ₂	No. of Al ₃ Ti or TiB ₂ units	No. of liquid Al atoms
TiB ₂ AlP	$Al(111) \ TiB_2(0001)$	910	P	$8_{[1000]} \times 12_{[11\bar{2}0]} \times 4_{[0001]}$	32	160
Al_3TiAlP	$Al(111) \ Al_3 Ti(112)$	910	P	$12_{[110]} \times 8_{[11\bar{2}]} \times 6_{[112]}$	144	144
TiB_2AlF	$Al(111) \ TiB_2(0001)$	910	F	$8_{[1000]} \times 12_{[11\overline{2}0]} \times 4_{[0001]}$	32	160
Al ₃ TiAlF	Al(111) Al ₃ Ti(112)	910	F	$12_{[110]} \times 8_{[11\bar{2}]} \times 6_{[112]}$	144	144

TABLE I. Systems and boundary conditions used in simulations.

Ti, and B we have used density-functional theory (DFT) to provide a robust description of the forces between the atoms. Because of recent advances in parallel computers and the development of efficient DFT computer codes, we have been able to perform molecular dynamics (MD) to simulate the nucleation of solid Al from the melt by Al₃Ti and TiB₂ substrates. We find that Al₃Ti is indeed a good nucleating material but also find that the precursor layer observed on TiB₂ could be strained Al on a Ti-terminated face rather than Al₃Ti.

II. METHODOLOGY

A. Simulation software

The calculations were performed with the Vienna ab initio simulation package (VASP). 13-16 In this code, a plane-wave basis set for the expansion of the wave functions is used. The rapid oscillations in the wave functions are treated using projector-augmented waves (PAWs), ^{17,18} and the contribution to the energy from electronic exchange and correlation is described using the PW91^{19,20} gradient-corrected density functional. Performance is improved through the use of an efficient second-order extrapolation of the charge density, parallel 3D fast Fourier transforms, and the mixed block Davidson method²¹ plus a residual minimization scheme using direct inversion in the iterative subspace²² for wavefunction optimization. An energy tolerance of 10⁻⁴ eV/atom was used as a test of charge self-consistency. The plane-wave cutoffs for liquid Al/TiB₂ and liquid Al/Al₃Ti were 536 eV and 329 eV, respectively. The simulations were performed with a $2 \times 2 \times 1$ k-point mesh.

B. Systems and conditions

Two substrates [Al₃Ti(112) and TiB₂ (0001)] were considered, as shown in Table I. To establish the correct cell sizes we constructed two cells: one of perfect crystalline Al₃Ti (in the D0₂₂) structure in contact with fcc Al forming an Al(111)||Al₃Ti(112) interface; the other of perfect hcp TiB₂ in contact with fcc Al forming an Al(111)||TiB₂ (0001) interface. The lattice parameters were a=b=3.85 Å, and c=8.58 Å for Al₃Ti (Ref. 23) and a=b=3.03 Å and c=3.23 Å for TiB₂.²⁴ The Al₃Ti region contains $12\times8\times6$ atomic layers and the TiB₂ region has $8\times12\times4$ layers. To generate the starting coordinates for the liquid Al we removed the substrate material (TiB₂ or Al₃Ti) and performed MD at 1273 K and an average pressure of 0 Pa using an Embedded Atom Method (EAM) potential²⁵ and the Hoover

NVT ensemble²⁶ as implemented in LAMMPS.²⁷ To ensure that the liquid Al had zero pressure after being reunited with its substrate, the computational cell was stretched slightly before adding the substrate back in. We believe the number of atoms used for the substrates and the liquid Al is adequate for obtaining useful information about nucleation: the substrates retain their solid structure, and the pair correlation function in the liquid region shows the system is disordered. Larger numbers of atoms are desirable, but unaffordable. Periodic boundary conditions were applied in the x and y directions. In the z direction periodic boundary conditions (PBCs) were used, but for one set of simulations there is no vacuum present (symbol P), while for the other set a vacuum region was inserted on top of the liquid Al (symbol F): see Table I.

We performed two types of simulation: one consisting of 160 liquid Al atoms on top of 32 TiB₂ units, the other with 144 liquid Al atoms combined with 144 Al₃Ti units. Using the reference melting point (912 K) calculated by Alfè *et al.*²⁸ using VASP with PAW and generalized gradient approximation (GGA), we studied α -Al nucleation at small undercoolings (\sim 2 K). The MD simulations were all performed at constant temperature (\sim 910 K) in the NVT ensemble, with a time step of 1 fs. We ran the simulations for between 2.0 and 2.85 ps in order to observe the ordering in the liquid Al close to the substrates.

C. Simulation hardware

The simulation of TiB₂ with liquid Al using periodic boundary conditions was performed on an IBM Blue Gene/L computer at Blue Gene Watson (BGW) in the IBM's Thomas J. Watson Research Center in Yorktown Heights, NY, USA. In total, 128 nodes (256 cores) were used, with each node containing two 700 MHz power 440 dual core processors and 512 MB of memory. The remaining simulations were carried out on a 16-rack IBM Blue Gene/P system in the Supercomputing Laboratory (KSL) at the King Abdullah University of Science and Technology (KAUST): each node has four 850 MHz PowerPC 450 quad core processors and 4 GB of memory.

