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The nucleation sequence of α-Al on TiB_2 particles in Al-Cu alloys

Jiehua Li[1]*, Fredrik S. Hage[2,3], Quentin M. Ramasse[2,4], Peter Schumacher[1, 5]

[1] Institute of Casting Research, Montanuniversität Leoben, Leoben, A-8700, Austria

[2] SuperSTEM Laboratory, SciTech Daresbury Campus, Keckwick Lane, Daresbury,
WA4 4AD, UK

[3] Department of Materials, University of Oxford, Oxford OX1 3PH, UK

[4] School of Chemical and Process Engineering & School of Physics and Astronomy,
University of Leeds, Leeds LS2 9JT, UK

[5] Austrian Foundry Research Institute, Leoben, A-8700, Austria

*Corresponding Author. Post address: Institute of Casting Research, Montanuniversität Leoben, A-8700, Leoben, Austria.

Tel.: +43-3842-402-3304; Fax: +43-3842-402-3302.

Email address: **jiehua.li@unileoben.ac.at** (Jiehua Li)

Abstract

The refinement of Al alloys by TiB_2 has been extensively investigated for decades, both in industry and academia. In order to achieve higher grain refinement potency, it is known that other solutes must be added alongside TiB_2, thus tailoring the heterogeneous nucleation at the interface between the TiB_2 particles and the Al matrix. Here, we report results from an atomic-scale experimental investigation of the heterogeneous nucleation interface of TiB_2 in Al-Cu based alloys as well as in an Al-5Ti-1B grain refiner employed in these Al-Cu based alloys. We focus on the effect of segregation of the main solute elements (Ti, Cu) to the interface of TiB_2 and attempt to disentangle this effect from other factors affecting the nucleation and growth. Significant Ti segregation in the form of a Ti-rich layer, identified as an Al_3Ti two-dimensional compound, was unambiguously observed on the basal plane of TiB_2 particles in the Al-5Ti-1B grain refiner, in agreement with prior literature. In the Al-Cu alloy system, prevalent Ti segregation was also observed on the basal plane of TiB_2, accompanied in cases when the Cu concentration is high by the presence of a further atomic-scale Cu-rich layer. Based on these observations, a possible nucleation sequence for the Al-Cu based alloys with the addition of Al-5Ti-1B grain refiner is proposed whereby Al nucleation occurs on an Ti-rich layer on the surface of TiB_2, which can then be preserved from a subsequent peritectic transformation by a surrounding eutectic reaction that forms a Cu-rich layer when sufficient Cu is present. This proposed nucleation sequence should help to link the absence or presence of Al_3Ti layers on the basal plane of TiB_2 to processing conditions in post-solidification studies. Although it is difficult to know with absolute certainty if a TiB_2 particle observed in the post-solidification microstructure was active or inactive for heterogeneous nucleation during the solidification process, this experimental study highlights the possible role of Cu segregation on grain refinement of Al-Cu alloys by the Al-5Ti-1B grain refiner.

Keywords: Al alloy; Heterogeneous nucleation; Growth restriction; Grain refinement; HAADF-STEM; EELS

1. Introduction

The grain refinement of Al alloys has been extensively investigated [1-4] with a view to improve their mechanical properties and castability, in particular for mass feeding. The addition of Al-Ti-B grain refiners such as Al-5Ti-1B in Al alloys has been widely used due to their higher nucleation potency and wider potential for industrial applications. However, the so-called Zr poisoning [5, 6] very often occurs in many different types of Al alloys (i.e. Al-Cu-Mg, Al-Zn-Mg-Cu alloys or Al-Si based alloys) where the Al-5Ti-1B grain refiner is employed. More importantly, the so-called Si poisoning [7] also occurs in Al-Si based alloys when the Si concentration is higher than 3.5 wt. %. This is of crucial importance as most foundry alloys are based on Al-Si based alloys with a Si concentration of about 7wt. %. A better understanding of the mechanisms on which the Al-5Ti-1B grain refiner relies is thus of great importance to further enhance its grain refinement efficiency in Al alloys.

