Mechanism for Zr poisoning of Al-Ti-B based grain refiners

Y. Wang a, C.M. Fang a, L. Zhou a, T. Hashimoto b, X. Zhou b, Q.M. Ramasse c, Z. Fan a,∗

a BCAST, Brunel University London, Uxbridge, Middlesex, UB8 3PH, UK
b School of Materials, University of Manchester, Manchester, M13 9PL, UK
c SuperSTEM, STFC Daresbury Laboratories, Keckwick Lane, Warrington, WA4 4AD, UK

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ABSTRACT

Al-Ti-B based master alloys have been widely used for grain refining of Al-alloys in industry for many decades. However, the effectiveness of such grain refiners is severely compromised when a few hundred ppm of Zr is present in the Al melt, and this phenomenon is referred to as Zr poisoning in the literature. So far the exact mechanisms for Zr poisoning are not clear albeit significant research effort on the subject in the last few decades. In this work we investigated the mechanism for Zr poisoning through extensive examinations of the Al/TiB2 interface using the state-of-the-art electron microscopy and ab initio molecular dynamics simulations. We found that the presence of Zr in Al melts leads to (i) the dissolution of the Al3Ti 2-dimensional compound (2DC) formed on the (0 0 0 1) TiB2 surface during the grain refinement process; and (ii) the formation of an atomic monolayer of Ti2Zr 2DC on the (0 0 0 1) TiB2 surface, which replaces the original Ti-terminated TiB2 basal surface. This monolayer of Ti2Zr not only has large lattice misfit (4.2%) with α-Al, but also is atomically rough, rendering the TiB2 particles impotent for heterogeneous nucleation of α-Al. This work, in combination of our previous work, demonstrates that heterogeneous nucleation can be effectively manipulated, either enhanced or impeded, by chemical segregation of selected alloying/impurity elements at the liquid/substrate interface.

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1. Introduction

Grain refinement during casting of engineering alloys is usually desirable, since it results in not only a fine and equiaxed grain structure but also a significant reduction of casting defects, which in turn leads to an improved engineering performance [1]. As a common practice in the metal casting industry, grain refinement is usually achieved by chemical inoculation through addition of grain refiners. Among a series of Al-Ti-B based grain refiners developed for Al-alloys, Al-5Ti-1B (all compositions are in wt.% unless otherwise specified) master alloy has been the most widely used grain refiner, which contains potent TiB2 particles for enhancing heterogeneous nucleation of α-Al grains [2]. Since the introduction of Al-Ti-B based grain refiners at the beginning of the 1950s [3], significant effort has been made to optimize their performance largely through a trial-and-error approach, and to understand the grain refining mechanisms, with both the theory and practice being extensively reviewed [2,4–7]. However, only recently has the mechanism for grain refinement been made clear; i.e., formation of an atomic monolayer of Al3Ti 2-dimensional compound (2DC) on the (0 0 0 1) TiB2 surface is responsible for the high potency of TiB2 particles for heterogeneous nucleation of α-Al [8].

Both alloying and impurity elements in Al-alloys are known to improve the grain refining effectiveness of Al-Ti-B master alloys. However, the presence of solute elements is not always beneficial and the interaction between solute elements and TiB2 particles sometimes renders TiB2 particles impotent for heterogeneous nucleation. It has been reported that, in the presence of certain alloying or impurity elements in Al-alloys, such as Zr, Cr and Li, and high levels of Si, the effectiveness for grain refinement of Al-Ti-B master alloys can be dramatically reduced, resulting in a coarse and columnar grain structure in some cases [9–26]. This adverse effect on grain refinement is often referred to as “poisoning” in the literature.

Zr itself is usually considered to be a favorable solute element for grain refinement of Al-alloys since it has a relatively large growth restriction factor [27,28], although its refining ability was found to be less than that of Ti [5,25]. When the concentration of Zr is higher than the peritectic composition (0.11%), Al1Zr forms as the primary phase, which acts as an effective substrate for heterogeneous nucleation of α-Al [29,30]. It has also been shown that the grain
refining effects of Zr and Ti are not additive and their combined effect is much less than either of the elements alone \cite{5,25}.

