Heterogeneous nucleation of solid Al from the melt by TiB$_2$ and Al$_3$Ti: An ab initio molecular dynamics study

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The nucleation of solid Al from the melt by TiB$_2$ is well established and is believed to involve the formation of Al$_3$Ti. 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 TiB$_2$ and Al$_3$Ti 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 TiB$_2$. 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 TiB$_2$ substrate. The Al interatomic distances at the Ti-terminated surface are similar to distances found in Al$_3$Ti; we suggest that the layer encasing TiB$_2$ observed experimentally may be strained Al on a Ti-terminated surface rather than Al$_3$Ti. For the Al$_3$Ti 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 TiB$_2$, and on Al$_3$Ti(112), with the ordering able to be stronger on the Al$_3$Ti 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.

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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$^1$ proposed that TiB$_2$ is an effective nucleant for primary α-Al in the melt, and now the addition of master Al-Ti-B alloys is almost universally practiced in Al alloy castings.$^2$ For example, Al-5 wt %Ti-1 wt %B master alloys are commercially available that contain submicron sized TiB$_2$ 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 Al$_3$Ti, TiB$_2$ and excess Ti. A number of studies$^3$–$^6$ have been carried out to try to identify the mechanism of α-Al nucleation. Mohanty and Gruzleski$^7$ designed an experiment to directly add TiB$_2$ 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 TiB$_2$ was pushed into the region between α-Al dendrites if no Ti was added, and that Al$_3$Ti layers were absent, suggesting that TiB$_2$ alone does not nucleate α-Al. On the other hand, they reported the presence of blocky Al$_3$Ti crystals in the center of each grain when both TiB$_2$ and solute Ti are present.

Schumacher and Greer$^8$ performed the first experiment to identify the nucleation agents for α-Al using high-resolution transmission electron microscopy. They added an Al-Ti-B alloy to molten Al$_3$SiNi$_5$Y$_8$Co$_2$, 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 TiB$_2$ to form layers, which they believed to be Al$_3$Ti, on which Al crystals then grew.$^8$ Their study provides direct evidence for the existence of layers which they state is Al$_3$Ti on top of TiB$_2$ prior to the nucleation of α-Al, and initiated subsequent experimental work$^9$ to identify the crystal orientation relationships between those phases. Recently, Inqhal$^10$ et al.$^{10-12}$ carried out in situ x-ray diffraction experiments on pure Al with different volume fractions of TiB$_2$ 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 Al$_3$Ti on the TiB$_2$. This gives strong support to the observation of Schumacher and Greer$^8$ that the nucleation of Al on TiB$_2$ requires a precursor layer of Al$_3$Ti.

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,
TABLE I. Systems and boundary conditions used in simulations.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>System</th>
<th>(T) (K)</th>
<th>(B.C.)</th>
<th>No. of planes in (\text{Al}_3\text{Ti}) or (\text{TiB}_2)</th>
<th>No. of (\text{Al}_3\text{Ti}) or (\text{TiB}_2) units</th>
<th>No. of liquid Al atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{TiB}_2\text{AlP})</td>
<td>(\text{Al}(111)\parallel\text{TiB}_2(0001))</td>
<td>910</td>
<td>P</td>
<td>(8_{(100)}\times12_{(112)}\times4_{(001)})</td>
<td>32</td>
<td>160</td>
</tr>
<tr>
<td>(\text{Al}_3\text{TiAlP})</td>
<td>(\text{Al}(111)\parallel\text{Al}_3\text{Ti}(112))</td>
<td>910</td>
<td>P</td>
<td>(12_{(110)}\times8_{(112)}\times6_{(112)})</td>
<td>144</td>
<td>164</td>
</tr>
<tr>
<td>(\text{TiB}_2\text{AlF})</td>
<td>(\text{Al}(111)\parallel\text{TiB}_2(0001))</td>
<td>910</td>
<td>F</td>
<td>(8_{(100)}\times12_{(112)}\times4_{(001)})</td>
<td>32</td>
<td>160</td>
</tr>
<tr>
<td>(\text{Al}_3\text{TiAlF})</td>
<td>(\text{Al}(111)\parallel\text{Al}_3\text{Ti}(112))</td>
<td>910</td>
<td>F</td>
<td>(12_{(110)}\times8_{(112)}\times6_{(112)})</td>
<td>144</td>
<td>164</td>
</tr>
</tbody>
</table>