Various theories regarding the mechanisms by which Al-Ti-B-based grain refinement occurs have been proposed. These include the so-called particle theory, phase diagram theory, duplet nucleation theory or peritectic hulk theory, as reviewed in Ref. [1]. Further theories such as the free growth theory [8-12], a modified free growth theory [13], the interdependence theory [4], an epitaxial model for heterogeneous nucleation on potent substrates [14], and a new concept for growth restriction during solidification [15] have also been put forward. Of note, the liquid structure (clustering and / or ordering) prior to nucleation [16] and the importance of the substrate (chemistry and structure) [17, 18] have been highlighted as important parameters for the heterogeneous nucleation and subsequent growth, which significantly affect the grain refinement.

Despite the differences among all these theories, it is generally accepted that Ti has multiple roles within the Al melt. Ti is present within TiB_2 particles, which act as the nucleation substrate. Excess Ti segregates at the surface of TiB_2 and thereby creates an enriched Ti region leading to the formation of a crystalline layer a few atoms thick identified as an Al_3Ti

compound, which has been shown to be of importance for the heterogeneous nucleation of Al on the stable boride substrates (TiB_2) [19-25]. Furthermore, excess Ti also acts as an effective growth restrictor [2, 4, 10, 11, 13, 19]. It is thought the combined effects of the enhancement of the heterogeneous nucleation potency and the growth restriction result in the formation of desirable, small uniform equiaxed Al grains.

The growth restriction can be defined as a physical quantity proportional to the initial rate of constitutional undercooling development and its value can be used directly as a criterion for the effectiveness of grain refinement in Al alloys containing strong potential nucleation particles [2, 15]. It is generally accepted that Ti has a stronger effect on the growth restriction in Al alloys than any other element such as Cu or Si, among others [2]. Furthermore, Ti is more likely to segregate to the TiB_2 / liquid-Al interface, affecting its structure as well as the constitutional undercooling at the solid-liquid interface [19, 24].

To date, more attention has been paid to cases where both Ti content and growth restriction increase concurrently [2, 11, 23]. By contrast, fewer studies have focused on cases where in spite of a decrease of Ti content the growth restriction remains unchanged. This latter aspect is of great importance for disentangling the multiple roles of excess Ti in Al alloys.

The present work focuses on an atomic-scale characterization of the interface between TiB_2 grain refiner particles and α-Al matrix in the Al-Cu alloy system produced by conventional die castings (rather than in metallic glasses, as studied elsewhere [24]). The reasons for the choice of the Al-Cu alloy system for this study are fivefold: (i) Cu is an important alloying element for industrial aluminum alloys (for instance, in 2xxx Al alloys); (ii) Cu is generally believed to have no significant poisoning action on Al-Ti-B refiners [2], in contrast to Si (thus precluding the use of the Al-Si-Ti system for our purposes [6, 7]); (iii) Cu has a wide hypo-eutectic range (up to 33 wt. %), making it possible to adjust the growth restriction over a wide range [2] as a function of other parameters such as the Ti solute excess; (iv) Cu has little solubility in a potential Ti-rich layer structure [2]; (v) the effect of Cu segregation on grain refinement of Al-Cu alloys by Al-5Ti-1B is not clear yet.

This work builds on prior atomic-scale experimental studies of the heterogeneous nucleation interface of TiB_2 in a commercial Al-5Ti-1B grain refiner, where a Ti-rich layer with a structure differing from that of "bulk" TiB_2 was observed on the basal plane of TiB_2 particles; this structure was previously identified as a so-called Al_3Ti two-dimensional compound (TDC) [25]. Models have been proposed for the effect of excess Ti on the interface of TiB_2 [26-28] and different excess Ti levels are believed to significantly affect the stability of Al_3Ti and therefore the solidification path [24]. In a number of highly efficient commercial Al-5Ti-1B grain refiners, about 2.8 wt.% excess Ti is present, resulting in conditions where Al_3Ti TDC is expected to be stable through the solidification process [24]. In contrast, in usual commercial Al-based alloys, less than 0.15 wt.% excess Ti is added, resulting in conditions where the Al_3Ti TDC is no longer expected to be stable [24]. To date, atomic-scale experimental observations of the heterogeneous nucleation interface of TiB_2 subjected to these low Ti excess industrial solidification conditions used in conventional die casting are still lacking. It should be noted here that no TiB_2 particle observed in post solidification microstructure can be identified with certainty as having been active in the nucleation process. Even for a TiB_2 particle observed in the center of an Al grain with a well-defined orientation relationship with the surrounding Al matrix, the possibility remains that it was entrained within the grain ahead of the solidification front during the solidification process instead of initiating the grain nucleation. This is in particular the case of very high TiB_2 concentrations, such as in the commercial Al-5Ti-1B grain refiner, where only a small proportion of particles is known to be active [2], but it may also hold more generally for post-solidification electron microscopy observations of these alloys.