To allow us to make efficient use of the parallel computing resources, we first tested the scaling of the code with respect to the number of nodes on the KSL Blue Gene/P system using the TiB_2AlP system (see Table I). We used parallelization over bands and plane-wave coefficients. The measured speedup is shown in Fig. 1, where we have defined the speedup to be $16 \times t_{16 \text{ cores}}/t_{n \text{ cores}}$, and $t_{16 \text{ cores}}$ and $t_{n \text{ cores}}$

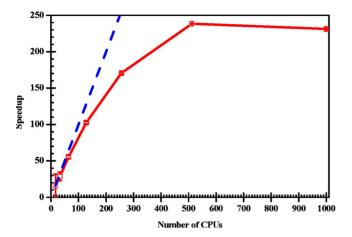


FIG. 1. (Color online) The simulation time for single step of ionic relaxation of TiB₂AlP system as a function of number of cores used on IBM Blue Gene, KSL, KAUST.

are the times to perform the calculation using 16 cores and n cores, respectively. For an ideal system the speedup should equal n. From Fig. 1, we see that speedup is useful up to 256 cores but falls off after that with no additional speedup if over 512 cores are used: this is plausible as our TiB₂AlP simulations contain only 256 atoms. We used 256 cores for all of our simulations.

D. Analysis of density profile

The results of our simulations have been analyzed by inspecting the density profile $(\rho(z))$ averaged over slices of the cell parallel to the solid/liquid (S/L) interface calculated using the following formula:^{29,30}

$$\rho(z) = \frac{\langle N_z \rangle}{A_{zz} \Delta z},\tag{1}$$

where $\langle N_z \rangle$ is the time averaged number of atoms in a bin of size Δz at z, and A_{xy} is the area of the S/L interface. The resulting profile is sensitive to the choice of bin size (Δz) ; to obtain a good spatial density distribution, the density fluctuations inside a bin have to be much smaller than the variation in the density between neighboring bins. In these calculations the number of bins was set at 300 (equivalent to a bin size of 0.11 Å), and the time average was taken over 50 snapshots separated by 0.05 ps. While this averaging time is less than a typical vibrational period (0.1-1 ps) it was kept this short to avoid averaging over the ordering events we are trying to observe.

E. Quantification of structural ordering

Because nucleation involves a transition from disordered liquid to ordered solid, a measure of the local ordering at the S/L interface is a very informative tool for interpreting the evolution of the interface. Many authors have proposed methods to characterize the short-range structural ordering during solidification, including the common neighbor analysis,³¹ the centrosymmetry parameter (CSP),³² the common neighborhood parameter,³³ and the ordering discrimina-

tor function.³⁴ We choose to use the CSP, as it is easiest to interpret. It gives a measure of how far a structure is from being centrosymmetric, with large values indicating large departures. Not only can liquid and solid be effectively distinguished using this parameter but also defect sites in the Al₃Ti substrate. For an fcc structure the CSP is defined as³²

$$\alpha = \sum_{i=1,6} |R_i + R_{i+6}|^2, \tag{2}$$

where R_i and R_{i+6} are bond vectors corresponding to the six pairs of opposite nearest neighbors, and the nearest neighbors are identified by finding the opposite atoms closest to the positions defined by the undistorted nearest-neighbor vectors. For bulk Al in the fcc structure, α =0, for the (001) surface α =24.9 Ų, for an intrinsic stacking fault α =8.3 Ų, for atoms midway between fcc and hcp α =2.1 Ų, and for liquid atoms with disordered structure $16 < \alpha < 24.9$ Ų.

Buta et al.³⁰ proposed a quantity that can measure both long- and short-ranged lateral order, namely the two-dimensional (2D) structure factor $S_{2D}(k)$,³⁵

$$S_{2D}(k) = \frac{1}{N} \sum_{i,j}^{N} \langle \exp i\vec{k} \cdot (\vec{r}_i - \vec{r}_j) \rangle$$

$$= \frac{1}{N} \sum_{i,j}^{N} \cos[k_x(x_i - x_j) + k_y(y_i - y_j)]. \tag{3}$$

This two-dimensional representation of the layer structure generates a periodic pattern similar to x-ray or neutron-scattering experiments: it gives the Fourier components of in-plane density fluctuations in the liquid computed from projections of the atomic positions onto the plane of the interface. This analysis allows us to identify lateral ordering within the interfacial layers on top of the $TiB_2(0001)$ and Al_3Ti (112) substrates.

III. RESULTS AND DISCUSSION

A. TiB₂ substrate

Using PBCs, the Al₃TiAlP simulation was performed at a temperature of 910 K, roughly corresponding to an undercooling of 2 K. (Note that the small cell size means that there will be a rise in the temperature at which the liquid is stable,³⁶ so the effective undercooling is greater than this.) There are two kinds of (0001) interface for the TiB₂ crystal: Ti-terminated and B-terminated. We intentionally add two Ti atoms to the liquid Al, with one in the bulk and the other next to the B terminated S/L interface. The purpose was to observe any effect from low concentrations of solute Ti.