Ti, and B have been 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 \(\text{Al}_3\text{Ti}\) and \(\text{TiB}_2\) substrates. We find that \(\text{Al}_3\text{Ti}\) is indeed a good nucleating material but also find that the precursor layer observed on \(\text{TiB}_2\) could be strained Al on a Ti-terminated face rather than \(\text{Al}_3\text{Ti}\).

II. METHODOLOGY

A. Simulation software

The calculations were performed with the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{13-16} In this code, a plane-wave basis set is used for the expansion of the wave functions is used. The rapid oscillations in the wave functions are treated using projector-augmented waves (PAWs),\textsuperscript{17,18} and the contribution to the energy from electronic exchange and correlation is described using the PW91\textsuperscript{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 method\textsuperscript{21} plus a residual minimization scheme using direct inversion in the iterative subspace\textsuperscript{22} 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/\(\text{TiB}_2\) and liquid Al/\(\text{Al}_3\text{Ti}\) were 536 eV and 329 eV, respectively. The simulations were performed with a \(2 \times 2 \times 1\) \textit{k}-point mesh.

B. Systems and conditions

Two substrates \([\text{Al}_3\text{Ti}(112)\text{ and TiB}_2 (0001)\text{]}\) were considered, as shown in Table I. To establish the correct cell sizes we constructed two cells: one of perfect crystalline \(\text{Al}_3\text{Ti}\) (in the \(\text{DO}_{22}\) structure in contact with fcc Al forming an Al(111)\parallel\text{Al}_3\text{Ti}(112)\) interface; the other of perfect hcp \(\text{TiB}_2\) in contact with fcc Al forming an Al(111)\parallel\text{TiB}_2 (0001)\) interface. The lattice parameters were \(a=b=3.85\) Å, and \(c=8.58\) Å for \(\text{Al}_3\text{Ti}\) (Ref. 23) and \(a=b=3.03\) Å and \(c=3.23\) Å for \(\text{TiB}_2\).\textsuperscript{24} The Al(112) region contains \(12 \times 8 \times 6\) atomic layers and the \(\text{TiB}_2\) region has \(8 \times 12 \times 4\) layers. To generate the starting coordinates for the liquid Al we removed the substrate material (\(\text{TiB}_2\) or \(\text{Al}_3\text{Ti}\)) and performed MD at 1273 K and an average pressure of 0 Pa using an Embedded Atom Method (EAM) potential\textsuperscript{25} and the Hoover NVT ensemble\textsuperscript{26} as implemented in LAMMPS.\textsuperscript{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 \(\text{TiB}_2\) units, the other with 144 liquid Al atoms combined with 144 \(\text{Al}_3\text{Ti}\) units. Using the reference melting point (912 K) calculated by Alfè \textit{et al.}\textsuperscript{28} using \textit{VASP} with PAW and generalized gradient approximation (GGA), we studied \(\alpha\)-Al nucleation at small undercoolings (\(~2\) K). The MD simulations were all performed at constant temperature (\(~910\) 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 \(\text{TiB}_2\) 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 \(\text{TiB}_2\)AlP 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 \(t_n\text{ cores}\)
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 TiB\(_2\)AlP 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 \( \langle \rho(z) \rangle \) averaged over slices of the cell parallel to the solid/liquid (S/L) interface calculated using the following formula:\textsuperscript{29,30}

\[
\rho(z) = \frac{\langle N_j \rangle}{A_{\text{int}} \Delta z},
\]

where \( \langle N_j \rangle \) is the time averaged number of atoms in a bin of size \( \Delta z \) at \( z \), and \( A_{\text{int}} \) is the area of the S/L interface. The resulting profile is sensitive to the choice of bin size (\( \Delta z \)); 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 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,\textsuperscript{31} the centrosymmetry parameter (CSP),\textsuperscript{32} the common neighborhood parameter,\textsuperscript{33} and the ordering discrimina-

\[\alpha = \frac{1}{N} \sum_{i=1}^{6} |R_i + R_{i+6}|^2,\]