Here, we use atomic resolution high angle annular dark field (HAADF) imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to address a number of these questions and to characterize the heterogeneous nucleation interface of TiB_2 particles in Al-Cu based alloys (and for reference in the commercial Al-5Ti-1B grain refiner), where the Ti solute excess is varied whilst keeping the growth restriction constant. This is achieved by carefully adjusting the overall chemical composition of the alloy, and the Cu and Ti concentrations in particular. We focus on the possible segregation of non-interacting solute elements, Ti and Cu, at the surface of TiB_2. The results confirm the formation of a Ti-rich layer on the basal plane of TiB_2 in the commercial Al-5Ti-1B grain refiner, with an atomic structure consistent with the previously identified Al_3Ti TDC. In the case of the Al-Cu alloy with high Cu content, a complex atomically-ordered structure was observed: the basal plane surface is covered by initial Ti-rich layers of a structure consistent with the Al_3Ti TDC observed in the reference grain refiner. Here, however, a further Al-rich (but Ti-poor) layer, followed by several ordered atomic planes of a Cu-rich atomically ordered structure are also observed covering both prism and basal planes. Based on these observations, a nucleation sequence in this Al-Cu alloy on the basal plane of TiB_2 is then proposed.

2. Experimental

2.1 Casting experiments

A series of experiments was designed to investigate the effect of Cu content on the grain refinement of the Al-Cu alloys by the Al-5Ti-1B grain refiner when the growth restriction remains constant, and to provide evidence of concurrent atomic-level structural changes as a function of Cu composition at the interface between the α-Al matrix and the TiB_2 grain-refiner particles. Al-Cu alloys with a precisely defined growth restriction of 19.6 K but different overall compositions (corresponding to alloys labelled 1-3) were prepared using commercial purity Al ingots (99.7%) and an Al-25Cu master alloy pre-prepared in induction melting using high purity Al (99.99%) and high purity Cu (99.999%). Compositions in wt. % are used throughout this work unless otherwise noted.

Each batch, weighing about 6 kg, was melted in a resistance furnace at 720 ºC. A reference sample was taken from the melt (before the addition of the grain refiner) in order to identify the grain size before inoculation. The nucleant particles (TiB_2) were added using a commercial grain refiner rod (Al-5Ti-1B). Additional excess Ti was added using an Al-10Ti master alloy. The concentrations of the nucleant particles (TiB_2) remained unchanged at about 0.01 wt. % TiB_2, which is much higher (10 times) than the conditions used in realistic industrial applications where concentrations are about 0.001 wt. %. The reason for a higher addition level of TiB_2 is twofold: (i) to ensure that there is enough TiB_2 in the Al melt for grain refinement, and (ii) to increase the probability of finding a representative number of TiB_2 particles in the TEM samples. The melt was stirred with a graphite rod for 20 s after inoculation to avoid settling. Samples were taken from the melt after 2, 5, 10, 20, 60, 90 and 120 min, to ensure sufficient time was given for the formation of the expected Ti-rich layers observed in previous literature reports at the surface of the boride particles. The samples were tested using a standard TP-1 test. The samples for grain size measurement were sectioned 38 mm away from the bottom surface. Standard metallographic procedures were followed to prepare these sections for grain size measurements. The samples were electro-polished using a mixture of 13 g boric acid, 35 g HF, 800 ml H_2O at a voltage of 20 V for 45 seconds. All images used for grain size measurements were taken from the centre of the samples using optical microscopy in a polarized mode at the same magnification. The reported grain sizes were measured from at least 20 images and 60 measurements using the line-intersect method. According to the grain size measurement results, the samples taken from the melt after 5 minutes were chosen as representative for further atomic resolution electron microscopy investigation.

