



Which wets TiB_2 inoculant particles: Al or Al_3Ti ?

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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 $\text{TiB}_2(0001)$ substrate (Ti or B) and the solid that forms on it (Al or Al_3Ti). 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_3Ti 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_3Ti 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 which these grain refiners nucleate α -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 [5–10] suggested that TiB_2 was the heterogeneous nucleant responsible for aluminium nucleation, by showing that thin ordered layers of Al_3Ti -like structure (presumed to be $\text{Al}_3[\text{Ti,Ta}]$), had formed off the (0001) face of a TiB_2 particle in a glass formed from $\text{Al}_{85}\text{Ni}_5\text{Y}_8\text{Co}_2$. 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 α -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_3Ti which nucleates off the TiB_2 forming a thin layer; Al then nucleates off the Al_3Ti layer [13]. The confidence in this Al_3Ti nucleation hypothesis is based on Schumacher's TEM experiments [5–10], 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 the those of bulk Al_3Ti were observed at the onset of aluminium solidification.

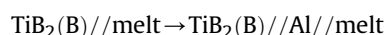
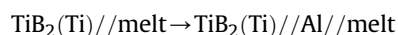
However, none of these experimental results are able to show the precise chemical composition of the nucleating layer. It is

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possible that what is being observed in these experiments is actually strained α -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_3Ti . 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) [17,16,18–21] 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_3Ti 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:



where the two species separated by//denote the characteristic interfaces of the system. The planes parallel to the interfaces are $\text{TiB}_2(0001)$, Al (111) and Al_3Ti (112), and the parenthesized element denotes the termination of the $\text{TiB}_2(0001)$ surface. Using DFT and thermodynamic arguments we address the following questions:

1. What are the $\text{TiB}_2//\text{Al}$ 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 $\text{TiB}_2//\text{Al}_3\text{Ti}$ interfacial energies (also accounting for the effects of interfacial strain) and how do they compare with those of $\text{TiB}_2//\text{Al}$?
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, ΔG_T , is defined for an initial system of N_{melt} mole-atoms of melt (original phase), transforming into N_{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_{solid} is small and completely wets, or wets with a very low contact angle, ΔG_T can be approximated by:

$$\Delta G_T = N_{\text{solid}}G_{\text{solid}} + N_{\text{melt}'}G_{\text{melt}'} - N_{\text{melt}}G_{\text{melt}} + \left[\gamma_{\text{solid}}^{\text{melt}'} + \gamma_{\text{sub}}^{\text{solid}} - \gamma_{\text{sub}}^{\text{melt}} \right] A_{\text{sub}} \quad (1)$$

where G_a is the bulk Gibbs energy per mole-atoms of species a , γ_b^a is

the interfacial energy between species a and b , and A_{sub} is the area of active substrate. For the nucleation reaction considered in this study, the nucleating solid refers to either Al or Al_3Ti , the melt refers to liquid Al with some small amount of dissolved Ti, before (*melt*) and after (*melt'*) the formation of the solid, and the substrate refers to the surfaces $\text{TiB}_2(\text{Ti})$ or $\text{TiB}_2(\text{B})$. In this study we are primarily interested in the difference in ΔG_T between Al_3Ti and Al wetting, given a particular TiB_2 substrate, and to see how these differences vary according to N_{solid} , X_{Ti} (the Ti concentration) or μ_{Ti} (the Ti chemical potential), and T (temperature).

The bulk Gibbs energies will be computed here using formulae from the literature [23–27], augmented with DFT to include strain effects. The three interfacial energies are determined as follows: $\gamma_{\text{sub}}^{\text{solid}}$ is obtained from DFT calculations reported here; $\gamma_{\text{solid}}^{\text{melt}'}$ is estimated by interpolating between literature values for similar interfaces where the melt is pure liquid Al and Al–Ti liquid with $X_{\text{Ti}} = 0.0169$ at.%; $\gamma_{\text{sub}}^{\text{melt}}$ is estimated through a simple model which involves the surface energies $\gamma_{\text{sub}}^{\text{vac}}$ and $\gamma_{\text{melt}}^{\text{vac}}$, 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 0 K, and with no atomic vibrations. Nevertheless it is possible, with our calculated and literature values, to form an approximate expression for ΔG_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_3Ti , the methods and parameters described in Kattner et al. [27] were used. We augment the solid Al and Al_3Ti Gibbs energies with the DFT 0 K 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 μ_{Ti} using $\mu_{\text{Ti}}^{\text{melt}} = \frac{\partial G_{\text{melt}}}{\partial N_{\text{Ti}}}$. This enables us to express the interfacial energies as a function 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, $a_{\text{Ti}} = \exp\left(\frac{\mu_{\text{Ti}} - \mu_{\text{Ti}}^{\text{bulk}}}{RT}\right)$, is approximately linear

in X_{Ti} : $a_{\text{Ti}} = \gamma_{\text{Ti}}X_{\text{Ti}}$, where γ_{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 γ_{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 0.001–0.01 at.%, which is broadly in line with that shown by Kostov et al. [28,29].

4. Interfacial energies

4.1. DFT method

To calculate $\gamma_{\text{sub}}^{\text{solid}}$, $\gamma_{\text{sub}}^{\text{vac}}$ (a term in our $\gamma_{\text{sub}}^{\text{melt}}$ model), and the strain energies that make part of G_{solid} , DFT simulations were performed using the ABINIT code [30–32], which implements a planewave basis set. A planewave energy cutoff of 30 Ha was used with a Projector Augmented Wave (PAW) [33–35] auxiliary energy cutoff of 60 Ha. The PBE Generalised Gradient Approximation (GGA)

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