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, \( \alpha = 0 \), for the (001) surface \( \alpha = 24.9 \text{ Å}^2 \), for an intrinsic stacking fault \( \alpha = 8.3 \text{ Å}^2 \), for atoms midway between fcc and hcp \( \alpha = 2.1 \text{ Å}^2 \), and for liquid atoms with disordered structure \( 16 < \alpha < 24.9 \text{ Å}^2 \).\textsuperscript{33}

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

\[
S_{2D}(k) = \frac{1}{N} \sum_{i,j} \exp(ik \cdot (\vec{r}_i - \vec{r}_j)) = \frac{1}{N} \sum_{i,j} \cos(k_x(x_i - x_j) + k_y(y_i - y_j)).
\]

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\(_3\)Ti (112) substrates.

III. RESULTS AND DISCUSSION

A. TiB\(_2\) substrate

Using PBCs, the Al\(_3\)TiAlP 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,\textsuperscript{36} so the effective undercooling is greater than this.) There are two kinds of (0001) interface for the TiB\(_2\) 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
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

![Fig. 2](image)

Sequential images and calculated density profile of solid Al nucleation from the melt on top of TiB$_2$ 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.

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 TiB$_2$ substrate is constant (1.6 ± 0.15 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 TiB$_2$ structure, giving an AlB$_2$ 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

![Fig. 3](image)

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.

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

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Neighbor distances</th>
<th>Interplanar spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$, $b$, $c$ (Å)</td>
<td>$r_{1\text{nn}}$ (Å)</td>
<td>$r_{2\text{nn}}$ (Å)</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Al$^a$</td>
<td>4.05 4.05</td>
<td>2.86 4.05</td>
</tr>
<tr>
<td>Al$_2$Ti$^b$</td>
<td>3.85 8.58</td>
<td>2.72 3.85</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>3.03 3.23</td>
<td>3.03 (Ti-Ti)</td>
</tr>
<tr>
<td>AlB$_2$</td>
<td>3.01 3.25</td>
<td>3.01 (Al-Al)</td>
</tr>
</tbody>
</table>

$^a$Reference 37.

$^b$Reference 23.

$^c$Reference 24.

$^d$Reference 38.
disordered layer. On the left-hand side (Ti-terminated surface) an fcc-like structure with an interplanar spacing of about 2.4 ± 0.5 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) 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 TiB2AlP 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 TiB2), 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 TiB2 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 TiB2 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 D022 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 room-temperature 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 pair-correlation 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. 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; [(d1)–(d4)] third layer in the liquid Al. Computed at \( t = 2.85 \) ps](image)
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 [Ti$_1$ and Ti$_2$ in the inset images in Fig. 5(b)]. We calculated the RDF for the first layer of liquid on top of the B-terminated TiB$_2$ surface and 12 Al atoms around the Ti$_2$ atom in the 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 TiB$_2$ surface is at a distance of 2.85 Å, close to the second neighbor Al-Al distance of 2.88 Å in Al$_3$Ti while the second peak is at 3.15 Å, which is close to the Al-Al distance in AlB$_2$. It might be that the presence of Ti is inhibiting the formation of the AlB$_2$ thin film by promoting the formation of an Al$_3$Ti, 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 Ti$_2$ has three peaks at 2.75, 3.65, and 4.75 Å, while $g(r)_{Ti-Al}$ around Ti$_2$ exhibits three peaks at 2.75, 3.25, and 4.95 Å. These do not match exactly separations in the Al$_3$Ti structure but are quite close.