2.2 TEM characterisation

Samples for electron microscopy observation were first mechanically polished until thin enough (about 50 μm in thickness) for a small 3mm diameter disc to be punched out, before being thinned to electron transparency using Ar ion polishing at 4 kV, with a 6 ° ion beam incidence. HAADF STEM imaging and EELS measurements were carried out using either a Nion UltraSTEM100 or a Nion UltraSTEM100MC aberration corrected STEM, equipped with a Gatan Enfina or Enfinium ERS EEL spectrometer, respectively. Specifically, a sample of the highest Cu-content Al-Cu alloy (alloy 1, taken from the melt after 5 minutes) was investigated using the UltraSTEM100 microscope operated at an acceleration voltage of 100 kV with an electron probe convergence semi-angle of 31 mrad, and an estimated minimum electron probe size of 0.8 Å. The commercial Al-5Ti-1B grain refiner was subsequently investigated as a reference using the UltraSTEM100MC microscope, operated at an acceleration voltage of 60 kV with an electron probe convergence semi-angle of 31.5 mrad, and an estimated electron probe size of 1.0 Å. The native energy spread of the cold field emission gun of both microscopes is 0.35 eV. The spectrometer collection semi-angle was 36 mrad (60 mrad) and the HAADF detector semi-angles were 83 - 185 mrad (100 – 230 mrad) for the UltraSTEM100 (UltraSTEM100MC) microscope. The HAADF images were produced by averaging several shorter exposure images (acquired consecutively, each with a ~1 μs pixel time) after rigid registration using the SDSD plug-in [29] for Gatan's Digital Micrograph (DM) software. All EELS data was de-noised using Principal Component Analysis (PCA) as implemented in the MSA plugin [30] for DM. All datasets de-noised using the PCA method were scrutinized for possible artefacts introduced by this process. EELS maps were created by subtracting the decaying background preceding each edge using a fitted power-law function and subsequent integration of the EELS edge intensity over a 50 eV window from each edge onset (B *K* (188 eV), Ti $L_{2,3}$ (456 eV), Cu $L_{2,3}$ (931 eV) and Al *K* (1560 eV) [31]). The intensities of the EELS maps are displayed on a false colour scale; a low intensity (black) corresponds to a lower relative concentration and an increased contrast (colour) corresponds to a relative increase in elemental concentration.

3. Results

Before turning our attention to the effect of Cu, it is important to revisit, as a reference, the case of the commercial Al-5Ti-B grain refiner, studied at length in the literature [25].

3.1 Heterogeneous nucleation interface of TiB_2 in the commercial Al-5Ti-1B grain refiner

Figure 1 shows HAADF STEM images (Figure 1a, b, f), EELS maps of Ti and B (Figure 1c), B (Figure 1d), Ti (Figure 1e) and Al (Figure 1g), and normalised HAADF and EELS (Al, Ti and B) line profiles (Figure 1h, i) of the basal plane of one TiB_2 particle in the commercial Al-5Ti-1B grain refiner. In a wider context, the basal plane of TiB_2 particle investigated in Figure 1b-i is indicated on the overview image in Figure 1a and Figure S1. Contrast in HAADF STEM images scales to a good approximation as $Z^{1.7}$, where Z is the atomic number [32]. This means for instance that in atomic-resolution images, columns containing Ti atoms within the Al matrix are distinguishable by a relative increase in HAADF image intensity compared to pure Al columns.

EELS maps and line profiles show the presence at the surface of the TiB_2 corresponding to its basal plane of an interfacial atomically ordered structure containing a significant amount of Ti. The outermost layer of the TiB_2 "bulk" crystal structure is indicated by blue arrows, while grey arrows indicate Ti rich columns (out of registry with the atomic structure of the rest of the TiB_2 particle) that appear to be part of this ordered surface layer, several atoms (3-4 atoms) thick. A gradual decrease in both HAADF and Ti signal suggests that the relative thickness (in the direction of the electron beam) of the Ti-rich structure decreases significantly with increasing distance from the nominal TiB_2 "bulk" surface. The results in Figure 1 are consistent with electron microscopy data supporting previous reports [25] of the presence of a so-called Al_3Ti TDC at the basal plane surface of TiB_2.

It should be noted that this Al_3Ti TDC was found to be quite sensitive to electron beam irradiation, see Figure S2. In order to mitigate beam-induced knock-on damage, HAADF images and EELS data were obtained at 60 kV (compared to the other STEM results presented below, obtained at 100 kV), and successive EELS datasets were not acquired from the exact same regions. Thus, the datasets used to generate Figure 1 a-e and Figure 1 f-g were acquired from neighbouring but not identical regions.

