Effect of Al-V-B grain refiner on refining aluminium alloys: estimation from \textit{ab initio} calculations

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Abstract. Ab initio calculations based on density functional theory were conducted to estimate the effect of Al-V-B grain refiner on refining aluminium alloys. Al-Ti-B, an industrial grain refiner, was investigated simultaneously to act as a reference. Six interfaces formed by (111) Al with (112) Al\textsubscript{3}V(Ti), V(Ti)-terminated (0001) V(Ti)B\textsubscript{2} and B-terminated (0001) V(Ti)B\textsubscript{2} were studied in detail. Interfacial lattice mismatch, work of adhesion and stain-free interfacial energy were calculated for each of these interfaces, respectively. Analysis of interfacial energy demonstrated that Al\textsubscript{3}V overlayers are less likely to form on the surface of (0001) VB\textsubscript{2} surface compared with the Ti-related system. By combination of interfacial lattice mismatch and work of adhesion, it was concluded that VB\textsubscript{2} is much more potent in refining aluminium alloys than TiB\textsubscript{2}, while Al\textsubscript{3}V is much weaker in nucleant potency compared with Al\textsubscript{3}Ti.

1. Introduction

Al foundry alloys have a broad application in the automotive and aerospace industries due to their superior corrosion and wear resistance, particularly high strengths after heat-treatment [1, 2]. It is known that the achievement of fine grain structure is beneficial to the soundness and mechanical properties of Al alloy castings [3]. In recent years, the focus of attention is on grain refining efficiency of Al-Ti-B master alloys since the master alloys are the most frequently used in the foundry [4-6]. However, in the cast Al-Si alloys the silicon-poisoning phenomenon significantly limits the degree of grain refinement achieved by adding Al-Ti-B master alloys to Al-Si casting alloys [7]. Therefore, researches were performed to overcome the Si poisoning effect and reduce the grain size of solidified Al-Si alloys [8, 9].

Ti element in Ti-based master alloy has a higher affinity with Si than Al, which leads to the formation of Ti silicide, and the aluminium melt gradually is depleted of Ti, reducing TiB\textsubscript{2} and Al\textsubscript{3}Ti substrates’ potency at pouring temperature of Al-Si alloy [10]. The Nb-based master alloys have seldom occurred the phenomenon of Si poisoning [11], but there is a serious precipitation phenomenon due to the sedimentation problem. Zhang \textit{et al.} [12] reported that a Al-V-B master alloys can overcome the Si poison effect on grain refinement and refine the grain structure of the Al-7wt\%Si alloy effectively through the experimental research. The mechanism of this phenomenon was not investigated clearly, and it is widely accepted that the \textit{ab initio} calculations with density functional theory [13, 14] can provide fundamental information at atomic or even electronic levels to investigate the heterogeneous nucleation mechanism. However, published papers about this issue are rarely retrieved.
The atomic geometry, interfacial adhesion and interfacial bonding nature play an important role in affecting nucleation potency of a heterogeneous substrate. Therefore, heterogeneous nucleation interfaces of Al/V(Ti)B₂ and Al/Al₃V(Ti) were extensively studied by using ab initio calculations, this work with the aim of estimating the potential and mechanism of Al-V-B as a grain refiner for aluminium alloys. Interfacial structure, adhesion strength and interfacial energy are obtained, which will be discussed in detail in the following sections.