However, Zr-containing Al-alloys are usually difficult to grain refine using the Al-Ti-B grain refiners. Jones and Pearson \cite{9} observed that it was not possible for the grain size of an Al-5Zn-1.5Mg-0.22Zr alloy to be refined below 250 µm by Al-5Ti-1B inoculation. By increasing the level of Al-5Ti-1B addition, the grain size was reduced to below 250 µm only when the holding time was shorter than 10 min, and a considerably larger grain size was observed in samples with prolonged holding time \cite{9}. Birch and Fishers \cite{10} reported the poisoning effect in Zr-containing commercial 7xxx Al-alloys inoculated with Al-5Ti-1B grain refiner, and similar observations were reported by Ahmadey et al. \cite{11} and Kearns and Cooper \cite{12} in 7050 Al-alloy containing 0.10–0.13% Zr. Results of Birch and Cowell \cite{13} and Abdel-Hamid \cite{14,15} also confirmed the poisoning effect of Zr in Al-alloys. Furthermore, it has been reported that the poisoning effect of Zr was promoted by the presence of Li as an alloying element in Al-alloys \cite{16}.

Impurities were found to affect Zr poisoning. Spittle and Sadli \cite{17} investigated the effect of Fe, Si, Cr, and Zr on the grain refinement of high purity Al (HP-Al) inoculated with Al-5Ti-1B grain refiner. They concluded that Zr addition results in a poisoning effect with the presence of Fe and Si. However, Zr alone in HP-Al was found to be beneficial to grain refinement by the Al-5Ti-1B grain refiner. In another report, Spittle and Sadli \cite{18} also studied the influence of various alloying elements, including 0.05% Zr, on the grain refinement of HP-Al, and found that the grain size of binary Al-alloys is strongly dependent on the magnitude of the constitutional undercooling parameter. Qiu et al. \cite{19} proposed a co-poisoning mechanism by Zr and Ti when a certain amount of Fe impurity was present in terms of crystallographic analysis. Johnson \cite{20} found that, for hypoperitectic Al-alloys, Zr and Ti in the liquid cooperated to promote grain refinement, while in hyperperitectic Al-alloys grain refinement deteriorated due to the formation of a mixed aluminiode phase, (Ti\textsubscript{1-x}Zr\textsubscript{x})Al\textsubscript{3}. It was speculated that the formation of the ternary aluminiode removes Ti dissolved in the melt, resulting in reduced growth restriction during the growth of α-Al dendrites.

A few hypotheses have been proposed to explain the poisoning effect of some solute elements on the grain refining effectiveness of Al-Ti-B master alloys. In their work on the effect of various alloying elements on grain refinement, Jones and Pearson \cite{9} attributed the poisoning effect of Zr to the formation of ZrB\textsubscript{2} coatings on the TiB\textsubscript{2} surface, because ZrB\textsubscript{2} is thermodynamically more stable than TiB\textsubscript{2}. They believed that ZrB\textsubscript{2} coatings prevent TiB\textsubscript{2} from acting as a nucleating site for the α-Al due to its larger lattice parameters than TiB\textsubscript{2}, although no evidence of the formation of ZrB\textsubscript{2} was presented. Trying to explain the poisoning effect of Zr and Cr, Abdel-Hamid \cite{14} proposed that some of the Ti atoms in Al\textsubscript{3}Ti and TiB\textsubscript{2} crystals were replaced by poisoning elements, such as Zr, Cr, etc., resulting in the formation of a less potent Al-Ti-Zr ternary compound. Murty and his co-workers \cite{5,21,22} shared this point of view in their explanation of the poisoning effect of Cr and Zr. The mechanism involving the formation of ternary aluminiodes was also supported by Johnson \cite{20} who suggested that the poisoning effect of Zr was associated with the reduced potency of Al\textsubscript{3}Ti through the formation of (Ti\textsubscript{1-x}Zr\textsubscript{x})Al\textsubscript{3}. Bunn et al. \cite{31} observed the presence of Zr in Al\textsubscript{3}Ti and attributed the poisoning effect to the modification of both Al\textsubscript{3}Ti and TiB\textsubscript{2} by Zr. In addition, the formation of (Ti\textsubscript{1-x}Zr\textsubscript{x})Al\textsubscript{3} would reduce the Ti concentration in the melt and thus the growth restriction, which is also believed to be an important factor for grain refinement. However, Bunn et al. \cite{31} realized that reduction in growth restriction arising from reduced solute concentrations in the melt was not the dominant factor in Zr poisoning and that the poisoning was mainly attributed to the interaction between Zr and the nucleating substrates. Another explanation for the poisoning effect of Zr and Cr was proposed by Jones in his hyper-nucleation theory \cite{32}, which involves the atomic size mismatch between Zr or Cr and the solvent Al.