Figure 2 shows HAADF STEM images (Figure 2a, b, f), EELS maps of Ti and B (Figure 2c), B (Figure 2d), Ti (Figure 2e) and Al (Figure 2g), and normalised HAADF and EELS (Al, Ti and B) line profiles (Figure 2h, i) of the prism plane of the same TiB_2 particle as shown in Figure 1 (overview image show in Figure 2a). In contrast to the basal plane data in Figure 1, the HAADF image contrast and Ti EELS signal on the prism plane lack the prominent and ordered features of the Al_3Ti TDC, suggesting no strong segregation of Ti on this surface has taken place (the gradual decay of the HAADF and Ti intensity EELS line profiles, in Figure 2h, can likely be attributed to projection / thickness effects). Some weak, partially ordered structures were occasionally observed on the prism plane of the TiB_2 particles: for completeness, an example image is shown in Figure S3, although the sensitivity to electron beam irradiation of these structures made atomically resolved EELS impractical.

The structural difference between the basal and prism planes of TiB_2, the former possessing a smaller mismatch to the proposed structure of the Al_3Ti TDC, is very likely to play a role in the observed difference in Ti segregation on these surfaces. Although, as noted above, it is difficult to establish with certainty the active role of any particle in heterogeneous nucleation from post solidification atomic-scale observation, the presence of an Al_3Ti TDC structure is thought to significantly increase the heterogeneous nucleation potency, thus resulting in preferential nucleation of α-Al on the basal plane of TiB_2. In what follows we therefore focus mainly on the structure and chemistry of the basal plane of TiB_2.

3.2 Grain refinement of Al-Cu based alloys with the Al-5Ti-1B grain refiner

Figure 3 shows the effect of excess Ti on the grain refinement of commercial purity Al-Cu alloys with different Cu concentrations (Alloys 1-3), where the growth restriction is kept constant at 19.6 K. The introduction of excess Ti (from 0.08 wt.% for Alloy 1 to 0.12 wt.% for Alloy 3) indeed refines the grain size overall. However, increasing the amount of excess Ti above 0.08 wt.% (as illustrated by Alloy 2 and Alloy 3 at 0.1 and 0.12 wt.%, respectively) results here in an increase in grain size: this is shown more clearly in Figure 3b. As both Cu and Ti concentrations are adjusted simultaneously to keep the growth restriction constant, there are several possible explanations for this observation. One the one hand, the increase in grain size may be attributable to the possible formation of a primary Al_3Ti phase (which is predicted to be thermodynamically favourable at these excess Ti concentrations), thus depleting the growth restriction. It should be noted here that the primary Al_3Ti phase is different from the Al_3Ti TDC on the surface of TiB_2. The formation of a primary Al_3Ti phase was indeed predicted using the Thermo-Calc software with the TTAL5 database for compositions corresponding to Alloy 2 and Alloy 3, respectively, as shown in Figures 4b, c. However, this was not the case for Alloy 1, as shown in Figure 4a. These predictions agree with the experimentally observed grain sizes (Figure 3). In order to avoid the effect of the formation of an Al_3Ti phase on the heterogeneous nucleation sequence, Alloy 1 is chosen for further detailed characterisation as it corresponds to an optimum Ti excess (0.08 wt.%) in which the formation of an Al_3Ti primary phase is not expected. It should be noted here that, apart from Alloy 3 with low Cu concentration, metastable Al_2Cu-Al eutectic is predicted in the late stage of solidification, as shown in Figures 4a, b.

Figure 5 shows an HAADF STEM image (Figure 5a) and EELS maps of B (Figure 5c), Ti (Figure 5d), Cu (Figure 5e), and Al (Figure 5f) obtained in Alloy 1, revealing a typical area seen in this sample with a large TiB_2 particle and of two smaller particles in its vicinity. A composite RGB chemical map, Figure 5b, further illustrates the relative Al, Cu and Ti compositions. In addition to the expected Ti and B content of the refiner particles (although the exact composition was not quantified here, it is reasonable to conclude that these are TiB_2 particles), it is interesting to note that the Cu solute in this sample seems to have formed Cu-rich aggregates with much higher relative Cu concentration than the surrounding Al matrix on both the prism and basal planes of the larger TiB_2 particle. The distribution of Cu must therefore be investigated in more detail.