2. Establishment of interfacial models of Al with Al₃V(Ti) and V(Ti)B₂

Atomistic geometries of the interfaces of Al with Al₃V, VB₂, Al₃Ti and TiB₂ were first determined. From previous experiments [15], orientation relationship (OR) of (0001)ᵥᵥᵥᵥ // (111)ₐₐₐₐ was confirmed. And on the surface of (0001) TiB₂, (112) Al₃Ti atomic layers were likely to appear which showed a relatively small mismatch with (111) Al [15]. Considering the similarity between Al₃Ti and Al₃V, (112) Al₃V is expected to form adhering to the (0001) VB₂ surface, which then may promote the nucleation of Al with (111) plane parallel to the substrate surface. Therefore, the OR of (112)ₐₐₐₐ // (111)ₐₐₐₐ is necessary to be examined. In-plane crystal orientation matching for the above two types of interfaces is <112₀>ᵥᵥᵥᵥ // <110>ₐₐₐₐ and <201>ᵥᵥᵥᵥ // <110>ₐₐₐₐ (or <110>ᵥᵥᵥᵥ // <110>ₐₐₐₐ), respectively [15]. Following the above ORs, interfacial models between Al and the four nucleant substrates were established (figure 1). For all the substrates and solid Al, 7-layer slabs were used to build the supercell, which have been tested to be sufficiently large to ensure the interaction between two surfaces to be negligible. A vacuum region with length larger than 15 Å was inserted into each supercell above the solid Al to separate it from the substrate. For the (0001) V(Ti)B₂ surface, two different terminations (V(Ti)-termination and B-termination) exist, which were both studied in this work, as shown in figure 1(b), (c), (e) and (f). We note that for each interfacial model, several stacking modes (ST) with high symmetry were considered as depicted by the solid circles that are connected by dashed lines in figure 2. This is helpful to find the interface structure with the lowest energy.

![Figure 1](image-url)

**Figure 1.** Atomic models of the six studied interfaces in this work. (a) to (f) are (112) Al₃Ti/ (111) Al, Ti-terminated (0001) TiB₂/(111) Al, B-terminated (0001) TiB₂/(111) Al, (112) Al₃V/(111) Al, V-terminated (0001) VB₂/(111) Al, and B-terminated (0001) VB₂/(111) Al interfaces, respectively.
The above established initial interfacial models (totally 12 models) were relaxed within the framework of density functional theory. Vienna Ab initio Simulation Package (VASP) was adopted to conduct these calculations [16, 17]. Projected-augmented waves (PAW) method [18, 19] was employed to deal with the relationship between valence electrons and the ionic cores. The Perdew-Burke-Ernzerhof functional with generalized gradient approximation (GGA-PBE) [20] was selected to approximate the exchange-correlation energy. We chose a plane wave cutoff energy of 400.0 eV for all the calculations. Gaussian smearing method with a smearing width of 0.01 eV was used in the self-consistent calculations to solve the ground state electronic density. The ionic relaxation continued until all forces were smaller than 0.01 eV·Å⁻¹, which was used to determine ground state energies and atomic geometries for each structure. $3 \times 3 \times 1$ and $7 \times 7 \times 1 \Gamma$-centered $k$-point meshes were used for Al₃V(Ti) and V(Ti)B₂ related interface calculations, respectively.

![Figure 2](image_url)  
**Figure 2.** Top view of (a) (0001) VB₂ surface and (b) (112) Al₃V surface with the possible stacking modes for (111) Al depicted by dashed lines and solid circles.

To estimate the nucleant potencies of Al₃V(Ti) and V(Ti)B₂ particles, lattice mismatch $f$ at the interfaces and interfacial energies were calculated based on the aforementioned interfacial models, which will be discussed in detail in the following sections.

### 3. Calculation of interfacial mismatch
Although (112) Al₃V(Ti), (0001) V(Ti)B₂ and (111) Al all show six-fold symmetry, their lattice parameters (or interatomic distances) are different which renders interfacial strain when the substrates are combined with the solid Al. During heterogeneous nucleation process of solid Al, interfacial strain hinders the formation of nuclei. Therefore, a smaller interfacial strain is expected for the substrate with high nucleant potency. Here, lattice mismatch $f$ was used to quantify the interfacial strain.

