Which wets TiB$_2$ inoculant particles: Al or Al$_3$Ti?

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Abstract

TiB$_2$ particles are proven effective nucleants of commercial purity aluminium, resulting in smaller grains and hence greater desired mechanical properties; however, there is uncertainty as to the mechanism by which it operates. Here we clarify what happens in the initial stages by computing the total Gibbs energy change associated with four possible nucleation mechanisms, each characterised by the termination of the TiB$_2$(0001) substrate (Ti or B) and the solid that forms on it (Al or Al$_3$Ti). The appropriate solid/solid interfacial energies are derived from Density Functional Theory (DFT) calculations, while the bulk energies are derived from thermodynamic data, supplemented with strain energies calculated from DFT. Solid/liquid interfacial energies are estimated using simple models with parameters based on the literature and DFT calculations. The results suggest that the Ti termination of TiB$_2$ is more stable than the B termination in the melt, and that the direct formation of Al off a Ti-terminated TiB$_2$ substrate is the most favourable mechanism for the nucleation of Al rather than the previously proposed formation of a Al$_3$Ti interlayer. On the B termination of TiB$_2$, Al formation is more stable for thick solid layers, but this is much more uncertain for thin solid layers where it is possible that Al$_3$Ti formation is more stable.

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1. Introduction

Aluminium alloys are widely used because they are light, strong, resistant to corrosion, and alumina is abundant in the Earth’s crust. The mechanical properties of an aluminium component depend on its microstructure, including the average size and shape of the grains, with smaller equiaxed grains generally leading to greater desirable properties such as improved yield strength and toughness due to the Hall-Petch effect [1, 2], together with reduced defects such as porosity [3] and hot tearing [4]. The addition of grain refiners to molten aluminium alloys is known to encourage significant reduction in grain size, and is common industrial practice. However, the mechanism by these grain refiners nucleate $\alpha$-Al is still disputed. Therefore, we require a fuller and more detailed understanding of the solidification process, starting with the system under study here: commercial purity (CP) aluminium together with its most commonly used grain refiner, the Al-Ti-B master alloy.

In the decades following the 1950s, grain refiner research focussed on observing results and trends, but did not study the mechanics of the process. However, in the 1990s several transmission electron microscope (TEM) experiments [5, 6, 7, 8, 9, 10] suggested that TiB$_2$ was the heterogeneous nucleant responsible for aluminium nucleation, by showing that thin ordered layers of Al$_3$Ti-like structure (presumed to be Al$_3$[Ti,Ta]), had formed off the (0001) face of a TiB$_2$ particle in a glass formed from Al$_{85}$Ni$_{5}$Y$_8$Co$_2$. It is, however, unclear what the consequence of using this metallic glass rather than molten CP Al is.

Other experiments showed that, in addition to TiB$_2$ particles, excess solute titanium in the melt was also needed for $\alpha$-Al nucleation to occur [11]. The role played by this excess Ti is not yet completely understood, but it is thought that in addition to acting as a diffusion restrictor [12], Ti is needed to form Al$_3$Ti which nucleates off the TiB$_2$ forming a thin layer; Al then nucleates off the Al$_3$Ti layer [13]. The confidence in this Al$_3$Ti nucleation hypothesis is based on Schumacher’s TEM experiments [5, 6, 7, 8, 9, 10], backed up by more recent
TEM experiments by Fan [14], and by in situ synchrotron X-ray diffraction experiments [15], where diffraction peaks corresponding to plane separations similar to those of bulk Al$_3$Ti were observed at the onset of aluminium solidification.

However, none of these experimental results are able to show the precise chemical composition of the nucleating layer. It is possible that what is being observed in these experiments is actually strained $\alpha$-Al, as suggested by Wang et al. [16], who proposed that the thin layers observed by Schumacher et al. [8] could be strained Al with the same interplanar separation as Al$_3$Ti. If this is the true mechanism, then the role of the excess Ti could be to ensure that TiB$_2$ particles become Ti-terminated. Other recent static and molecular dynamics calculations using Density Functional Theory (DFT) [17, 16, 18, 19, 20, 21] show that solid Al adheres well to the Ti-terminated face of TiB$_2$, and above the melting point liquid Al shows significant ordering close to this interface, which suggests it is plausible that Al could nucleate without an Al$_3$Ti layer. None of these computational studies, however, address the role of excess Ti on the heterogeneous nucleation process.

In this paper, we calculate the total Gibbs energies before and after nucleation, of four hypothetical aluminium nucleation mechanisms:

\begin{align*}
\text{TiB}_2(\text{Ti})/\text{melt} & \rightarrow \text{TiB}_2(\text{Ti})/\text{Al}/\text{melt} \\
\text{TiB}_2(\text{B})/\text{melt} & \rightarrow \text{TiB}_2(\text{B})/\text{Al}/\text{melt} \\
\text{TiB}_2(\text{Ti})/\text{melt} & \rightarrow \text{TiB}_2(\text{Ti})/\text{Al}_3\text{Ti}/\text{melt} \\
\text{TiB}_2(\text{B})/\text{melt} & \rightarrow \text{TiB}_2(\text{B})/\text{Al}_3\text{Ti}/\text{melt}
\end{align*}

where the two species separated by // denote the characteristic interfaces of the system. The planes parallel to the interfaces are TiB$_2$(0001), Al (111) and Al$_3$Ti (112), and the parenthesized element denotes the termination of the TiB$_2$(0001) surface. Using DFT and thermodynamic arguments we address the following questions:

1. What are the TiB$_2$/Al interfacial energies if we account for the effects of
strain within the interfacial plane, and is the strain energy in the interfacial plane significant?

2. What are the TiB₂//Al₃Ti interfacial energies (also accounting for the effects of interfacial strain) and how do they compare with those of TiB₂//Al?

3. Based on the evidence provided both here and in the literature, which of the four nucleation mechanisms is the most favourable?