Intermediate magnification chemical maps of the basal (Figure S4) and prism (Figure S5) planes of the TiB_2 particle shown in Figure 5 indicate that, in addition to the larger Cu-rich aggregates, there is a ~ 2 nm Cu-rich layer covering the particle. As this Cu-rich layer may play a significant role in grain refinement, probing the atomic-scale structure and chemistry of the basal and prism plane TiB_2-Al interface is highly desirable. Figure 6 shows atomic resolution HAADF STEM images (Figure 6a, d), EELS maps for Ti and B (Figure 6b), Al and Cu (Figure 6e), and normalised line profiles of HAADF images and the Ti and B (Figure 6c) and Cu and Al EELS signals (Figure 6f) of the basal plane of one of these TiB_2 particles. Here, and in what follows, although all maps were acquired in the very same region (and in fact immediately next to each other, as suggested by the white rectangles on Figures 5a and 5d depicting the region over which the EELS spectrum images were recorded), the wide energy loss range required to document all ionisation edges made it necessary to obtain two consecutive EELS maps, for B and Ti on the one hand, and for Cu and Al on the other. It is however reasonable to assume that the chemical profiles are representative of the interface chemistry, such that the two datasets can be interpreted together to infer the relative spatial localisation and relative composition of the observed structures. These maps reveal that on top of the outermost TiB_2 surface layer (indicated by blue arrows as a guide to the eye), there is an Al and Ti rich region (assumed to be an Al_3Ti TDC layer, by analogy with the case of the Al-5Ti-1B case studied earlier; it is indicated by a grey arrow as a guide to the eye), followed by an Al-rich layer with a much lower relative Ti content (red arrows), and finally a Cu-rich layer, several atomic planes (2-3 atoms) thick, exhibiting a clear ordered crystal structure. The various surface layers appear not to fully cover the entire basal plane of the TiB_2 particles: this is illustrated further in Figure S6 which shows how the Cu-rich layer is imaged more clearly using a different defocus value, taking advantage of the depth sectioning capabilities provided by the large convergence angle probe used here. This partial coverage is unlikely to be due to beam damage, as the structures in this sample seemed less prone to damage (see Figure S7; this is possibly due to a thicker sample) than in the case of the Al-5Ti-1B grain refiner sample (see Figure S2).

For completeness, Figure 7 shows EELS maps and HAADF images of the prism plane of the same TiB_2 particle shown in Figure 6. Similar to the basal plane, an Al-rich layer is covered by a Cu-rich layer. However, in general agreement with our observations of the prism plane of TiB_2 in the commercial Al-5Ti-1B grain refiner (Figure 2), Figure 7 suggests that no Al_3Ti TDC is present in this case. In spite of the difference between the two alloys, this would seem to be consistent with the conclusion that in both cases the heterogeneous nucleation of Al occurs preferentially on the basal plane of TiB_2. We attribute this to the segregation of Ti on the basal plane forming an Al_3Ti TDC, thanks to a favourable structural match at this interface.

4. Discussion

As demonstrated in Figure 3, the presence of excess Ti (0.8 wt.%) results in a smaller grain size when the growth restriction is kept constant (19.6 K). It is generally accepted that the grain refinement of Al alloys can be attributed to two key factors: nucleation potency and growth restriction. Nucleation potency is believed to be dependent on the number, size and size distribution of the nucleants (TiB_2 in the present investigation). For the grain refinement of the Al-Cu based alloys studied here, the nucleation potency of TiB_2 can be regarded as unchanged because we used the same nominal amounts of TiB_2 (0.01 wt. %) throughout and Al-5Ti-1B grain refiner rods. Furthermore, it has been reported [2, 8] that only the largest TiB_2 particles (*i.e.*, less than 2 % of the total number of particles in a typical case) can be activated during the refinement of Al grains. We surmise therefore that the number of TiB_2 particles with a large size [12] is not a dominant factor in the grain refinement we report here because a sufficient number of TiB_2 particles (0.01 wt. %) were added in all three samples during Al melting. Growth restriction on the other hand, is believed to depend mainly on the alloying elements themselves. Of all the alloying elements, Ti has the strongest growth restriction effect (15.38 K for 0.1 wt. % Ti) [2, 8]. Cu is also known to have a positive, albeit small, growth restriction effect (0.21 K for 0.1 wt. % Cu) [2, 8]. Increasing the Cu content therefore increases the growth restriction. By increasing the Cu content, it is therefore possible to compensate for a smaller amount of Ti excess while retaining identical growth restriction characteristics, and in turn to observe good grain refinement, as shown in Figure 3. It has also been reported [2, 11, 15] that when there is no strong interaction between the elements, the total growth restriction for all elements (ΣQ, used here as the main measure of growth restriction, listed in Table 1) is additive. However, it has also been reported [11, 33] that the prediction of the total growth restriction from the additive elements (ΣQ) is not applicable in cases where the primary phase is not α-Al. A phase other than α-Al forming initially may impair the grain refinement by poisoning the nucleation on inoculants particles and / or by removing solute from solution thus reducing the growth restriction [2]. While this may seem to be a concern here, it should be noted that the respective contents of Ti in samples Alloy 2 (0.1 wt.%) and Alloy 3 (0.12 wt.%) are typical of industrial applications for the grain refinement of cast Al alloys. The excess Ti remaining in the melt (*i.e.*, apart from that consumed through the formation of Al_3Ti primary phases) must therefore promote, rather than poison, the nucleation on inoculants particles. This suggestion stems from the observation of much smaller grain sizes (about 62 ± 4.9 μm) for samples such as Alloy 1 compared to the grain size reported in the case of other Al alloys with less excess Ti and fewer inoculants particles (e.g. 1 ppm, 10 ppm, with grain sizes of about 150 μm [1,3]). Therefore, the formation of a bulk primary Al_3Ti phase can be expected to mainly reduce the growth restriction but not to affect the heterogeneous nucleation sequence on TiB_2 particle.