In addition to the pair distribution function, we also quantified the centro symmetry parameter 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 Ti$_1$-Ti$_4$ in Fig. 6]. We plotted the distribution of ordering over this period in Fig. 6(b). Ti$_1$ is slightly less ordered compared to the liquid Al$_b$ atoms because the mean $\alpha$ value is smaller. Surprisingly, Ti$_2$ shows the same degree of ordering as the Al atoms Al$_a$ on top of the Ti-terminated surface of TiB$_2$. This means that Ti$_2$ promotes the surrounding atoms to form an fcc structure inside the bulk liquid. Atoms at the Ti-terminated surface (Ti$_3$) are more disordered as compared to the Ti atoms in the middle of the TiB$_2$ substrate (Ti$_4$). 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 Al$_{a,b}$ and Ti$_{1-4}$ thus supports the experimental findings that formation of an fcc-like structure is promoted by the presence of Ti atoms.3–6
The interplanar spacing for the Al$_3$Ti substrate retained its bulk value, just as we saw for the TiB$_2$ structure. In contrast to the TiB$_2$ substrate shown in Fig. 2, fcc-like structural ordering is initiated and propagates into the liquid on both sides of the Al$_3$Ti 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 Al$_3$Ti substrate for 1 ps, the maximum density of the first ordering layer (308 mol/l) on top of the Al$_3$Ti 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 Al$_3$Ti 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 Al$_3$Ti substrate. Using the outermost layer of the Al$_3$Ti 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 Al$_3$Ti 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 Al$_3$Ti. This might explain why Al$_3$Ti is a powerful nucleant that easily initiates the formation of fcc Al solid from the melt.

C. Comparison of the B-terminated TiB$_2$ and Al$_3$Ti (112) surface

For both TiB$_2$AlP and Al$_3$TiAlP we calculated the initial pressure and final pressure. We found positive pressures (about $5.0 \times 10^8$ Pa) at the beginning and negative pressures (about $-3.0 \times 10^9$ 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 TiB$_2$. In order to make a better comparison of the relative effectiveness of Al$_3$Ti and TiB$_2$ 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 TiB$_2$AlP and Al$_3$TiAlP systems...
were simulated to compare the efficiency with which TiB$_2$ and Al$_3$Ti 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 TiB$_2$ basal plane and the Al$_3$Ti 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 TiB$_2$, solid Al can only nucleate from the melt on top of the B-terminated TiB$_2$ 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 TiB$_2$ 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 AlB$_2$ 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 Al$_3$Ti(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 embedded atom method for the Al-Ti system. Using the same conditions and configuration (Al$_3$TiAl$_2$F), we found that continuous growth of solid Al on Al$_3$Ti(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 Al$_3$TiAl$_2$F system.

Our preliminary TiB$_2$Al$_2$F and Al$_3$TiAl$_2$F 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 TiB$_2$ basal plane, and it does not display the fluctuations in order seen in the liquid on the Al$_3$Ti(112) substrate. In addition, the d spacing in the new solid phases differ on the two kinds of substrate. Liquid Al on Al$_3$Ti(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$_3$Ti(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-
coolings (~2 K) on different kinds of substrates including Al$_3$Ti and TiB$_2$, 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 TiB$_2$ and Al$_3$Ti substrates at temperatures below the Al melting point. Lattice parameters differ on two kinds of termination surfaces of TiB$_2$, promoting new structure ordering with different potentials to grow. The liquid→solid transformation process on top of the B-terminated (0001) basal plane of TiB$_2$ does not promote fcc-like ordering, instead it tries to form an AlB$_2$ structure to replicate the TiB$_2$ 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 between fcc Al and TiB$_2$. At small undercooling, liquid Al close to the Al$_3$Ti (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 Al$_3$TiAlF (as estimated from classical MD using an EAM potential) is too great to be done by ab initio MD using our available resources. Nevertheless, this preliminary study exposes promising features through our direct comparison of Al$_3$Ti (112) with TiB$_2$ (0001). We find some evidence that Al$_3$Ti (112) is a more powerful nucleant than TiB$_2$ (0001) with signs that continu-
ous growth of fcc structure on top of Al$_3$Ti (112) is possible. This can be seen as supporting the accepted view that “free growth” occurs on Al$_3$Ti (112) which coats TiB$_2$, as suggested by previous experiments. 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.

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