Although the exact mechanism for the poisoning effect is so far unclear, it is generally accepted that poisoning is mainly due to the interaction of these alloying elements, Zr, Cr, Si and Li, with the nucleating particles, such as Al\textsubscript{3}Ti and TiB\textsubscript{2} \cite{9,14,31,33}. It is anticipated that such interaction may give rise to the formation of complex aluminides, borides and silicides, which have a poor potency for nucleating α-Al grains, on the surface of nucleating particles.

The loss of nucleation potency through poisoning is known to be time dependent; i.e., grain size increases with holding time after addition of grain refiner. Experimental work \cite{9,31} showed that the poisoning effect increases with holding time after the addition of Zr, being consistent with progressive substitution of Ti atoms with Zr atoms. In general, loss of nucleation potency by poisoning is non-recoverable, unlike gravity-induced fading (i.e., settling of nucleant particles), which can be recovered by stirring the melt prior to casting.

Zr is an important trace alloying element in some 2xxx and 7xxx series Al-alloys due to its contribution to dispersion strengthening and impedance of dynamic recrystallization. For example, typical 7xxx series alloys contain about 0.12% Zr for dispersion strengthening. Problems can be encountered during direct chill (DC) casting of such alloys, where the performance of Al-Ti-B grain refiner is significantly reduced due to the Zr poisoning effect. Considerable work has been carried out to reduce or eliminate such poisoning. Increasing the addition level of Al-5Ti-1B master alloy has been shown to be a way to improve the grain refining response \cite{9,33}, although the accumulation of non-active TiB\textsubscript{2} particles in the alloy causes serious concern. Another approach to overcome the problem is to use alternative grain refiners, such as Al-Ti-C based master alloys \cite{34–38}. As a promising grain refiner, Al-Ti-C master alloy has been reported to be resistant to Zr poisoning to a certain extent, although there are some controversies between different investigators \cite{38}. In a 7xxx Al-alloy containing 0.06% Zr, addition of Al-3Ti-0.15C master alloy has been shown to result in a very fine grain structure without twin columnar growth \cite{34}. Schneider et al. \cite{35} also found that the grain refining effect of Al-5Ti-0.25C grain refiner was better than that of Al-5Ti-0.2B in a Zr-containing 7050 alloy at the same addition level. However, experimental study \cite{37} has demonstrated that Al-Ti-C master alloy may be poisoned in the presence of Zr. The grain refining ability of Al-5Ti-0.4C master alloy (0.2% addition) was reported to diminish when 0.12% Zr was added to the melt \cite{38}. It was suggested that Zr interacted with both TiAl\textsubscript{3} and TiC phases.

In the present work, extensive electron microscopy has been carried out focusing on the Al/TiB\textsubscript{2} interface, in order to reveal any possible modification caused by interaction between Zr and TiB\textsubscript{2} at the interface. An ab initio molecular dynamics method is employed to simulate the structure and stability of the segregation layer at the interface at temperature above the liquidus of Al in accordance with the experimental observation. Mechanism underlying Zr poisoning is discussed in the context of Zr segregation at the Al(liquid)/TiB\textsubscript{2} interface and its consequence on the potency of TiB\textsubscript{2} particles for heterogeneous nucleation of α-Al.

2. Experimental

2.1. Materials

Commercial purity aluminium (CP-Al, > 99.86% Al) and Al-10Zr master alloy were used for all the experiments in this work. TiB\textsubscript{2}
particles were introduced to the CP-Al melt through the addition of 0.1% of commercial Al-5Ti-1B grain refiner rods supplied by LSM (Rotherham, UK). In order to assess the effect of Zr on the effectiveness of the grain refiner, Zr was added to the CP-Al melt at concentrations between 0.058% and 0.450%. The chemical compositions and impurities of the materials used in this work are given in Table 1.