Given the set of parameters explored in this study, it is possible to propose three different scenarios about the heterogeneous nucleation sequence on TiB_2 particle. Firstly, the presence of Cu but the absence of any excess Ti results in a lack of an Al_3Ti TDC structure on the surfaces of the TiB_2 particles. The heterogeneous nucleation of Al then occurs *via* the formation of a heterogeneous cap of Al at higher undercooling, followed by a progressive to total Al coverage of the TiB_2 particle surface. In this case, the solute Cu acts as a growth restrictor and is not involved in the heterogeneous nucleation. Secondly, in the presence of both excess Ti and solute Cu the solidification path can be described as follows: firstly, an Al3Ti TDC forms respectively survives from the surface of the TiB_2 particles, covering its basal plane (not the prism plane). Subsequently, the Al_3Ti TDC transforms *via* a peritectic reaction with the liquid and Al and subsequent peritectic transformation. The presence or absence of an Al_3Ti TDC in the post-solidification microstructure could be dependent on the completion of this peritectic transformation. In most cases, the Al_3Ti TDC will have been involved in a peritectic reaction to form an Al-rich layer. Figure 1 shows clearly that the Al_3Ti TDC comprises 3-4 atomic layers; the Al-rich layer is most locally indistinguishable from the surrounding Al matrix. In contrast, when the TiB_2 particle was an active nucleation site, the peritectic transformation will completely consume the Al_3Ti TDC so that none remains in the post solidification microstructure, which could explain the absence of any observed Al_3Ti TDC in some literature reports [2, 4]. The solute Cu acts here as a growth restrictor and is not involved in the heterogeneous nucleation. This scenario may be more likely to apply to cases with lower Cu concentrations in the Al-Cu alloys (e.g. Alloy 3), by comparison with third case below. Thirdly, in the presence of excess Ti and of a large concentration of solute Cu facilitating the observation of metastable eutectic Al-Cu, an Al_3Ti TDC layer (only 1-2 atomic layers as shown in Figure 6b, c, thinner than that in Figure 1 (3-4 atomic layers)) covers the basal plane of the TiB_2 particle, but in contrast to the second case, while a peritectic reaction does occur between the Al_3Ti TDC and the Al liquid, forming an initial Al-rich layer, a subsequent eutectic reaction then results in the formation of a Cu-rich layer (metastable Al_2Cu eutectic, only 1-2 atomic layers as shown in Figure 6e, f) on the top of this Al-rich layer (only 1 atomic layer as shown in Figure 6e, f), effectively stopping any complete peritectic transformation from consuming the underlying Al_3Ti TDC and facilitating the observation of Al-rich layer. Although many parameters are at play, and a completely unambiguous validation of this third scenario is difficult, a similar eutectic reaction sequence was proposed in the Al-Zn-Mg-Cu based alloy with Sc, Ti and Zr additions [34]. Here primary $Al_3(ZrTi)$ firstly forms, followed by a subsequent eutectic reaction ($L \rightarrow Al + Al_3Sc$) forming a Al-rich layer for each Sc-rich layer eutectic structure until the size of the nucleated particle ($Al_3(ScTiZr)$) is large enough so that Al can grow from its surface. In this case, the eutectic reaction ($L \rightarrow Al + Al_3Sc$) is involved in the heterogeneous nucleation. By analogy it is reasonable to propose in our case that the eutectic reaction (L→Al + Cu-rich layer) can also occur at the interface of TiB_2. The occurrence of the peritectic reaction between the Al_3Ti TDC layer and the Al liquid, combined with the absence of the subsequent peritectic transformation, would also be consistent with the observation of an Al_3Ti TDC structure in metallic glass experiments (which, due to high cooling rates, cannot sustain a peritectic transformation) [24]. In this case, the Al_3Ti TDC remains present in the post-solidification microstructure, which can help rationalize the observation of this Al_3Ti TDC in previous reports [8-12, 21-24] and in the present investigation (Figure 6). In the third case, solute Cu not only acts as a growth restrictor but it is also involved in the heterogeneous nucleation sequence. Higher Cu concentrations in the Al-Cu alloys (*i.e.* Alloy 1) may make this scenario more likely. Regardless, for all three cases, the TiB_2 particle would be regarded as active for grain refinement. Once more, however, the observation of particles consistent in their structure or chemistry with these three cases does not rule out the possibility that they could have been pushed ahead of the solidification front and finally be located along grain boundaries, or been entrained within the α-Al grain and located inside the α-Al grain. In such scenarios, these TiB_2 particles were not be active as heterogeneous nucleation sites.