For the V(Ti)B₂/Al interfaces, $f$ was calculated using the following equation:

$$f = \frac{d_{11\bar{2}0}_{\text{V(Ti)B}_2} - d_{1\bar{1}0}_{\text{Al}}}{d_{1\bar{1}0}_{\text{Al}}} \times 100\%, \tag{1}$$

where $d_{11\bar{2}0}_{\text{V(Ti)B}_2}$ and $d_{1\bar{1}0}_{\text{Al}}$ are interatomic distances along the $<11\bar{2}0>_{\text{V(Ti)B}_2}$ and $<1\bar{1}0>_{\text{Al}}$ directions, respectively. For the Al₃V(Ti)/Al interface, $f$ has the following formula:

$$f = \frac{1}{3} \left( \frac{d_{1\bar{1}0}_{\text{Al}} - d_{1\bar{1}0}_{\text{Al}}}{d_{1\bar{1}0}_{\text{Al}}} + \frac{2}{3} \frac{d_{20\bar{1}}_{\text{Al}} - d_{1\bar{1}0}_{\text{Al}}}{d_{1\bar{1}0}_{\text{Al}}} \right) \times 100\%. \tag{2}$$
In the above equation, \(d <110>_{\text{Al}_3V(Ti)}\) and \(d <20\overline{1}>_{\text{Al}_3V(Ti)}\) denote the interatomic distances in the \(<110>\) and \(<20\overline{1}>\) directions of the \(\text{Al}_3V(Ti)\) substrate. The prefactors 1/3 and 2/3 in the above equation are determined due to the fact that for the OR between \((112)\ \text{Al}_3V(Ti)\) and \((111)\ \text{Al}\), 1/3 of the in-plane crystal orientation matches are \(<110>_{\text{Al}_3V(Ti)} // <110>_{\text{Al}}\), while the rest are \(<20\overline{1}>_{\text{Al}_3V(Ti)} // <110>_{\text{Al}}\).

The calculated interatomic distances based on \textit{ab initio} simulations and the corresponding interfacial lattice mismatches are listed in table 1.

| Parameters | Al   | VB\(_2\) | Ti\(_B2\) | Al\(_3V\) | Al\(_3Ti\) |
|------------|------|----------|-----------|-----------|------------|
| \(d (\text{Å})\) | \(<110>\) | \(<1120>\) | \(<1120>\) | \(<110>\) | \(<20\overline{1}>\) | \(<20\overline{1}>\) | \(<110>\) | \(2.86\) | \(3.00\) | \(3.03\) | \(2.66\) | \(2.80\) | \(2.72\) | \(2.89\) |
| \(f(\%)\) | —    | 4.9      | 5.9       | -3.7      | -0.93      |

In table 1, lattice mismatches of Al with the four substrates are compared. A positive value of \(f\) means the solid Al is stretched, while a negative value suggests the solid Al is compressed. Clearly illustrated by table 1 is that Al\(_3Ti\) has the smallest lattice mismatch with Al while Ti\(_B2\) exhibits the largest \(f\). This finding has already been verified for a number of times by previous experimental and theoretical analyses, and it explains why the appearance of an Al\(_3Ti\) layer on the surface of Ti\(_B2\) substrate can significantly enhance the nucleant potency of Ti\(_B2\). More interesting are the \(f\) values of Al with V-based compounds. It is found that the absolute values of \(f\) for VB\(_2\) and Al\(_3V\) approach, which implies that effect of Al\(_3V\) on enhancing the nucleant potency of VB\(_2\) may be much weaker than the Ti-based system. Additionally, a slight decrease of \(f\) is found when replacing Ti\(_B2\) by VB\(_2\). The above discussion based on interfacial lattice mismatch predicts that for the Al-V-B master alloys, VB\(_2\) alone may play an indispensable role in refining the aluminum alloys even without the help of Al\(_3V\) overlayers.