2. Modelling the nucleation of aluminium

Heterogeneous nucleation is the initial formation of a new phase out of an original phase, occurring on a substrate. There are a wide range of methods for studying nucleation that are outside the purview of this paper. The interested reader is advised to follow the many good articles cited in this paper, as well as recent books on nucleation, such as that by Greer & Kelton [22]. The total change in Gibbs energy of this process, $\Delta G_T$, is defined for an initial system of $N_{\text{melt}}$ mole-atoms of melt (original phase), transforming into $N_{\text{solid}}$ mole-atoms of solid (new phase) on a substrate, and $N_{\text{melt}'}$ mole-atoms of the remaining unsolidified melt, which might have a slightly different composition to the starting melt. If $N_{\text{solid}}$ is small and completely wets, or wets with a very low contact angle, $\Delta G_T$ can be approximated by:

$$
\Delta G_T = N_{\text{solid}} G_{\text{solid}} + N_{\text{melt}} G_{\text{melt}} + N_{\text{melt}'} G_{\text{melt}'} + \left[ \gamma_{\text{solid}} + \gamma_{\text{sub}} - \gamma_{\text{sub}} \right] A_{\text{sub}}
$$

(1)

where $G_a$ is the bulk Gibbs energy per mole-atoms of species $a$, $\gamma_{ab}$ is the interfacial energy between species $a$ and $b$, and $A_{\text{sub}}$ is the area of active substrate. For the nucleation reaction considered in this study, the nucleating solid refers to either Al or Al₃Ti, the melt refers to liquid Al with some small amount of dissolved Ti, before ($\text{melt}$) and after ($\text{melt}'$) the formation of the solid, and the substrate refers to the surfaces TiB₂(Ti) or TiB₂(B). In this study we are primarily interested in the difference in $\Delta G_T$ between Al₃Ti and Al wetting, given
a particular TiB$_2$ substrate, and to see how these differences vary according to $N_{solid}$, $X_{Ti}$ (or $\mu_{Ti}$), and $T$ (temperature).

The bulk Gibbs energies will be computed here using formulae from the literature [23, 24, 25, 26, 27], augmented with DFT to include strain effects. The three interfacial energies are determined as follows: $\gamma_{solid}^{sub}$ is obtained from DFT calculations reported here; $\gamma_{solid}^{melt}$ is estimated by interpolating between literature values for similar interfaces where the melt is pure liquid Al and Al-Ti liquid with $X_{Ti} = 0.0169$ at.%; $\gamma_{sub}^{melt}$ is estimated through a simple model which involves the surface energies $\gamma_{sub}^{vac}$ and $\gamma_{melt}^{vac}$, calculated using DFT and interpolated literature values respectively. We note that the values of $N$ and $A$ are interrelated and depend on assumptions made about the size and shape of the substrate, and of the solid that forms on the substrate.

Note that a central approximation of this paper is the use of static DFT energies – i.e. at 0K, and with no atomic vibrations. Nevertheless it is possible, with our calculated and literature values, to form an approximate expression for $\Delta G_T$, especially since our main goal is a comparison between different mechanisms.

3. Bulk Gibbs Energies

The Gibbs energies of the bulk phases – the $G$’s in Eq. 1 – are calculated using the temperature dependent Gibbs energy expressions of the pure elements from the SGTE databases [23], which are empirical equations fitted to the numerous heating and cooling experiments in the literature. To calculate the Gibbs energy of the multi-component phases, the melt (liquid Al with dissolved Ti) and bulk Al$_3$Ti, the methods and parameters described in Kattner et al. [27] were used. We augment the solid Al and Al$_3$Ti Gibbs energies with the DFT 0K strain energies from the next section.

Furthermore, the bulk Gibbs energy of the melt is used to obtain the relationship between Ti concentration $X_{Ti}$ and the chemical potential $\mu_{Ti}$ using $\mu_{Ti}^{melt} = \frac{dG^{melt}}{dN_{Ti}}$. This enables us to express the interfacial energies as a func-
tion of $X_{Ti}$, thereby making all the variables of Eq. 1 functions of the same Ti concentration variable. The chemical potential is a non-linear function of concentration, but locally the activity, $a_{Ti} = \exp\left(\frac{\mu_{Ti} - \mu_{Ti}^{bulk}}{RT}\right)$, is approximately linear in $X_{Ti}$: $a_{Ti} = \gamma_{Ti}X_{Ti}$, where $\gamma_{Ti}$ (not to be confused with interfacial energy) is the activity coefficient, a dimensionless factor that is a function of $X_{Ti}$ and temperature. The activity $\gamma_{Ti}$ is calculated to be about $2.5 \times 10^{-5} - 3.0 \times 10^{-5}$ around the melting point of Al, at typical melt Ti concentrations of 0.001 to 0.01 at.%, which is broadly in line with that shown by Kostov et al. [28, 29].

4. Interfacial energies

4.1. DFT method

To calculate $\gamma_{solid}^{sub}$, $\gamma_{vac}^{sub}$ (a term in our $\gamma_{melt}^{sub}$ model), and the strain energies that make part of $G_{solid}$, DFT simulations were performed using the ABINIT code [30, 31, 32], which implements a planewave basis set. A planewave energy cutoff of 30 Ha was used with a PAW [33, 34, 35] auxiliary energy cutoff of 60 Ha. The PBE GGA functional [36] was used for the exchange and correlation energy. Monkhorst-Pack grids [37] of $6 \times 6 \times 6$ k points for bulk materials, and $6 \times 6 \times 1$ k points for slabs were employed. Band occupations were calculated using the cold smearing function of Marzari [38]. SCF calculations were converged to within $10^{-9}$ Ha, while atomic and geometric relaxations were carried out using the BFGS method [39] to within a tolerance of $5 \times 10^{-5}$ Ha/Bohr per atom for the bulk and surface energy calculations, and $5 \times 10^{-4}$ Ha/Bohr per atom for the larger, interface calculations. These parameters were chosen after performing extensive convergence tests, to ensure measurable quantities are converged to experimental accuracy: 0.01 J/m$^2$ for the TiB$_2$ surface energies, 0.05 J/m$^2$ for the Al surface energy and TiB$_2$/Al interfacial energies, 0.2 J/m$^2$ for the Al$_3$Ti surface energy, and 0.1 J/m$^2$ for the TiB$_2$/Al$_3$Ti and interfacial energies; 0.01 Å for lattice constants.
4.2. Strain effects