In Fig. 2, three typical snapshots of liquid Al on top of TiB_2 at 910 K are shown together with the corresponding density profiles, $\rho(z)$, averaged over a period of 0.05 ps. The TiB_2 region has two Ti planes and two B planes, producing one Ti-terminated surface and one B-terminated surface. This is then surrounded by liquid Al atoms at the beginning of the simulation [Fig. 2(a)]. The calculated density profile perpendicular to the S/L interface shows the Ti (magenta dotted

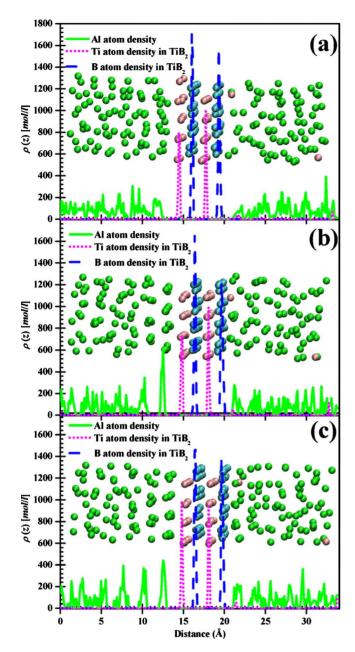


FIG. 2. (Color online) Sequential images and calculated density profile of solid Al nucleation from the melt on top of TiB₂ substrate at T=910 K using periodic boundary condition. (a) t_s =0.05 ps; (b) t_s =1.42 ps; (c) t_s =2.85 ps.

lines) and B (blue dashed lines) planes, in contrast to the random positions of the Al (green straight lines) atoms in the liquid. However, ordered structure is visible in the liquid Al by 1.42 ps [Fig. 2(b)]. Solidlike structural ordering is initiated in the first liquid layer on top of the TiB₂ substrate, and then propagates outward into the bulk liquid. However, the ordering is different on the B- and Ti-terminated surfaces. On the B-terminated surface only one Al ordered layer forms, which is followed by another layer that is quite disordered. On the Ti-terminated surface the ordering extends three or more layers into the liquid [see Fig. 2(c)]. In both cases the density oscillations dampen gradually from the S/L interface to a uniform distribution when liquid phase dominates.

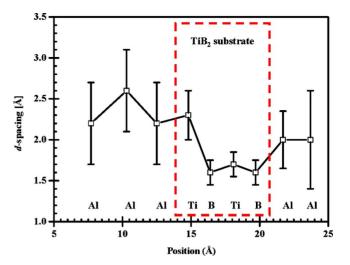


FIG. 3. (Color online) d spacing as a function of atomic position. A bin size of 0.11 Å was used to build the histogram from which the peak positions were found. The error bars are found from the half width at half maximum of the peaks.

Using a bin size of 0.11 Å, we calculated the distribution of interplanar spacing (d spacing) normal to the S/L interface, as shown in Fig. 3. The d spacing at position z is defined as the distance between the peak at z and the first peak to its left. First we note the interplanar spacing within the TiB₂ substrate is constant $(1.6 \pm 0.15 \text{ Å})$ and very similar to the bulk value of 1.62 Å (see Table II), confirming that our thin slab is sufficient for this simulation. Two different interplanar spacings are observed in the peak positions of the ordered Al layers. On the right-hand side (B-terminated surface), the Al atoms are situated at the same positions that Ti would occupy in the TiB2 structure, giving an AlB2 crystal structure with an interplanar spacing of 1.9 ± 0.4 Å. This is expanded by about 25% compared with the bulk value of 1.63 Å (see Table II); the reason for this is probably that the structure cannot grow further, so the solidlike Al region is strongly perturbed by the neighboring liquid Al. However, this needs further analysis and will be examined in more detail in future work. Presumably it is the absence of B that inhibits growth beyond about one ordered layer plus one

TABLE II. Lattice constants, neighbor distances, and interplanar spacings for key structures.

	Lattice parameters		Neighbor distances		Interplanar spacing	
	a,b (Å)	с (Å)	r _{1nn} (Å)	r _{2nn} (Å)	Index	<i>d</i> (Å)
Ala	4.05	4.05	2.86	4.05	(111)	2.34
Al ₃ Ti ^b	3.85	8.58	2.72	3.85	(112)	2.31
TiB ₂ ^c	3.03	3.23	3.03 (Ti-Ti)		(0001)	1.62
AlB ₂ d	3.01	3.25	3.01 (Al-Al)		(0001)	1.63

^aReference 37.

^bReference 23.

^cReference 24.

^dReference 38.

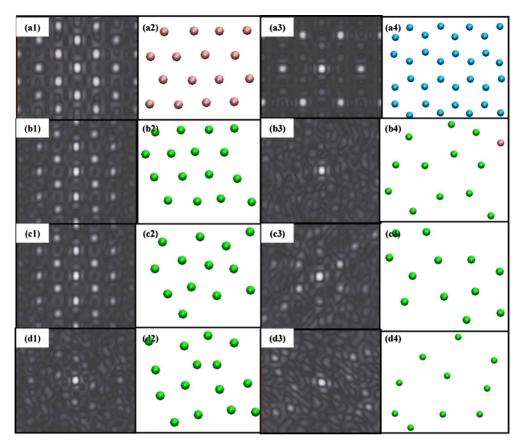


FIG. 4. (Color online) Two-dimensional structure factor and corresponding ordering layers on the Ti side [(a1) and (a2)] and B side [(a3) and (a4)] of TiB2. [(a1) and (a2)] Ti layer; [(a3) and (a4)] B layer, [(b1)–(b4)] first layer in the liquid Al; [(c1)–(c4)] second layer in the liquid Al; [(c1)-(c4)] third layer in the liquid Al. Computed at t=2.85 ps

disordered layer. On the left-hand side (Ti-terminated surface) an fcc-like structure with an interplanar spacing of about $2.4\pm0.5\,$ Å is nucleated in the liquid and extends into the liquid for at least three layers. This d spacing is very similar to the room temperature experimental interplanar spacing of Al $(111)^{39}$ of 2.34 Å (see Table II).