4. Quantification of interfacial affinity

The affinity between the substrate and Al also plays a vital role in affecting nucleant potency. Interfacial affinity describes the tendency to form an interface and embodies the stability of it. Work of adhesion \(W_{ad}\) and strain-free interfacial energy \(\gamma\) (or interfacial chemical energy) were together used to quantify the interfacial affinity. \(W_{ad}\) is expressed as follows:

\[
W_{ad} = \frac{1}{A} (E_{\text{inter}} - E_{\text{sub}} - E_{\text{Al}}). \tag{3}
\]

In equation (3), \(A\) is the total area of the interface; \(E_{\text{inter}}, E_{\text{sub}}\) and \(E_{\text{Al}}\) are the ground state total energies of the interface, substrate (Al\(_3V(Ti)\) or V(Ti)B\(_2\)) and Al slab, respectively. \(W_{ad}\) has another expression which connects \(\gamma_{ad}\) with the surface energies of the substrate \(\sigma_{\text{sub}}\) and Al \(\sigma_{\text{Al}}\):

\[
W_{ad} = \gamma_{ad} - \sigma_{\text{sub}} - \sigma_{\text{Al}}. \tag{4}
\]

Using equation (4), \(\gamma_{ad}\) can be calculated through \(\gamma_{ad} = W_{ad} + \sigma_{\text{sub}} + \sigma_{\text{Al}}\).

Surface energies of (111) Al and (112) Al\(_3V(Ti)\) are easy to acquire since these surfaces are stoichiometric, while those of the non-stoichiometric (0001) V(Ti)B\(_2\) surfaces are influenced by the chemical potential of the individual element. We have taken the (0001) VB\(_2\) surface as an example to demonstrate how the non-stoichiometric surface energy was calculated, which was readily applied for the calculation of (0001) Ti\(_B2\) surface energy. Surface energy of (0001) VB\(_2\) surface is derived as
\[ \sigma_{\text{VB2}} = \frac{1}{A} (E_{\text{slab}} - N_V \mu_{\text{VB2,s}}^V - N_B \mu_{\text{VB2,s}}^B), \]  

where \( A \) is the total surface area of (0001) VB2 surface; \( E_{\text{slab}} \) denotes the ground state total energy of the (0001) VB2 slab; \( N_V \) and \( N_B \) are the number of V and B atoms in the slab, respectively; \( \mu_{\text{VB2,s}}^V \) and \( \mu_{\text{VB2,s}}^B \) indicate the chemical potentials of V and B in the surface slab, respectively. Considering the equilibration between surface and bulk VB2, it is assumed that \( \mu_{\text{VB2,s}}^V = \mu_{\text{VB2,b}}^V \) and \( \mu_{\text{VB2,s}}^B = \mu_{\text{VB2,b}}^B \), where \( \mu_{\text{VB2,b}}^V \) and \( \mu_{\text{VB2,b}}^B \) are the chemical potentials of V and B in bulk VB2 [21]. For bulk VB2, an equation can be established:

\[ \mu_{\text{VB2}}^b = \mu_{\text{VB2,s}}^V + 2 \mu_{\text{VB2,b}}^V = \mu_{\text{VB2,s}}^B + 2 \mu_{\text{VB2,b}}^B, \]  

in which \( \mu_{\text{vb2}}^v \) is the chemical potential of a unit of VB2, which is readily calculated from the \textit{ab initio} simulations. Combining equation (5) and (6), \( \sigma_{\text{VB2}} \) can be written as:

\[ \sigma_{\text{VB2}} = \frac{1}{A} [E_{\text{slab}} - \frac{1}{2} N_B \mu_{\text{VB2,b}}^V + (\frac{1}{2} N_B - N_V) \mu_{\text{VB2,s}}^V] \]  

Now, \( \mu_{\text{vb2}}^v \) is still needed to be determined for the calculation of \( \sigma_{\text{VB2}} \). According to Han et al. [21], \( \mu_{\text{vb2}}^v \) is indeed in a range determined by the following formula:

\[ \Delta H_f \leq \mu_{\text{VB2,s}}^V - \mu_{\text{v,b}}^V \leq 0. \]  

In equation (8), \( \mu_{\text{vb2}}^v \) is the chemical potential of a V atom in bulk V and \( \Delta H_f \) is the formation enthalpy of VB2. Both \( \mu_{\text{vb2}}^v \) and \( \Delta H_f \) were obtained from \textit{ab initio} calculations.