The solid forming on the substrate (TiB$_2$(Ti) or TiB$_2$(B)) is assumed to be coherent and dislocation free, based on TEM images [8]. The solid is assumed to stretch to accommodate the strain, since the TiB$_2$ substrate is a very large particle (on the atomic scale) of a stiff ceramic [40]; the solid is a thin layer of a less stiff material [41, 42]. Although dislocations will form as the solid becomes thicker, we are interested only in the region close to the interface i.e. the case when the strained phases are in equilibrium with the liquid and the substrate. Thus while we shall continue to refer to the solid as either Al or Al$_3$Ti, we shall really mean strained Al or strained Al$_3$Ti, which ensures that $\gamma_{\text{solid}}^{\text{sub}}$ is correctly defined as being independent of the amount of solid. It is shown in section 5 that strain significantly alters the predicted interfacial energy.

4.3. Ti Chemical Potential

In order to calculate the surface and interfacial energies of TiB$_2$ by DFT, we require knowledge of the Ti chemical potential, $\mu_{Ti}$, as there is an exchange of Ti between the melt and the nucleated solid, and possibly the substrate. This chemical potential is sensitive to the Ti concentration in the melt ($X_{Ti}$). At thermodynamic equilibrium $\mu_{Ti}$ should be constant over the entire system; however, as solid forms our system will not be at equilibrium and $\mu_{Ti}$ will vary with position. As the Ti reservoir is the Ti in the melt, whose composition remains practically constant, we will take $\mu_{Ti}$ to be that for the melt. In the systems we are studying, there are limitations that restrict the range of $\mu_{Ti}$ (and $X_{Ti}$), which are inferred from the stability of TiB$_2$ particles, which do not dissolve in the melt, and the absence of pure Ti or B [43]. Combining the $\mu_{Ti}$ and $\mu_B$ ranges with simple thermodynamic expressions of the formation of TiB$_2$, leads to the expression, $\Delta G_{F}^{TiB_2} < \Delta \mu_{Ti} < 0$, where $\Delta \mu_{Ti} = \mu_{Ti} - \mu_{Ti}^{\text{bulk}}$, and $\Delta G_{F}^{TiB_2}$ is the Gibbs energy of formation of TiB$_2$ (a detailed derivation was done by Han [43]).
4.4. Bulk calculations

A unit cell of each material in its most stable bulk phase at 0K was simulated: fcc for Al; face-centered tetragonal DO$_{22}$ for Al$_3$Ti [44]; hexagonal for TiB$_2$; hcp for Ti; and a 12-atom rhombohedral cell ($\alpha$-phase) for B \(^1\). The strained bulk states were simulated using 6-layer unit cells of Al(111) and Al$_3$Ti(112), which were allowed to fully relax in the z-direction, but held fixed in the x-y plane to match the ‘a’ lattice parameter of TiB$_2$ (3.031 Å), thus matching the strained bulk state of Al and Al$_3$Ti present in the surface and interfacial slabs presented in section 4.5.

Table 1 shows the lattice constants obtained from the relaxed bulk simulations, which are later used to define certain cell dimensions in the surface and interface simulations. In addition, the table below shows the calculated energies of bulk formation for TiB$_2$ and Al$_3$Ti (those for Al, Ti and B are zero by definition), and the strained forms of Al and Al$_3$Ti.

The lattice constants agree closely with experiment, with all errors being less than 0.05 Å, and many being less than 0.01 Å. The formation energies of relaxed TiB$_2$ and Al$_3$Ti are also close to the experimental values. Table 1 shows that strained Al and Al$_3$Ti have significantly higher energies than their relaxed counterparts, and that the strain induced on the solid to match the TiB$_2$ substrate is greater for Al$_3$Ti than for Al: their bulk strain energies are: $\Delta G_{\text{strain}}^{\text{Al}} = +2.2$ kJ/mol-atoms and $\Delta G_{\text{strain}}^{\text{Al$_3$Ti}} = +16$ kJ/mol-atoms. This significant difference in strain energy is likely caused by Al$_3$Ti having a tetragonal structure rather than a regular fcc one like Al, which has two important consequences: firstly, the first Al$_3$Ti (112) plane, unlike Al (111), does not exactly align with the perfect hexagonal structure of TiB$_2$(0001); secondly, whilst the Al (111) planes are

\(^1\alpha\)-B is not quite the B ground state, but it is used because it is much simpler than the real ground state, the $\beta$-phase ($\sim$105 atoms per unit cell) whilst the difference in energy per atom between $\alpha$-B and $\beta$-B is very small. Recent DFT calculations [45] found the difference in energy per atom between $\alpha$-B and $\beta$-B to be only 0.29 kJ/mol, which would make less than 0.01 J/m$^2$ difference to the final interfacial energies.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice constant (Å)</th>
<th>Formation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated</td>
<td>experimental</td>
</tr>
<tr>
<td>Al</td>
<td>a = 4.051</td>
<td>a = 4.0496 [46]</td>
</tr>
<tr>
<td>Ti</td>
<td>a = 2.933</td>
<td>a = 2.9506 [46]</td>
</tr>
<tr>
<td></td>
<td>c = 4.657</td>
<td>c = 4.6835</td>
</tr>
<tr>
<td>B</td>
<td>a = 5.049</td>
<td>a = 5.064 [47]</td>
</tr>
<tr>
<td>Al₃Ti</td>
<td>a = 3.853</td>
<td>a = 3.8537 [48]</td>
</tr>
<tr>
<td></td>
<td>c = 8.632</td>
<td>c = 8.5839</td>
</tr>
<tr>
<td>TiB₂</td>
<td>a = 3.0314</td>
<td>a = 3.0236 [40]</td>
</tr>
<tr>
<td></td>
<td>c = 3.2228</td>
<td>c = 3.2204</td>
</tr>
</tbody>
</table>

Table 1: The lattice constants and formation energies obtained from bulk calculations at 0 K and prior experiments.

vertically aligned, repeating every three planes, the Al₃Ti (112) planes lean at about 5 degrees from the vertical. Subsequently, fixing the Al₃Ti (112) planes to conform to TiB₂(0001) results in compression of some of the atoms in the plane and extra induced strain to straighten the slab.