Precisely what would happen if the simulation were run longer is unclear. It took 1 month to complete 2.85 ps for the TiB_2AlP system of, and we are currently unable to take this further. However, one message is clear: Al grows much more readily on the Ti-terminated surface than on the B-terminated one.

In order to compare the ordering as a function of distance away from the two types of substrate surfaces (Ti- and B-terminated TiB_2), we calculated the two-dimensional structural factor at time t=2.85 ps as shown in Fig. 4 Hexagonal patterns are observed on both surfaces. Figure 4b2 confirms that Al forms (111) fcc planes on the Ti-terminated surface while on the B-terminated surface Fig. 4b4 shows that the Al atoms roughly occupy the Ti sites of the TiB_2 structure.

Using the three layers of atoms on the Ti-terminated surface shown in Figs. 4b2–4d2, and the three layers on the B-terminated surface shown in Figs. 4b4–4d4, we calculated the radial distribution function (RDF) of Al-Al pairs on both sides of the TiB₂ substrate as shown in Fig. 5(a). The RDF for the Ti-Ti, Ti-B, and B-B pairs in the TiB₂ substrate were

also obtained, together with the RDF of Al-Al pairs in the bulk liquid (excluding the six layers close to TiB_2 substrate). No ordering beyond the first neighbor shell is observed in the bulk liquid or near the B-terminated surface. Structural ordering out to about the third neighbor shell is seen in the first three Al layers near the Ti-terminated surface, with strong peaks appearing at 2.75 and 3.85 Å. These correspond well to two neighbor separations in the $D0_{22}$ Al₃Ti structure (2.72 and 3.85 Å), which might explain the apparent presence of Al₃Ti in the experimental x-ray spectra. $^{10-12}$

There is also a weaker peak at 3.25 Å, whose significance is as follows. A surprising feature of the nearest-neighbor distance (2.75 Å) is that it is 4% smaller than the bulk roomtemperature spacing of 2.86 Å while the effective lattice constant (measured by the interplanar spacing and the substrate lattice constants) is rather similar to that for the room temperature solid on the Ti surface. We credit this to the dynamics of the Al atoms being captured in the paircorrelation function in a different way than in the average one-dimensional density. The two can be seen to be compatible as the longer distance (3.25 Å), when averaged with the shorter distance (2.75 Å) gives an average (3.00 Å) very similar to the Ti-Ti distance (3.03 Å) in the substrate, which we expect to define the average in-plane Al-Al distance. On the B-terminated surface, the RDF for Al-Al only has clear peaks at 2.75 and 3.05 Å, matching both the first neighbor in liquid Al and the first neighbor in AlB₂ (the liquid Al forms

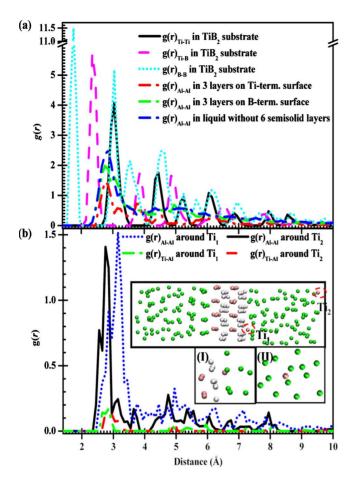


FIG. 5. (Color online) (a) The RDF of Ti-Ti, Ti-B, B-B in the solid substrate and Al-Al in the solidlike films on both sides of ${\rm TiB_2}$ and the bulk liquid which are calculated from the last 100 MD steps at 910 K. (b) The RDF of Al-Al and Ti-Al around the Ti atoms in the liquid with insert images (I and II) showing different ordering behaviors of atoms around Ti atoms.

a thin film of AlB_2 on top of TiB_2). In the substrate, the RDF of Ti-Ti pairs has five peaks at 3.05, 4.45, 5.25, 6.05, and 6.85 Å within the cutoff of 10.0 Å, and four nearest neighbors were identified for Ti-B pair which were at distances of 2.35, 3.85, 4.85, and 6.55 Å.

We now investigate the ordering of atoms around the two added Ti atoms [Ti₁ and Ti₂ in the inset images in Fig. 5(b)]. We calculated the RDF for the first layer of liquid on top of the B-terminated TiB₂ surface and 12 Al atoms around the Ti₂ atom in the bulk liquid, as shown in Fig. 5(b). The first peak of $g(r)_{Al-Al}$ in the first layer of liquid on the B-terminated TiB₂ surface is at a distance of 2.85 Å, close to the second neighbor Al-Al distance of 2.88 Å in Al₃Ti while the second peak is at 3.15 Å, which is close to the Al-Al distance in AlB₂. It might be that the presence of Ti is inhibiting the formation of the AlB₂ thin film by promoting the formation of an Al₃Ti, which might also explain why the 2D structure factor in Fig. 4b3 is not as clear as the second layer in Fig. 4c3. From Fig. 5(b) we see that $g(r)_{Al-Al}$ around Ti₂ has three peaks at 2.75, 3.65, and 4.75 Å, while $g(r)_{\text{Ti-Al}}$ around Ti₂ exhibits three peaks at 2.75, 3.25, and 4.95 Å. These do not match exactly separations in the Al₃Ti structure but are quite close.