2.2. Grain size assessment

The standard TP-1 test [39] was used to assess the grain size by providing a consistent cooling rate of 3.5 K/s at the central region of the cross-section 38 mm from the bottom of the TP-1 cast sample. Al-Zr melts with varying Zr concentrations were held isothermally at 800 °C for 4 h followed by the addition of 0.1% Al-5Ti-1B grain refiner. After holding for 1 more hour, the Al-Zr alloy melt inoculated with Al-5Ti-1B master alloy was cast into the pre-heated TP-1 mould (350 °C) which was immediately cooled by water spray with a controlled water flow rate of 3.8 l/min. Such TP-1 tests were also carried out on CP-Al with no addition of Zr for comparison.

Quantitative metallography for grain size assessment was performed by examining the grain structure of the transverse section 38 mm from the base, and the longitudinal section of the lower part formed by examining the grain structure of the transverse section 38 mm from the base, and the longitudinal section of the lower part. The specimens for the grain size assessment were prepared using standard metallographic techniques. Electro-polishing was performed prior to anodizing with Barker’s reagent (5 ml HBF4 + 200 ml distilled water) to show the grains with different orientations. A Zeiss optical microscope fitted with the Axio Vision 4.3 image analysis system was used for the grain size assessment under polarized light. A mean linear intercept technique was used to quantify the grain size with measurement of at least 500 grains.

2.3. High resolution TEM/STEM

A pressurised melt filtration technique was used to collect the TiB2 particles introduced to the alloy melt through the addition of the commercial Al-5Ti-1B grain refiner, in order to facilitate direct examinations using advanced electron microscopy. In this process, Al-Zr alloy melt inoculated with 0.2% Al-5Ti-1B grain refiner was transferred into the crucible in the pressure chamber. Argon was introduced to force the melt to flow through a porous filter attached to the bottom of the crucible. TiB2 particles were thus collected above the filter together with the residual melt. The solidified material immediately above the filter, which contained the locally concentrated TiB2 particles, was subjected to examination. A detailed description of the melt filtration technique can be found elsewhere [40,41].

Thin foil specimens for transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were prepared from 3 mm diameter discs sliced from the filtered residue material. The discs were ground to a thickness less than 60 μm before further thinning by Ar ion beam milling using a Gatan precision ion polishing system (PIPS) under a voltage of 1.0–5.0 kV and an incident beam angle of 3–5°. Traditional high resolution TEM analysis was conducted on a JEOL 2100F microscope operated with an accelerating voltage of 200 kV. Atomic resolution STEM with Z-contrast high-angle annular dark filed (HAADF) imaging was carried out on an aberration (Cs)-corrected FEI Titan 80–200 instrument equipped with Super-X energy dispersive x-ray spectroscopy (Super-X EDS) system, operated with an accelerating voltage of 200 kV. Further STEM of a higher resolution was conducted using Nion Ultra-STEM 100 instrument (2nd generation) at the SuperSTEM Centre (Daresbury, UK). This microscope was equipped with a field emission gun operated at 100 kV, and a Nion spherical aberration (Cs) corrector and electron energy loss spectroscopy (EELS) system. Super-X EDS mapping and atomic resolution EELS mapping were conducted to obtain compositional profiles across Al/TiB2 interface.

Simulation of STEM-HAADF images was conducted using the QSTEM multislice simulation package developed by Koch [42], and the simulated results were compared to the STEM HAADF images obtained experimentally using Cs-corrected high resolution STEM.

2.4. Ab initio molecular dynamics simulations

Ab initio molecular dynamics (MD) simulations were carried out using the code VASP (Vienna ab initio Simulation Package) [43,44], which employs the ab initio density functional theory (DFT) within the projector-augmented wave (PAW) framework [45,46]. The exchange and correlation terms were described using the generalized gradient approximation (GGA-PBE) [47]. A cut off energy of 320 eV and only Γ-point in the BZ [48] were used. The liquid Al was generated by equilibrating for about 10 picoseconds (ps) at 3000 K, followed by cooling down to and equilibrated at a designated temperature for 10ps. The liquid Al obtained in this way was brought in contact with the TiB2 substrate and then equilibrated at the same temperature for 10ps to ensure equilibrium. The time-averaged method was employed to take samples with over several ps (2000–3000 steps, 1.5fs/step) to satisfy the statistics. The substrate and liquid atoms were fully relaxed during the simulations.