It is important to note that by using 0K strain energies we have neglected differences in the strain that might arise due to thermal expansion and compositional disorder [27], instead assuming the ideal lattice occupancies in the DFT cells. The 0K strain energies will be used with the temperature-dependent relaxed bulk energies for Al and Al₃Ti derived in section 3. This should not significantly affect the main results, since the experimentally determined lattice expansion coefficients for Al and TiB₂ [50, 40] and the theoretically determined values for Al₃Ti [51] show that going from 0K to the melting temperature of Al would result in fairly small reductions in lattice mismatch for both Al (111) (~ +5.5% to +4.2%) and Al₃Ti (112) (~ +11.2% to +10.7% and +4.7% to +4.6%). Furthermore, the Al mismatch, already lower than the Al₃Ti mismatch at 0K, is reduced by a greater amount at the Al melting point, hence the main result of this paper, that TiB₂(Ti)//Al is the favoured nucleation mechanism, would
likely be reinforced if thermal expansion was taken into account.

4.5. Surface and interfacial energy calculations

The following single material surface slabs were simulated: Al(111), strained Al(111), Al₃Ti(112), strained Al₃Ti(112), TiB₂(Ti), and TiB₂(B). The supercells for TiB₂(Ti) and TiB₂(B) were seven layer slabs, containing 10 and 11 atoms respectively (the same as simulated by Han [43]), while the Al and Al₃Ti supercells were six layer slabs, containing 6 and 24 atoms respectively (the Al₃Ti supercells contain 4 atoms per layer, as each layer must have 1 Ti atom for every 3 Al atoms). The strained Al and Al₃Ti supercells differ from their relaxed counterparts by having the cell parameters in the plane of the interfaces fixed to match those of the TiB₂ slabs.

Four interfacial supercells were simulated, each a slab containing seven layers of TiB₂ adhered to six layers of strained solid, Al (111) or Al₃Ti (112). Hence a 16 atom TiB₂(Ti)//Al, a 17 atom TiB₂(B)//Al, a 64 atom TiB₂(Ti)//Al, and a 68 atom TiB₂(B)//Al₃Ti supercell were simulated.

The vacuum added to each surface and interface supercell was least 13 Å thick, sufficient to prevent interaction between periodic images. The number of layers of each material was tested for convergence to ensure a good representation of the bulk material, while still remaining small enough for a full accuracy run: seven layers of TiB₂, six layers of Al, six layers of Al₃Ti, and six Al layers’ worth of vacuum were found to converge γ to 0.05 J/m² for TiB₂//Al and 0.2 J/m² for TiB₂//Al₃Ti (these are conservative estimates), while the difference in γ between systems, which is more important, converged even more tightly.

The surface and interfacial energies are calculated by the common method of subtracting away appropriate amounts of bulk energy, dividing by the area, and then, for interface systems, subtracting any excess surface energy[52]. For example, the interfacial energy calculated from the TiB₂(Ti)//Al slab is:

\[ \gamma_{\text{TiB}_2(Ti)}^{Al} = \frac{1}{A} \left( E^{\text{slab}} - \left\{ 3\mu_{\text{Ti},\text{B}_2} + \mu_{\text{Ti}}^{\text{slab}} + 6\mu_{\text{Al}}^{\text{bulk}} \right\} - \left( \gamma_{\text{vac}}^{\text{TiB}_2(Ti)} + \gamma_{\text{vac}}^{\text{Al}} \right) \right) \]

The \( \mu_{\text{Ti}} \) term is needed because the TiB₂(Ti) substrate in the supercell does not
Table 2: Relaxed and strained surface energies of the solid, Al and Al\textsubscript{3}Ti, calculated from our slab simulations, compared with other simulation results.

<table>
<thead>
<tr>
<th>Solid surface</th>
<th>Relaxed $\sigma$ (Jm\textsuperscript{-2})</th>
<th>Strained $\sigma$ (Jm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Previous work</td>
</tr>
<tr>
<td>Al (111)</td>
<td>0.82</td>
<td>0.939[53]</td>
</tr>
<tr>
<td>Al\textsubscript{3}Ti (112)</td>
<td>0.97</td>
<td>0.92[54]</td>
</tr>
</tbody>
</table>

contain a whole number of TiB\textsubscript{2} units (this is discussed in Han’s TiB\textsubscript{2} surface study [43]). Thus $\gamma$ for all systems involving a TiB\textsubscript{2} substrate are functions of $\mu_{Ti}$, and are thus expressed as a range, going from minimum $\mu_{Ti}$ to maximum $\mu_{Ti}$.

4.6. Surface and interfacial energy results

The surface energies of TiB\textsubscript{2}, $\gamma_{TiB_2(Ti)}^{vac}$ and $\gamma_{TiB_2(B)}^{vac}$, were calculated to be $5.47 - 2.23$ J/m\textsuperscript{2} and $2.99 - 6.23$ J/m\textsuperscript{2} respectively, which is in very close agreement with Han’s results [43]. The surface energies of relaxed and strained Al and Al\textsubscript{3}Ti are shown in table 2.

It is interesting to note that, although the surface energy of strained Al is less than that of strained Al\textsubscript{3}Ti, (strained to achieve coherency with a TiB\textsubscript{2} substrate that is), compared to its relaxed counterpart, the strain seems to have a greater comparative effect on Al than on Al\textsubscript{3}Ti, which is the reverse trend to what was seen for the bulk energy discussed in the previous section.

Our calculated interfacial energies are shown in table 3, and plotted in figure 1 (the plot treats the strained bulk as the reference system). Note that the negative values of interfacial energies shown in these tables and graphs are actually unphysical, but we have kept them to help the reader fully see and compare each plot.