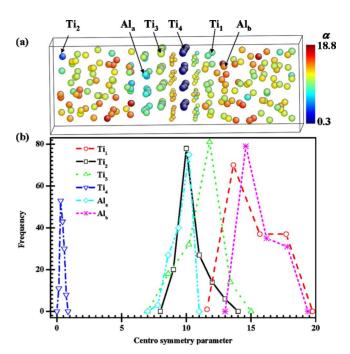


FIG. 6. (Color online) (a) The atoms colorized by their averaged centro symmetry parameter (α) over the last 200 fs showing the ordering of Al atoms on the Ti-terminated surface (Al_a), disordered liquid Al (Al_b), three different positions of Ti atoms including a single Ti atom on the B-terminated surface (Ti₁), in bulk liquid (Ti₂), at the surface of the TiB₂ substrate (Ti₃), and in the middle of the TiB₂ substrate (Ti₄). (b) The distribution of α for each atom type.

In addition to the pair distribution function, we also quantified the centro symmetry parameter (α) distribution for each atom over the last 200 fs of simulation [Fig. 6(a)] with the color showing the averaged degree of ordering. This parameter is close to zero for an fcc crystal and is greater than 16 when the atoms are in a disordered state such as liquid. Clearly, the Al atoms on top of the Ti-terminated surface tend to form several ordered layers. The degree of ordering on the B-terminated surface decreases dramatically as it moves from the first layer into the liquid. Interestingly, four different z positions of Ti atoms show completely different degrees of ordering (compare Ti₁-Ti₄ in Fig. 6). We plotted the distribution of ordering over this period in Fig. 6(b). Ti₁ is slightly less ordered compared to the liquid Alb atoms because the mean α value is smaller. Surprisingly, Ti₂ shows the same degree of ordering as the Al atoms (Al_a) on top of the Ti-terminated surface of TiB2. This means that Ti2 promotes the surrounding atoms to form an fcc structure inside the bulk liquid. Atoms at the Ti-terminated surface (Ti₃) are more disordered as compared to the Ti atoms in the middle of the TiB₂ substrate (Ti₄). However, this degeneration of ordering has successfully transferred ordering from the Ti substrate into the liquid Al gradually. This analysis of the structural ordering observed on Ala,b, and Ti1-4 thus supports the experimental findings that formation of an fcc-like structure is promoted by the presence of Ti atoms.³⁻⁶

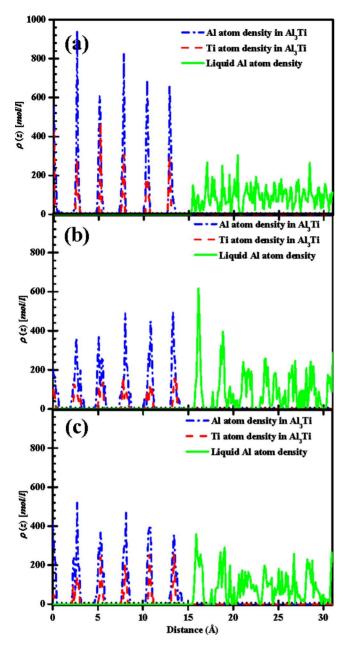


FIG. 7. (Color online) Calculated density profile of solid Al nucleation from the melt on top of the Al₃Ti substrate at T=910 K using periodic boundary condition. (a) t_s =0.05 ps; (b) t_s =1 ps; (c) t_s =2 ps.

B. Al₃Ti substrate

As for the TiB₂AlP simulation, we performed *ab initio* MD at 910 K using an *NVT* ensemble in a system (Al₃TiAlP) containing both a solid slab of Al₃Ti and liquid Al; the solid substrate forms an interface with the liquid at its (112) surfaces on both sides. The Al₃Ti structure has no compositional variation between the two (112) surfaces. The time to complete a 2 ps simulation with 288 atoms was one month on 256 cores. We obtained 2000 atomic configurations which were then analyzed by calculating the density profile along the direction perpendicular to the S/L interface. The resulting plots of Al and Ti atom densities in the Al₃Ti substrate and the Al atom density in the liquid are shown in Fig. 7.