![Figure 3](image_url)

\textbf{Figure 3.} Surface energies of (a) (0001) V(Ti)B2 and (b) (112) Al3V(Ti) surfaces.

Figure 3 depicts the calculated surface energies of the (0001) V(Ti)B2 and (112) Al3V(Ti) surfaces. A prominent feature shown in figure 3 is that the surface energies of the (112) Al3V(Ti) surfaces are much lower than those of the (0001) V(Ti)B2 surfaces. This finding well explains why Al3V(Ti) overlayers are likely to form on the (0001) V(Ti)B2 surface, because such structures significantly reduce the surface energies of the borides. Another finding from figure 3 is that surface energies of the (0001) V(Ti)B2 are closely related to the chemical potential of the V(Ti) atoms in the surface slabs. More
importantly, surface energies of V(Ti)-terminated and B-terminated surfaces are in the same range, and thus both of these two types of surfaces are likely to exist.

Prior to the calculation of interfacial energy, $W_{ad}$ for the six interfaces were computed firstly, as shown in figure 4, in which terminations of the (0001) V(Ti)B$_2$ surfaces are indicated by the element symbols in parentheses. To compute $W_{ad}$, ground state total energies $E_{inter}$ of the six interfaces need to be determined. As the first step, the equilibrated interface structures were obtained using the approach introduced in section 2. At the (112) Al$_3$V(Ti), we found that (111) Al stacking in the ST2 manner (figure 2) was energetically more favorable. At the (0001) V(Ti)B$_2$ surface, ST2 (atop V(Ti) atoms) and ST1 (atop B atoms) are the stacking modes with the lowest energy for B and V(Ti)-terminated substrates, respectively. $E_{inter}$ were extracted from these interfacial structures and then put into equation (3) to calculate $W_{ad}$. Contrary to $\sigma$ (figure 3), $W_{ad}$ for the (112) Al$_3$V(Ti) substrate is obviously larger than that for the (0001) V(Ti)B$_2$ substrate nevertheless of Ti(V) or B termination. Basically, $W_{ad}$ quantifies the energy releasing from combining two slabs (in this work, substrate and Al slabs) to form an interface. A smaller $W_{ad}$ suggests that it is energetically more favorable to form the corresponding interface. Therefore, (0001) Al slab is more readily to form an interface with V(Ti)B$_2$ substrates, especially when it is terminated by V(Ti), compared with the Al$_3$V(Ti) substrate.

![Figure 4. Work of adhesion for the interfaces of (111) Al with (0001) V(Ti)B$_2$ and (112) Al$_3$V(Ti). Contents in the parentheses indicate the surface termination of the V(Ti)B$_2$ substrates.](image-url)