Our values for TiB\textsubscript{2}(Ti)//Al and TiB\textsubscript{2}(B)//Al are in close agreement with those from previous simulations [17], while there are no published interface calculations for the Al\textsubscript{3}Ti systems that we are aware of. As explained in section 2, the use of the strained bulk energies to calculate the interfacial energy makes
Table 3: Calculated ranges of values for the interfacial energies - the first number in the range is for $\mu_{Ti} = -0.12$ Ha/atom. (-310 kJ/mol-a.); the second number is for $\mu_{Ti} = 0$ Ha/atom (0 kJ/mol-a.).

<table>
<thead>
<tr>
<th>System</th>
<th>Previous work</th>
<th>This work (inc. $xy$ strain)</th>
<th>This work (exc. $xy$ strain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB$_2$(Ti)//Al</td>
<td>3.25 -- -0.08 [17]</td>
<td>3.04 -- -0.20</td>
<td>2.62 -- -0.62</td>
</tr>
<tr>
<td>TiB$_2$(B)//Al</td>
<td>1.12 -- 4.45 [17]</td>
<td>0.99 -- 4.23</td>
<td>0.57 -- 3.82</td>
</tr>
<tr>
<td>TiB$_2$(Ti)//Al$_3$Ti</td>
<td>-</td>
<td>3.61 -- 0.37</td>
<td>2.93 -- -0.31</td>
</tr>
<tr>
<td>TiB$_2$(B)//Al$_3$Ti</td>
<td>-</td>
<td>0.46 -- 3.71</td>
<td>-0.21 -- 3.03</td>
</tr>
</tbody>
</table>

Figure 1: Interfacial energy versus Ti chemical potential for the four interfacial systems. The energies of formation of Al$_3$Ti, both relaxed and strained, are shown by the vertical dotted lines.
a significant difference to the results, which figure 2 demonstrates. The small
difference between our strain-included $\gamma$ and those of Han may be at least partly
explained by Han’s use of ultrasoft pseudopotentials, in contrast to our use of
PAW.

The results from figure 1 suggest three main findings concerning $\gamma_{\text{sub}}^{\text{solid}}$:

1. Both solid Al and Al$_3$Ti form a more stable interface with TiB$_2$(Ti) than
TiB$_2$(B) at higher Ti chemical potentials; at lower Ti chemical potentials,
TiB$_2$(B) forms the more stable interface.

2. The TiB$_2$(Ti) substrate forms more stable interfaces with Al than with
Al$_3$Ti; conversely, TiB$_2$(B) forms more stable interfaces with Al$_3$Ti than
Al.

3. We see that for higher Ti concentrations ($\Delta \mu_{Ti} \gtrsim -184$ kJ/mol, which
around the melting point equates to \( X_{Ti} \geq 0.0003\text{at.\%} \) the most stable interface is \( \text{TiB}_2(\text{Ti})/\text{Al} \); for lower Ti concentrations (\( \Delta \mu_{Ti} \leq -184 \text{kJ/mol} \) or \( X_{Ti} \leq 0.0003\text{at.\%} \) the most stable is \( \text{TiB}_2(\text{B})/\text{Al}_3\text{Ti} \). However, bulk \( \text{Al}_3\text{Ti} \) is not stable in this range, but only stable when \( \Delta \mu_{Ti} > -90 \text{kJ/mol} \).

It therefore seems that based on the GS substrate//solid interfacial energies alone, \( \text{TiB}_2(\text{Ti})/\text{Al} \) is the most favorable system.

4.7. Solid-liquid interfacial energies

We now consider the solid-liquid interfacial energies \( \gamma_{\text{melt}} \) and \( \gamma_{\text{melt}}^{\text{sub}} \). The \( \gamma_{\text{solid}} \) values, \( \gamma_{\text{Al}}^{\text{melt}} \) and \( \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}} \), are estimated as follows: \( \gamma_{\text{Al}}^{\text{melt}} \) at 660K was taken as a linear interpolation between literature values of \( \gamma_{\text{Al}}^{\text{Al(l)}} \) (0.131 J/m\(^2\) – the average of 0.121 J/m\(^2\) \cite{55} and 0.141 J/m\(^2\) \cite{56}) and \( \gamma_{\text{Al}}^{\text{melt}(X_{Ti}=0.0169\%)} \) (rounded up to 0.171 J/m\(^2\) \cite{57}). The effect of strain – we are actually dealing with \( \gamma_{\text{Al-strained}} \) – was estimated by calculating the difference that straining Al makes to the Al(111)//vacuum surface energy, \( \{\sigma_{\text{Al-strained}}^{\text{vac}} - \sigma_{\text{Al-relaxed}}^{\text{vac}}\} \), and was found to be 0.258 J/m\(^2\) (see table 2). This results in an estimate for \( \gamma_{\text{Al}}^{\text{melt}} \) of 0.389 J/m\(^2\). For \( \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}} \), a similar method was used, except that the two values to interpolate between were themselves estimated, due to a lack of literature values, using \( \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}(X_{Ti}=0.0169\%)} \approx \gamma_{\text{Al}}^{\text{melt}(X_{Ti}=0.0169\%)} + \left( \gamma_{\text{Al}_3\text{Ti}}^{\text{Al(l)}} - \gamma_{\text{Al}_3\text{Ti}}^{\text{Al}_3\text{Ti}} \right) \). 