3. Results

3.1. Confirmation of Zr poisoning

Prior to investigation of the poisoning mechanism, it is important to confirm the Zr poisoning effect through designed solidification experiments. Fig. 1a and d shows the macrostructure of CP-Al solidified under TP-1 conditions. Both the transverse and longitudinal sections show a coarse columnar grain structure. Addition of 0.1% commercial Al-5Ti-1B grain refiner to the CP-Al melt resulted in a fine and fully equiaxed grain structure (Fig. 1b and e), with the average grain size being 175 ± 25 μm. This suggests that the commercial Al-5Ti-1B grain refiner used in this experiment is effective for grain refinement of CP-Al. However, the macrostructure of Al-0.058Zr alloy inoculated with 0.1% Al-5Ti-1B grain refiner has a coarse columnar grain structure (Fig. 1c and f). This indicates that the effectiveness of the grain refiner was reduced dramatically due to the presence of 580 ppm Zr in the melt, confirming the poisoning effect of Zr. With further increase of Zr concentration up

| Table 1 Compositions (wt.%) of commercial purity Al (CP-Al), Al-5Ti-1B grain refiner and Al-10Zr master alloy used in this work. |
|-----------------|---|---|---|---|---|---|---|---|
| Alloy           | Fe | Si | V  | Zn | Ni | Cu | Cr | B | Zr | Al  |
| CP-Al           | 0.08 | 0.03 | –  | 0.003 | 0.005 | 0.001 | 0.001 | 0.006 | –  | –  | Bal. |
| Al-5Ti-1B       | 0.09 | 0.08 | 0.04 | –     | –     | –     | 4.80  | 0.85  | –  | –  | Bal. |
| Al-10Zr         | 0.08 | 0.03 | –  | 0.01  | –     | 0.04  | 0.02  | –  | 9.90 | –  | Bal. |
to 0.45%, the macrostructures of Al-Zr alloys inoculated with 0.1% Al-5Ti-1B grain refiner remain coarse and columnar, and the width of the columnar grains increases with increasing Zr concentration (Fig. 2). This suggests that the effect of Zr poisoning increases with increasing Zr concentration.

3.2. Segregation of Zr atoms on TiB₂ surface in dilute Al-Zr alloys

The reference point for our investigation is the TiB₂ particles brought into the Al melt by the commercial Al-5Ti-1B grain refiner. It was confirmed in our previous work [8] that the TiB₂ particles in such grain refiner are extremely potent for heterogeneous nucleation of α-Al due to the presence of Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface. High temperature, high concentration of Ti and prolonged reaction time in the fabrication processing of the grain refiner ensures the formation of the Al₃Ti 2DC. A well-defined orientation relationship (OR): (0 0 0 1)[1 1 -2 0] TiB₂//(1 1 1) [0 -1 1] Al was observed readily in the CP-Al sample inoculated by the Al-5Ti-1B grain refiner.

In order to examine any possible modification of the TiB₂ surface due to the presence of Zr in the alloy melt, TiB₂ particles in the Al-Zr alloy were collected and examined in detail by SEM and TEM/STEM, focusing on their faceted surfaces. It was confirmed that the terminating facets of the TiB₂ particles are {0 0 0 1} basal and {1 0 -1 0} prismatic planes. Their average size is 0.2–3.2 μm in diameter, which is the typical size range observed in a commercial Al-5Ti-1B grain refiner [49]. No obvious change in size and morphology was observed before and after the Zr addition by SEM examination. However, TEM/STEM examination has revealed several interesting facts: (i) the well-defined OR between TiB₂ and Al was not observed in the Al-Zr alloy inoculated by Al-5Ti-1B refiner, although as many as 100 TiB₂ particles in total were examined in multiple thin foil TEM specimens; (ii) the original Al₃Ti 2DC was not observed on (0 0 0 1) TiB₂ surface; and (3) the original Ti-terminated (0 0 0 1) TiB₂ surface is replaced by a new segregation layer.