Whether the TiB_2 particle is active or not mainly depends on the particle size [8, 9]. When the solidification temperature is in contact with liquidous, all Al_3Ti TDC covered TiB_2 particle will form an Al-rich layer via a peritectic reaction. Subsequently, when the solidification temperature decreases below liquidous, depending on the size of TiB_2 particles, some larger TiB_2 particles will become active as nucleation sites and lead to free growth of Al. This will facilitate the peritectic transformation of the remaining Al_3Ti TDC, which leads to the absence of Al_3Ti TDC in the post solidification microstructure. While, for the smaller TiB_2 particles on which no free growth is expected, when the smaller TiB_2 particles are not nucleation sites, the Al_3Ti TDC and Al-rich layer will remain, however the Al-rich layer will become indistinguishable from the surrounding Al matrix and the observation of the Al_3Ti TDC will greatly depend on the experimental TEM techniques used. In contrast, when the smaller TiB_2 particles are nucleation sites for subsequent eutectic reaction in Al-Cu alloys, the Al-rich layer acts as a nucleation site for the eutectic reaction (Al-Cu eutectic) and thereby can become clearly distinguishable using suitable TEM techniques.

5. Conclusion

We have presented an atomic-scale experimental investigation of a number of key parameters controlling heterogeneous nucleation at the interface of TiB_2 grain refiner particles in the Al-Cu alloy system, with particular focus on the segregation of solute elements (Ti, Cu). Some conclusions can be drawn as follow:

1. As a starting point, we were able to unambiguously confirm the segregation of Ti on the basal plane of TiB_2, but not on the prism plane, in the commercial Al-5Ti-1B grain refiner which was used in the creation of three Al-Cu based alloys studied here. This segregation is shown to consist mainly in the formation of a structure consistent with the so-called Al_3Ti TDC in earlier literature reports, located on the basal plane of the TiB_2 particles.
2. As excess solute Ti can enhance the heterogeneous nucleation and act as a growth restrictor, two related and interdependent, yet distinct roles, three Al-Cu alloys were designed to vary the excess Ti at the same overall growth restriction (19.6 K). In the case of an Al-Cu alloy with a high solute Cu and a relatively low amount of excess Ti (i.e. Alloy 1), similar Ti segregation in the form of an Al_3Ti TDC structure on the basal plane of TiB_2 is accompanied by the formation of an additional Cu-rich layer covering the entire particle. On the basis of this observation, one possible heterogeneous nucleation sequence has been proposed, which can interpret the absence and presence of the Al_3Ti TDC on TiB_2 particle in Al alloys, in particular to Al-Cu alloys here.
3. The formation of this Cu-rich layer may be closely dependent on the Cu concentration, and future studies varying this parameter while attempting to keep other factors constant would thus be required. However, the present investigation provides a clearer picture of the heterogeneous nucleation sequence of α-Al on TiB_2 in Al-Cu alloys.

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