Modelling \( \gamma_{\text{sub}}^{\text{melt}} \). To estimate the interfacial energy between the melt and the substrate we have built a simple model. We start by expressing \( \gamma_{\text{sub}}^{\text{melt}} \) as follows:

\[
\gamma_{\text{sub}}^{\text{melt}} = \gamma_{\text{sub}}^{\text{vac}} + \gamma_{\text{melt}}^{\text{vac}} + \Delta \gamma_{\text{sub}}^{\text{melt}} \tag{3}
\]

where \( \Delta \gamma_{\text{sub}}^{\text{melt}} \) is the difference in total interfacial and surface energies caused by the immersion of the substrate into the melt. For \( \gamma_{\text{vac}}^{\text{sub}} \) we use the 0K interfacial energies obtained from the DFT surface energy calculations (see table 2). For \( \gamma_{\text{melt}}^{\text{vac}} \) we start with \( \gamma_{\text{Al(l)}}^{\text{melt}} \) as 1 J/m\(^2\) \cite{58, 59, 60} and use the same linear interpolation as for \( \gamma_{\text{solid}}^{\text{melt}} \) above, and then add the 0K difference between the
strained and relaxed solid Al surface energies, which is 0.14 J/m$^2$ (see table 2). The energy changes caused by $\Delta \gamma_{\text{melt}}$ are based only on the amount of ordering of the liquid at the substrate, based on the results of DFT MD simulations by Wang [16] and Zhang [18, 21]. An ordering function is used, $a(z)$, to quantify the state of the liquid at a distance $z$ from the substrate (0 is perfect disorder, i.e. liquid; 1 is perfect order, i.e. solid), and is approximated by an exponential function, $a(z) = \exp(-kz)$ where $k$ is a disordering parameter. Based on Wang’s [16] diagrams of the nuclei’s final positions and the density profile away from the interface, $k$ was set to $0.25 \times 10^{-10}$ m$^{-1}$ and $1 \times 10^{-10}$ m$^{-1}$ for TiB$_2$(B) and TiB$_2$(Ti). The interfacial free energy is then computed using the procedure detailed in the supplementary material, and is a function of $a(z)$, and thus ultimately a function of $k$. Our final expression for $\gamma_{\text{melt}}$ is:

$$\gamma_{\text{melt}} = \gamma_{\text{vac}} + \gamma_{\text{melt}} - b\rho_{\text{liq}} \left( \frac{8}{3} \rho_{\text{liq}} \Delta\rho + \frac{1}{4} \right) k^{-1} \tag{4}$$

where $b$ is the temperature dependent Gibbs energy of fusion of the Al liquid, $\rho_{\text{liq}}$ is the density of Al liquid, and $\Delta\rho = \rho_{\text{solid}} - \rho_{\text{liq}}$ with $\rho_{\text{solid}}$ being the density of the solid. While very simple, this model contains two important elements: firstly, the interfacial energy varies with respect to $X_{Ti}$, because $\gamma_{\text{vac}}$ and $\gamma_{\text{melt}}$ vary with $X_{Ti}$; secondly, it contains an element, $\Delta \gamma_{\text{melt}}$, that lowers $\gamma_{\text{melt}}$ in proportion to the amount of ordering seen at the substrate i.e. more ordering, means a lower $\gamma_{\text{melt}}$. Figure 3 shows the interfacial energy derived from the model using the values of $k$ given above.

The plots for $\gamma_{\text{melt}}$ are quite similar to those of $\gamma_{\text{solid}}$ (and $\gamma_{\text{vac}}$), but shifted about 3.5 - 4 J/m$^2$ (1 J/m$^2$) higher. The crossover point occurs at about $\mu_{Ti} = -200$ kJ/mol, which around the melting point of Al corresponds to $X_{Ti} = 1 \times 10^{-7}$ to $1 \times 10^{-6}$. In a typical industrial melt $X_{Ti}$ is about $1 \times 10^{-5}$ to $1 \times 10^{-4}$, hence TiB$_2$(Ti) is predicted to be the more stable substrate prior to nucleation, and hence, the two nucleation mechanisms starting with TiB$_2$(Ti)\//melt appear to be the most likely nucleation mechanisms. However, the possibility that TiB$_2$(B) substrates might still be present is discussed in the analysis section.
Figure 3: The interfacial energy between TiB₂ substrates and the melt, $\gamma_{\text{melt}}$, plotted against $\mu_{\text{Ti}^\text{sub}} - \mu_{\text{Ti}^\text{bulk}}$, according to our model.
4.8. Finite temperature corrections to interfacial energy

One major limitation of the $\gamma_{\text{solid}}^{\text{sub}}$ and $\gamma_{\text{melt}}^{\text{sub}}$ figures is that they were calculated using GS DFT simulations, and so do not include finite temperature effects. Further DFT perturbation calculations (DFPT), implementing the harmonic approximation, can be used to estimate the finite temperature effects. However, at the temperatures considered here (close to the melting point), the harmonic approximation breaks down and further anharmonic effects need to be considered, which would be very computationally demanding and beyond the scope of this paper. However, some preliminary DFPT calculations using an LDA exchange correlation functional and norm-conserving pseudopotentials were carried out to see qualitatively how the finite temperature corrections affect the initial substrate//melt system and the $\Delta G_T$ for the nucleation of Al. These preliminary results suggest that the final conclusion, which predicts the TiB$_2$(Ti)//Al nucleation mechanism as the most favoured, would not be affected by the finite temperature corrections. Please see the supplementary material for more details. For this study, the GS results shown in sections 4 and 4.7 are used for the $\Delta G_T$ analysis in section 5.

5. $\Delta G_T$ Analysis

The interfacial energies from section 4 and the bulk energies from section 3 are now inserted into Eq. 1 to calculate the total Gibbs energy of solid formation, and analyse it as a function of solid thickness $n$, Ti concentration $X_{Ti}$, and temperature $T$. It must be emphasised that this analysis does not say anything about the critical point of nucleation, that is, the most stable number of layers of solid. According to Eq. 1, above the melting point and even slightly below it, one layer of solid should be the most stable arrangement, because the first layer reduces the overall Gibbs energy by reducing the total interfacial energy, while the formation of further layers of solid would only increase the total Gibbs energy, because the formation of strained solid, Al or Al$_3$Ti, is positive (see table 1). Yet Eq. 1 is derived from macroscopic equilibrium thermodynamics,
and it is unclear how closely very thin layers of solid obey these rules. Hence, the analysis will consider separately a thin layer system (1 atomic layer) and a thick layer system (6 atomic layers), in order to more clearly identify where any uncertainty in the conclusions lies.