The interplanar spacing for the Al₃Ti substrate retained its bulk value, just as we saw for the TiB2 structure. In contrast to the TiB2 substrate shown in Fig. 2, fcc-like structural ordering is initiated and propagates into the liquid on both sides of the Al₃Ti substrate as shown by the structuring of the liquid Al density profile after only 1 ps [Figs. 7(a) and 7(b)]. There are periodic oscillations in the density of the substrate corresponding to (112) planes of atoms [Ti (red) and Al (blue), and their d spacing is 2.34 Å initially, expanding to 2.68 Å after heating to 910 K. After holding the liquid Al on both sides of the Al₃Ti substrate for 1 ps, the maximum density of the first ordering layer (308 mol/l) on top of the Al₃Ti substrate in Fig. 7(b) almost reaches the same value as the sum of the densities for Al and Ti in the substrate (363 mol/l). The ordering phase has the same interplanar spacing as the Al₃Ti substrate. A longer holding time allows more solid phase to grow on both sides, and when the two solid phases meet in the middle, stress is created as they are not perfectly registered. From Figs. 7(c) and 7(b), we see that this leads a new loss of order.

In order to observe how the ordering extends into the liquid we calculated the 2D structure factor using Eq. 8. As shown in Fig. 8(a), the snapshot of the last configuration clearly shows ordering in the first three layers on top of Al₃Ti substrate. Using the outmost layer of the Al₃Ti structure [Fig. 8d1] and the three liquid Al layers closest to it [Figs. 8a1–8c1], we calculated a 2D structure factor for each slice, as shown in Figs. 8a2–8d2. The structure of the atoms in the first layer [Fig. 8c2] matches that of the Al₃Ti substrate [Fig. 8d2] while the ordering decays as we move further into the liquid, as shown in Figs. 8a2 and 8b2. It is clear that liquid Al forms an fcc structure with a lattice constant similar to that for Al₃Ti. This might explain why Al₃Ti is a powerful nucleant that easily initiates the formation of fcc Al solid from the melt.

C. Comparison of the B-terminated TiB₂ and Al₃Ti (112) surface

For both TiB₂AlP and Al₃TiAlP we calculated the initial pressure and final pressure. We found positive pressures (about 5.0×10^8 Pa) at the beginning and negative pressures (about -3.0×10^9 Pa) at the end of the simulations; these are both uncomfortably large, and might help explain the large Al interplanar spacing on the B surface of TiB2. In order to make a better comparison of the relative effectiveness of Al₃Ti and TiB₂ in nucleating solid Al from the melt we need to eliminate these stresses. Their origin is the interaction between the two growing ordered regions produced by the periodic boundaries. The sharp change in pressure occurs because solid Al nucleates on both sides of the substrates, and the whole system contracts to accommodate the solidification shrinkage. One approach might be to use constant pressure (NPT) MD instead of constant volume (NVT) MD. However, our version of VASP does not provide this feature. Instead we add a vacuum region on top of the liquid, keeping only one interface in each system, thereby allowing stress to be released along the direction perpendicular to the interface. Using this methodology the TiB₂AlF and Al₃TiAlF systems

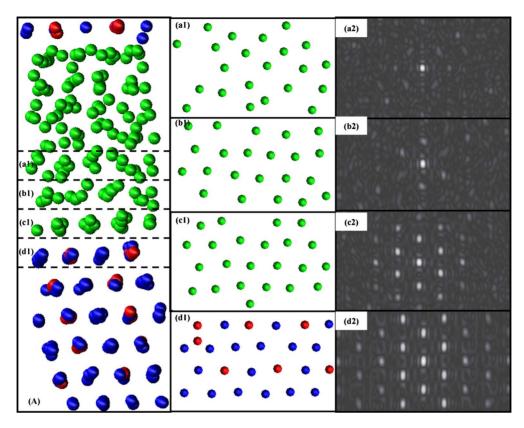


FIG. 8. (Color online) Structural ordering at the beginning of continuous growth on Al₃Ti (112) surface at 910 K. (a) a snapshot at t_s =2 ps, and projections of the outer four layers [(a1)–(d1)] and the corresponding time-averaged structure factors for 50 MD steps [(a2)–(d2)]. Ti and Al atoms in Al₃Ti structure are in red (gray) and blue (dark), respectively. Liquid Al atoms are in green (light gray).

were simulated to compare the efficiency with which TiB_2 and Al_3Ti nucleate solid Al from the melt.

The density profiles, $\rho(z)$, computed at three times (0.05, 1, and 2 ps) and averaged over a period of 0.05 ps for a simulation at 910 K, are shown in Fig. 9. They reveal structural ordering on top of both the TiB₂(0001) basal plane and the Al₃Ti(112) surface. Three typical snapshots of the atomic positions are also shown for these times. Because there is a vacuum region separating the liquid Al and Ti-terminated surface of TiB2, solid Al can only nucleate from the melt on top of the B-terminated TiB₂ surface. At the beginning of the simulation a disordered phase is clearly seen from the random oscillations in the density profile [Fig. 9(a)]. After 1 ps solid films start forming on top of the B layer in the TiB2 substrate as seen in Fig. 9(b). The d spacing was measured to be 1.79 Å, a bit larger than the interplanar spacing of the AlB₂ structure of 1.63 Å at room temperature due to thermal expansion at high temperature. After 2 ps, a second solid layer is stabilized, with an interlayer spacing of 2.12 Å.