Equation (4) was used together with the already obtained results of $\sigma$ (figure 3) and $W_{ad}$ (figure 4) to calculate the interfacial energy $\gamma$. Surface energy of (111) Al is also required for this calculation, which was computed to be 0.904 J m$^{-2}$ based on the ab initio method. The calculated $\gamma$ for the six interfaces (figure 1) are exhibited in figure 5. $\gamma$ embodies the stability of an interface. An interface presenting a smaller $\gamma$ is more likely to exist compared with its counterpart with a larger $\gamma$. This is important when analyzing which of the terminations (V(Ti) or B) is more likely to appear when Al is present. From figure 5, it is observed that with $\mu_v^{\text{V(Ti)}}$ (\$\mu_h^{\text{V(Ti)}}\$) increasing, $\gamma$ of the V(Ti)-terminated (0001) V(Ti)B$_2$/Al interface decreases gradually which even reaches zero when $\mu_v^{\text{V(Ti)}}$ (\$\mu_h^{\text{V(Ti)}}\$) is near $\mu_v^{\text{Ti}}$ (\$\mu_h^{\text{Ti}}\$). Meanwhile, $\gamma$ of the interface with the B-terminated substrate increases. Obviously, $\mu_v^{\text{V(Ti)}}$ (\$\mu_h^{\text{V(Ti)}}\$) is influenced by the concentration of V(Ti) at the interface, which is difficult to measure. However, some experiment results may provide some hints on the more exact $\mu_v^{\text{V(Ti)}}$ (\$\mu_h^{\text{V(Ti)}}\$) range. Normally, an excess of solute Ti atoms is guaranteed when designing the Al-Ti-B master alloys to ensure an excellent grain refining effect. As observed in previous experimental investigations [22], these free Ti solute atoms partially segregate to the surface of the TiB$_2$ resulting an increase of local Ti concentration, which then
renders the increase of $\mu_{TiB_2}^{n}$ to approach $\mu_{b}^{n}$. When $\mu_{TiB_2}^{n}$ is larger than $A_Ti$ in figure 5(b), the Ti-terminated TiB$_2$ surface becomes more stable. And if $\mu_{TiB_2}^{n}$ is beyond $B_Ti$ (figure 5(b)), formation of the Al$_3$Ti layer is not possible. In the experiments of Fan et al. [22], a Ti-terminated TiB$_2$ was observed which was covered by an Al$_3$Ti monolayer at the TiB$_2$/Al interface. This finding suggests that $\mu_{TiB_2}^{n}$ is actually between $A_Ti$ and $B_Ti$. For the V-related interfaces, interval between $A_V$ and $B_V$ is obviously smaller than that between $A_Ti$ and $B_Ti$. This makes $\mu_{V}^{V_2}$ easier to pass $B_Ti$ as the concentration of V increases at interface when formation of Al$_3$V overlayer is energetically unfavorable. In fact, some experimental results can evidence such a conjecture. Zhang et al. [12] found in their pioneering investigation of Al-V-B grain refiners that VB$_2$ alone seems to be the potent nucleants instead of the Al$_3$Ti particles.

![Figure 5. Interfacial energies of the interfaces of (111) Al with (a) (0001) V(Ti)B$_2$ and (b) (112) Al$_3$V(Ti).](image)

5. Discussion

According to classical nucleation theory, nucleant potency for heterogeneous nucleation can be quantified by contact angle $\theta$, which is defined as follows:

$$\cos \theta = \frac{\gamma_{sl} - \gamma_{ns}}{\gamma_{sl}}.$$  \hspace{1cm} (9)

In this equation, $\gamma_{sl}$, $\gamma_{ns}$ and $\gamma_{ns}$ are the interfacial energies of solid/liquid, nucleant/liquid, and nucleant/solid interfaces, respectively. In the case of estimating potency of nucleant substrates, $\gamma_{sl}$ is the same for all the substrates. Therefore, the larger ($\gamma_{sl} - \gamma_{ns}$) is, the higher the potency will be. A substantial difference between nucleant/liquid and nucleant/solid interfaces is the existence of interfacial strain at the nucleant/solid interface, which is effectively quantified by $f$. Another difference is embodied in the chemical bonding feature [23, 24] that can be qualitatively reflected by $W_{ad}$. Therefore, by combination of $f$ and $W_{ad}$, the nucleant potency of the substrates in Al-V(Ti)-B master alloys can be estimated. Al$_3$V show much worse nucleant potency than Al$_3$Ti, because $W_{ad}$ of for these two substrates are nearly the same while interfacial strain of Al$_3$V/Al is much larger than the interface containing Al$_3$Ti. On the contrary, VB$_2$ is more potent than TiB$_2$ with the former presenting smaller $f$ and $W_{ad}$ than the latter.
6. Conclusion

*Ab initio* calculations were conducted to estimate the effect of Al-V-B grain refiner on refining aluminium alloys with a comparison to the Al-Ti-B grain refiner. We found VB$_2$ in Al-V-B can play a much more important role in refining Al than TiB$_2$ in Al-Ti-B, and nucleant potency of Al$_3$V is much weaker than Al$_3$Ti. These findings theoretically explain the previous experimental observation that VB$_2$ alone instead of together with Al$_3$V refines an aluminium alloy.

Acknowledgments

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