We make assumptions about the size, shape, and number density of TiB$_2$ substrates, based on estimates by Greer [61]: the average diameter of the substrate = 3$\mu$m, the particle density = $1 \times 10^{14}$ particles/m$^2$, and the fraction of active particles = 0.001. This gives a total active substrate area = $4.93 \times 10^{-7}$m$^2$/mol-atoms of melt. The value of these constants does significantly influence the absolute values of $G_T$ and $\Delta G_T$, but they have a negligible effect on the difference in $\Delta G_T$ between the 4 systems. Throughout, unless specified otherwise, $X_{Ti}$ is taken to be fixed at a typical value of $5 \times 10^{-5}$ mole fraction (0.01wt%) used in industry, and the temperature is taken to be 950K, which is approximately when wetting on the substrate is first observed [15].

5.1. $G_T$ and $\Delta G_T$ vs n layers

Figure 4 shows the absolute values of $G_T$ plotted against the number of layers $n$. We see that under typical melt conditions, TiB$_2$(Ti)//melt is the most stable starting system before nucleation, and TiB$_2$(Ti)//Al//melt is the most stable after nucleation. Hence this plot supports TiB$_2$(Ti)//melt $\rightarrow$ TiB$_2$(Ti)//Al//melt as the most likely nucleation mechanism. Interestingly, if the starting system is TiB$_2$(B)//melt, it is much less clear whether TiB$_2$(B)//Al//melt or TiB$_2$(B)//Al$_3$Ti//melt would be the most stable system after nucleation. The evidence above suggests that thin layers of solid Al$_3$Ti might be more stable than thin layers of solid Al, on a TiB$_2$(B) substrate.

Figure 5 shows the difference in values of $\Delta G_T$, the Gibbs energy change due to nucleation, plotted as functions of $n$, the number of layers of solid. It shows the most likely solid, Al or Al$_3$Ti, given a particular starting substrate - a negative value indicates that solid Al formation is more stable, whereas a positive value indicates that solid Al$_3$Ti formation is more stable. There is a clear trend that as $n$ increases, formation of Al becomes more and more
Figure 4: The total Gibbs energy, $G_T$, of the initial and final systems. The absolute value of $G_T$ is arbitrary: here the value for the initial TiB$_2$(Ti)//melt system is chosen as zero. Note: the TiB$_2$(Ti)//Al$_3$Ti//melt and TiB$_2$(B)//Al$_3$Ti//melt lines are very similar and are overlapping on this plot.
Figure 5: The difference in $\Delta G_T$ between formation of $n$ layers of Al and Al$_3$Ti, for both substrates, at two different temperatures. The vertical line in both graphs represents the minimum number of layers of solid beyond which subsequent layers are bulk-like, according to our DFT calculations.

favourable over Al$_3$Ti.

5.2. $\Delta G_T$ vs $X_{Ti}$ and $T$

Figure 6 shows the effects of varying $X_{Ti}$ and $T$, for thin and thick layers of solid. As expected from the Al-Ti phase diagram, an increase in $X_{Ti}$ increases the stability of Al$_3$Ti relative to Al. In the range of $X_{Ti}$ shown here, which is typical of an industrial aluminium melt, and for much higher $X_{Ti}$, the Al-favouring trends shown in figure 5 do not change – that is, for 6 atomic layers on TiB$_2$(B), and any amount of solid thickness on TiB$_2$(Ti), it remains that Al is much more stable than Al$_3$Ti. However, for thin layers of solid forming on TiB$_2$(B), Al$_3$Ti appears to be more stable, although there is significant un-
Figure 6: The difference in $\Delta G_T$ for the formation of 1 and 6 layers of Al and Al$_3$Ti on both substrates, plotted against $X_{Ti}$, at two different temperatures.

certainty in which solid is more stable. It is quite possible that the cross-over point – below which thin layers of Al$_3$Ti would cease to be more stable than thin layers of Al – might lie within an industrially relevant composition. Direct evidence for the TiB$_2$(B)//Al$_3$Ti mechanism was not seen in Wang’s DFT MD simulation, but it is possible that a longer simulation with more Ti atoms in the liquid at the TiB$_2$(B) surface might show at least one Al$_3$Ti layer form spontaneously at the surface. The effect of decreasing temperature decreases slightly the likelihood of Al forming: this effect becomes more noticeable for thicker amounts of solid.
5.3. $\Delta G_T$ sensitivity to $\gamma_{\text{melt}}$ values

This and the next subsection look at how sensitive the $\Delta G_T$ results are to the $\gamma_{\text{melt}}$ values, which were calculated relatively roughly compared to the $G$ and $\gamma_{\text{solid}}$ values. Figure 7 shows the effects of varying the estimates for $\gamma_{\text{melt}}$, specifically the difference $\gamma_{\text{Al}}^{\text{melt}} - \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}}$. The plot shows that for both thick and thin layers of solid on a TiB$_2$(Ti) substrate, quite large variations in $\gamma_{\text{Al}}^{\text{melt}} - \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}}$ from the value we used (-0.208 J/m$^2$, shown by the crosses) would not alter the original conclusion that thick layers of Al are more stable than Al$_3$Ti on both TiB$_2$ substrates. However, for thin layers on a TiB$_2$(B) substrate, the more stable solid is reasonably sensitive to variations in $\gamma_{\text{Al}}^{\text{melt}} - \gamma_{\text{Al}_3\text{Ti}}^{\text{melt}}$—a shift to -0.35 J/m$^2$ would make Al more stable than Al$_3$Ti.
Figure 8 looks at the effect of varying the solid//liquid interfacial energy of our starting system, $\gamma_{\text{melt}}^{\text{sub}}$, specifically $\gamma_{\text{TiB}_2(\text{Ti})}^{\text{melt}} - \gamma_{\text{TiB}_2(\text{B})}^{\text{melt}}$. Previous graphs have plotted the $\Delta G_T$ difference between Al and Al$_3$Ti mechanisms, *given a particular substrate* - that is the more useful comparison if we assume that in our real system all or almost all of the substrates have the same termination. However, we may wish to consider the possibility that both substrates are available in the melt. In this case, we would want to know, *given a particular nucleating solid*, what is the more favourable substrate, and this is what figure 8 shows. The plot suggests that the precise value of $\gamma_{\text{TiB}_2(\text{Ti})}^{\text{melt}} - \gamma_{\text{TiB}_2(\text{B})}^{\text{melt}}$ is important in determining the favoured substrate. It is very likely, given our values for $\gamma_{\text{Al}}^{\text{TiB}_2}$ and $\gamma_{\text{vac}}^{\text{TiB}_2}$, that $\gamma_{\text{TiB}_2(\text{Ti})}^{\text{melt}} - \gamma_{\text{TiB}_2(\text{B})}^{\text{melt}}$ is also negative in typical industrial $X_{\text{Ti}}$ and $T$. Our default results confirm that Al nucleation clearly favours TiB$_2$(Ti) as a substrate, and Al$_3$Ti nucleation favours TiB$_2$(B). These results are fairly stable with respect to errors in our $\gamma_{\text{TiB}_2(\text{Ti})}^{\text{melt}} - \gamma_{\text{TiB}_2(\text{B})}^{\text{melt}}$ estimation. However, $\gamma_{\text{sub}}^{\text{melt}}$ was estimated using the ordering of liquid Al atoms only, and not Al atoms with some dissolved Ti. Understanding how the presence of Ti atoms affects this ordering is an interesting topic of ongoing research [21].