Atomic scale examination of this new segregation layer (STEM HAADF images in Fig. 3) reveals that it is an atomic monolayer of chemical segregation on the (0 0 0 1) TiB₂ surface, as evidenced by the atomic columns having a brighter contrast than that of the Ti columns in TiB₂ when the TiB₂ is viewed along both [1 1 -2 0] (Fig. 3a) and [1 0 -1 0] (Fig. 3c) directions. The α-Al is oriented away from any low index zone direction in both Fig. 3a and c, suggesting that this particular TiB₂ particle did not participate in grain initiation during solidification. The higher brightness of atom columns in the segregation layer indicates that heavier (than Ti) atoms exist in these columns (large green spheres represent heavier atom X in Fig. 3b and e). Particularly, on tilting the specimen by 30° from [1 1 -2 0] to [1 0 -1 0] TiB₂, the brightness of the segregation layer is no longer uniform as shown more clearly by the SuperSTEM HAADF image in Fig. 3d. Instead, it has a periodic variation with two darker atomic columns between the two brighter atomic columns as
illustrated schematically in Fig. 3e. The periodic variation in brightness in the HAADF image indicates that there are at least two types of atoms in the segregation layer, with their arrangement being ordered in 2D. In addition, experimental measurement shows that the spacing between the segregation layer and its closest Ti layer in TiB₂ was slightly larger than the spacing between two Ti layers in TiB₂, i.e., 0.34 ± 0.01 nm compared with 0.32 nm. These results suggest that the surface segregation layer is an ordered 2DC, in which the atoms are arranged in a hexagonal configuration, following that of Ti atoms in the (0 0 0 1) TiB₂ terminating plane.

High resolution Super-X EDS analysis using aberration (Cs)-corrected STEM instrument was performed to identify the chemical nature of the segregation layer on the TiB₂ surface. An example of such analysis is given in Fig. 4. The elemental mapping across the Al/TiB₂ interface shows the segregation of Zr atoms (Fig. 4b) at the interface, corresponding to the brighter contrast of the segregation layer in the HAADF image (Fig. 4a). No Zr segregation was observed on {1 0 -1 0} prismatic planes of the TiB₂ particles in this work, suggesting that segregation of Zr atoms is selective, depending on atomic configuration of the terminating surfaces of TiB₂. In addition, the presence of Al and Ti atoms in the segregation layer cannot be conclusive due to the existence of Al in the Al matrix and Ti in the TiB₂ substrate (Fig. 4c and d). Furthermore, particular attention was paid to the potential segregation of the main impurity elements in the alloy, such as Fe and Si. The EDS mapping results in Fig. 4e and f do not suggest any existence of either Fe or Si in the segregation layer.

Intuitively, one would not expect that the basal surface of all the TiB₂ particles to be entirely covered by the Zr-containing segregation layer. Indeed, it was occasionally found that some of TiB₂ particles were covered only partially by the segregation layer on their (0 0 0 1) surface. For instance, Fig. 5 shows that Zr segregation occurs on the left hand side of the (0 0 0 1) TiB₂ surface, confirmed by the specific periodic pattern of brightness in the HAADF image in Fig. 5a and the corresponding Zr elemental map from Super-X EDS analysis in Fig. 5b. Again Fig. 5c and d shows no existence of Fe or Si in the segregation layer.

3.3. Chemistry and structure of Zr segregation layer

From the above experimental findings by the direct STEM observation and EDS analysis (Figs. 3–5), the segregation layer has the following unique characteristics: (i) it is an atomic monolayer; (ii) it is a 2-dimensional compound (2DC) in which the atoms have a hexagonal arrangement; and (iii) it contains Zr and one or more other elements. Based on the compositions of CP-Al and the master alloys used in this work (Table 1), other possible elements in the segregation layer may include Ti, Al, Fe and Si. However, Fe and Si are ruled out by the EDS results (Figs. 4 and 5). The possibility of Al can also be eliminated by the fact that Al atoms do not substitute Ti atoms in the Ti-terminated (0 0 0 1) TiB₂ surface as presented in our previous work [8], and this is consistent with the thermodynamic
Fig. 4. (a) High resolution STEM HAADF image across Al/TiB₂ interface viewed along [1 1 -2 0] TiB₂ direction, and (b–f) Super-X EDS elemental mapping of (b) Zr (cyan), (c) Al (green), (d) Ti (red), (e) Fe (purple) and (f) Si (yellow) across the interface, showing Zr segregation but no segregation of Fe and Si at the interface between Al and (0 0 0 1) basal plane surface of TiB₂. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. (a) High resolution STEM HAADF image across Al/TiB₂ interface viewed along [1 0 -1 0] TiB₂ direction, and (b–d) Super-X EDS elemental mapping (from the marked area in (a)) of (b) Zr (cyan), (c) Fe (purple) and (d) Si (yellow) across the interface, showing the on-going Zr segregation process on the (0 0 0 1) surface of a TiB₂ particle evidenced by the periodic pattern of brightness in (a) the HAADF images and the Zr composition profile in (b) the EDS map on the left hand part of the TiB₂ surface. No segregation of Fe and Si is observed at the interface. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
analysis that TiB$_2$ is more stable than AlB$_2$ (ZrB$_2$ is thermodynamically more stable than TiB$_2$ [9]). Therefore, the only possibility left is that the segregation layer contains 2 elements: Zr and Ti, with the atomic ratio of Zr/Ti being 1:2 according to the brightness pattern in the HAADF images (Fig. 3a, 3c and 3d). Based on the above analysis, it can be concluded that the segregation layer is Ti$_2$Zr 2DC.