The liquid Al on top of Al₃Ti(112) orders rapidly within 1 s, with ordering extending over several layers as shown by comparing Figs. 9(d) and 9(e). However, this order is transient, as can be seen by comparing Figs. 9(e) and 9(f). We hypothesize that this is because there are long-range fluctuations in the liquid Al that take time to dampen out. In order to obtain an estimate of the total time required to reach a stable configuration we performed classical molecular dynamics using an empirical potential derived from the embed-

ded atom method for the Al-Ti system.²⁵ Using the same conditions and configuration (Al₃TiAlF), we found that continuous growth of solid Al on Al₃Ti(112) occurs after 7.5 ps and complete solidification occurs within 14.5 ps. Therefore, more simulation time must be allowed if the optimal configuration for continuous growth is to be obtained by relaxation for Al₃TiAlF system.

Our preliminary TiB_2AlF and Al_3TiAlF calculations, which each took 1 month on 256 cores, provide us with qualitative information about the effectiveness of two different substrates for nucleating solid Al from the melt. Only two to three ordering layers ever appeared on the B-terminated surface of TiB_2 [see Fig. 9(c)] and it does not display the fluctuations in order seen in the liquid on the $Al_3Ti(112)$ substrate [see Fig. 9(f)]. In addition, the d spacing in the new solid phases differ on the two kinds of substrate. Liquid Al on $Al_3Ti(112)$ forms close-packed (111) planes of fcc structure with an interlayer spacing of about 2.74 Å. Therefore, α -Al appears to nucleate much more readily on $Al_3Ti(112)$ than on the B-terminated TiB_2 (0001) basal plane, though we cannot draw strong conclusions from these short simulations.

IV. SUMMARY AND CONCLUSION

We have investigated heterogeneous nucleation of α -Al from the Al melt upon cooling by means of *ab initio* molecular dynamics simulations (PAW with GGA as implemented in VASP). By calculating the density profile at negligible under-

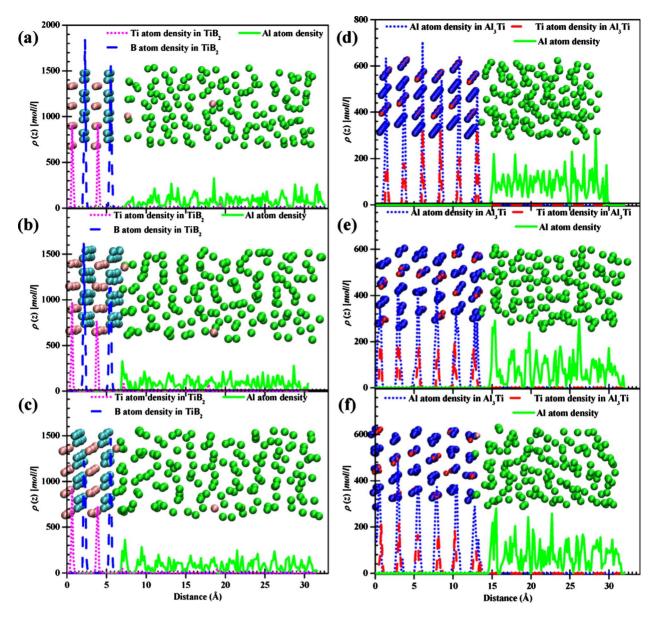


FIG. 9. (Color online) Sequential images and calculated density profile of solid Al nucleation from the melt on top of TiB₂ and Al₃Ti substrates at T=910 K using the free surface condition. (a) TiB₂ substrate, t_s =0.05 ps; (b) TiB₂ substrate, t_s =1 ps (c) TiB₂ substrate, t_s =2 ps, (d) Al₃Ti substrate, t_s =0.05 ps; (e) Al₃Ti substrate, t_s =1 ps; (f) Al₃Ti substrate, t_s =2 ps.

coolings (\sim 2 K) on different kinds of substrates including Al₃Ti and TiB₂, we have successfully obtained quantitative information of heterogeneous nucleation mechanism of α -Al from the Al melt. Structural ordering was clearly seen in the liquid close to the TiB₂ and Al₃Ti substrates at temperatures below the Al melting point. Lattice parameters differ on two kinds of termination surfaces of TiB₂, promoting new structure ordering with different potentials to grow.²⁹ The liquid \rightarrow solid transformation process on top of the B-terminated (0001) basal plane of TiB₂ does not promote fcc-like ordering, instead it tries to form an AlB₂ structure to replicate the TiB₂ lattice. The Ti-terminated surface has greater potential to nucleate α -Al, but did not promote continuous growth of Al (111) in 2.85 ps: this is probably due to the strain energy associated with the lattice mismatch be-

tween fcc Al and TiB_2 . At small undercooling, liquid Al close to the Al_3Ti (112) substrate readily transforms into a solid fcc-like structure.

Interestingly, arbitrary stresses introduced by the interaction between the two ordered regions under periodic boundary conditions prevent complete solidification. We found that these artificial forces can be removed by inserting a vacuum region on top of the liquid. However, the computational cost to reach complete solidification for Al₃TiAlF (as estimated from classical MD using an EAM potential) is too great to be done by *ab intio* MD using our available resources. Nevertheless, this preliminary study exposes promising features through our direct comparison of Al₃Ti (112) with TiB₂ (0001). We find some evidence that Al₃Ti (112) is a more powerful nucleant than TiB₂ (0001) with signs that continu-

ous growth of fcc structure on top of Al_3Ti (112) is possible. This can be seen as supporting the accepted view that "free growth" occurs on Al_3Ti (112) which coats TiB_2 , as suggested by previous experiments. ^{40–43} However, these simulations suggest a second possibility, namely, that strained Al grows on the Ti-terminated surface of TiB_2 , and it is this surface on which growth occurs.