6. Conclusions

Four potential mechanisms for the nucleation of aluminium were investigated and compared. Four interfaces were simulated using DFT, each involving a substrate, TiB$_2$(Ti) or TiB$_2$(B), and a nucleated solid, Al or Al$_3$Ti. Each interfacial energy was calculated as a function of the Ti chemical potential, itself a function of Ti concentration ($X_{\text{Ti}}$) and temperature ($T$) in the melt. The interfacial energy was then combined with Gibbs energy data from the literature to assess the nucleating potential of each mechanism. The following conclusions are made:

1. Regarding the stability of the interfaces at 0K: the TiB$_2$(Ti)//Al interface is more stable than TiB$_2$(Ti)//Al$_3$Ti for all values of $X_{\text{Ti}}$; the TiB$_2$(B)//Al$_3$Ti interface is more stable than TiB$_2$(B)//Al for all values
Figure 8: The difference in $\Delta G_T$ between formation of a solid on $\text{TiB}_2$(Ti) and $\text{TiB}_2$(B), plotted against the difference in the starting solid-liquid interfacial energy $\gamma^\text{melt}_{\text{TiB}_2(Ti)} - \gamma^\text{melt}_{\text{TiB}_2(B)}$. The left half of the graph represents cases where $\text{TiB}_2$(Ti) has the lower interfacial energy with the melt; the right half likewise for $\text{TiB}_2$(B). This difference in $\Delta G_T$ is plotted for each solid separately, at $T=950\text{K}$, for three different $X_{Ti}$. 
of $X_{Ti}$; the most stable interface at 0K is TiB$_2$(Ti)/\!/Al for $X_{Ti} \geq 0.0003$ at.\%, and TiB$_2$(B)/\!/Al$_3$Ti for $X_{Ti} \leq 0.0003$ at.\%. Strain plays a significant role in the value of the interfacial energy, adding about 0.5 J/m$^2$ to TiB$_2$/\!/Al interfacial energies.

2. The results here suggest that any possible Al$_3$Ti layers that do form, on either substrate, are likely to be very thin, and probably significantly thinner than any Al layers that might form.

3. TiB$_2$(Ti) is more stable in the melt than TiB$_2$(B) prior to nucleation. In this case, formation of Al is more stable than Al$_3$Ti formation, for thin and thick solid layers. However, if TiB$_2$(B) is present in the melt prior to nucleation, then only for thick solid layers is formation of Al is more stable over Al$_3$Ti, whilst for thin solid layers, it is unclear whether formation of Al or Al$_3$Ti is more stable, but our results slightly favour Al$_3$Ti.

The results and analysis as they stand point towards a mechanism wherein either something similar to pure Al, rather than Al$_3$Ti, nucleates off a TiB$_2$(Ti) substrate, or else a mixture of Al and Al$_3$Ti, perhaps an intermediate Al-Ti structure, nucleates off a TiB$_2$(B) substrate. Given the non-uniform and locally varying nature of real-life interfaces, it is a possibility that any combination of these mechanisms are active at once throughout the melt. One thing all the suggested mechanisms have in common, however, is Ti contact with both B and Al, whether in the last Ti layer of TiB$_2$, or in the first layer of Al$_3$Ti.

To get closer to a firm conclusion several extensions to this work could be made. Firstly, the liquid-solid interfacial energies, which were modelled quite simply in this study, need to be calculated accurately as a function of $X_{Ti}$ and $T$. Secondly, all interfacial energies, which were fully or partially calculated at 0 K in this study, should be calculated at finite temperature. Finally, while the classical model has been useful to observe general trends between the four systems, in response to several parameters, ultimately large scale long running DFT MD calculations of TiB$_2$ substrates in the presence of liquid melt need to be run.
Acknowledgements

The authors would like to acknowledge financial support from ESPRC (grant numbers EP/I02249X/1 and GR/T26344/1), and further financial support from the ExoMet Project (which is co-funded by the European Commission in the 7th Framework Programme (contract FP7-NMP3-LA-2012-280421), by the European Space Agency and by the individual partner organisations), and the Research Complex at Harwell. The authors would like to further acknowledge the use of the CX1 high performance computer at Imperial College London, and thank Simon Burbidge for his invaluable help and advice on CX1, and Junsheng Wang for his previous work which lead to this current study. This work was made possible by the facilities and support provided by the Diamond-Manchester Collaboration and the Research Complex at Harwell, funded in part by the EPSRC (EP/I02249X/1).


[30] ABINIT code, a common project of the Universite Catholique de Louvain, Corning Incorporated, and other contributors (URL: http://www.abinit.org).


[34] N. Holzwarth, pAW atomic data for element B - Generated by AtomPAW (N. Holzwarth)+ AtomPAW2Abinit v3.2.1.