To conclude, while these simulations have raised interesting possibilities, we recognize that they are just a first step. Longer and larger simulations are needed, as well as further experimentation, to fully understand the mechanisms of nucleation.

ACKNOWLEDGMENTS

The authors would like to acknowledge funding and computational resources provided by the King Abdullah University of Science and Technology.

- ¹ A. Cibula and R. W. Ruddle, J. Inst. Met. **76**, 361 (1949).
- ²A. L. Greer, Philos. Trans. R. Soc. London, Ser. B **361**, 479 (2003).
- ³B. Cantor and R. D. Doherty, Acta Metall. **27**, 33 (1979).
- ⁴K. A. Q. O'Reilly, B. Cantor, and P. G. Enright, Scr. Metall. Mater. 28, 173 (1993).
- ⁵B. Cantor, Mater. Sci. Eng., A **226-228**, 151 (1997).
- ⁶B. Cantor, Philos. Trans. R. Soc. London, Ser. A **361**, 409 (2003).
- ⁷P. S. Mohanty and J. E. Gruzleski, Acta Mater. **44**, 3749 (1996).
- ⁸P. Schumacher and A. L. Greer, in *Light Metals*, edited by W. Hale (TMS, Anaheim, USA, 1996), p. 745.
- ⁹P. Schumacher and B. J. McKay, J. Non-Cryst. Solids **317**, 123 (2003).
- ¹⁰N. Iqbal, N. H. van Dijk, S. E. Offerman, M. P. Moret, L. Kat-german, and G. J. Kearley, Acta Mater. 53, 2875 (2005).
- ¹¹N. Iqbal, N. H. van Dijk, S. E. Offerman, N. Geerlofs, M. P. Moret, L. Katgerman, and G. J. Kearley, Mater. Sci. Eng., A 416, 18 (2006).
- ¹²N. Iqbal, N. H. van Dijk, S. E. Offerman, M. P. Moret, L. Kat-german, and G. J. Kearley, J. Non-Cryst. Solids 353, 3640 (2007).
- ¹³G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- ¹⁴G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
- ¹⁵G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
- ¹⁶G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- ¹⁷P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- ¹⁸G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
- ¹⁹J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- ²⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 48, 4978 (1993).
- ²¹E. R. Davidson, in *Methods in Computational Molecular Physics*, edited by G. H. F. Diercksen and S. Wilson, Vol. 113 of NATO Advanced Study Institute, Series C: (Plenum, New York, 1983), p. 95.

- ²²D. M. Wood, J. Phys. A 18, 1343 (1985).
- ²³P. Norby and A. Norlund Christensen, Acta Chem. Scand., Ser. A 40a, 157 (1986).
- ²⁴R. G. Munro, J. Res. Natl. Inst. Stand. Technol. **105**, 709 (2000).
- ²⁵R. R. Zope and Y. Mishin, Phys. Rev. B **68**, 024102 (2003).
- ²⁶W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
- ²⁷S. Plimpton, P. Crozier, and A. Thompson, LAMMPS, http://lammps.sandia.gov, Sandia National Laboratories, Albuquerque, NM, USA, 2009).
- ²⁸D. Alfè, L. Vočadlo, G. Price, and M. Gillan, J. Phys.: Condens. Matter 16, S973 (2004).
- ²⁹ A. Hashibon, J. Adler, M. W. Finnis, and W. D. Kaplan, Comput. Mater. Sci. **24**, 443 (2002).
- ³⁰D. Buta, M. Asta, and J. J. Hoyt, Phys. Rev. E **78**, 031605 (2008).
- ³¹ J. D. Honeycutt and H. C. Andersen, J. Phys. Chem. **91**, 4950 (1987)
- ³²C. L. Kelchner, S. J. Plimpton, and J. C. Hamilton, Phys. Rev. B 58, 11085 (1998).
- ³³ H. Tsuzuki, P. S. Branicio, and J. P. Rino, Comput. Phys. Commun. **177**, 518 (2007).
- ³⁴J. Morris and X. Song, J. Chem. Phys. **119**, 3920 (2003).
- ³⁵M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
- ³⁶J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan, Phys. Rev. B 49, 3109 (1994).
- ³⁷ CRC Handbook of Chemistry and Physics, edited by D. R. Lide (CRC Press, Boca Raton, 2009).
- ³⁸I. Loa, K. Kunc, K. Syassen, and P. Bouvier, Phys. Rev. B 66, 134101 (2002).
- ³⁹ A. Smakula and J. Kalnajs, Phys. Rev. **99**, 1737 (1955).
- ⁴⁰I. Maxwell and A. Hellawell, Acta Metall. **23**, 229 (1975).
- ⁴¹ A. L. Greer, A. M. Bunn, A. Tronche, P. V. Evans, and D. J. Bristow, Acta Mater. 48, 2823 (2000).
- ⁴²P. Schumacher, A. L. Greer, J. Worth, P. V. Evans, M. A. Kearns, P. Fisher, and A. H. Green, Mater. Sci. Technol. **14**, 394 (1998).
- ⁴³M. Easton, Metall. Mater. Trans. A **36A**, 1911 (2005).