The atomic arrangement in the Ti$_2$Zr 2DC can therefore be constructed, as shown in Fig. 6. Fig. 6a and b shows the atomic arrangement of (0 0 0 1) TiB$_2$ plane and Ti$_2$Zr 2DC, respectively, whilst Fig. 6c and d shows the side view of the Ti$_2$Zr 2DC on the top of TiB$_2$ viewed along [1 1 -2 0]TiB$_2$ and [1 0 -1 0]TiB$_2$ directions, respectively. It is seen in Fig. 6b that, in the Ti$_2$Zr 2DC, every atomic column along direction A has the same Ti:Zr ratio (2:1), whilst there are two Ti atomic columns between the Zr ones along direction B (directions A and B are paralleled to [1 1 -2 0]TiB$_2$ and [1 0 -1 0]TiB$_2$ directions, respectively). Such atomic configuration produces the uniform and periodic Z-contrast brightness pattern as shown in Fig. 6c and d, which are consistent with those observed experimentally along these two directions (Fig. 3a, 3c and 3d). Fig. 6e presents a 3D construction of the Ti$_2$Zr 2DC on the (0 0 0 1) TiB$_2$ surface. The full coherency between Ti$_2$Zr 2DC and the Ti-terminated (0 0 0 1) TiB$_2$ surface suggest that the “lattice parameters”, i.e., the inter-atomic spacing, for the Ti$_2$Zr 2DC equals to the a-value ($a = 0.3030$ nm) of the lattice constants of TiB$_2$.

Using the QSTEM multi-slice simulation package developed by Koch [42], simulation of STEM HAADF images was performed in order to validate the established characteristics of the segregation layer. A hybrid lattice structure composing of the Ti$_2$Zr 2DC on the (0 0 0 1) TiB$_2$ surface was established according to the analysis above, as shown schematically in Fig. 6. The parameters used for the simulation were Cs = –0.1 mm, Cc = 1.4 mm, Defu–schezer convergent angle = 20 mrad, specimen thickness = 50 nm. Fig. 7 compares the simulated STEM HAADF images with the experimental ones, along both [1 1 -2 0] and [1 0 -1 0] directions of TiB$_2$. The good agreement between the simulated images and the STEM HAADF images in Fig. 7 confirmed that the segregation layer is Ti$_2$Zr 2DC with an atomic configuration as shown in Fig. 6b.

### 3.4. The nature of Ti$_2$Zr 2DC

To understand the influence of TiB$_2$ substrate with Ti$_2$Zr 2DC on heterogeneous nucleation of $\alpha$-Al, knowledge of the atomic ordering in the liquid Al adjacent to the TiB$_2$ substrate at a temperature close to the alloy liquidus is important. Therefore, ab initio MD simulations were performed for the Al(liquid)/TiB$_2$ (Ti$_2$Zr 2DC) system at 900 K, 1000 K and 1200 K, respectively. A snapshot of the system equilibrated at 1000 K viewed along the [1 0 -1 0] TiB$_2$ direction is shown in Fig. 8a. Fig. 8b shows the atomic density profiles of the liquid Al adjacent to the Al(liquid)/TiB$_2$ (Ti$_2$Zr 2DC) interface equilibrated at the three different temperatures. It is seen from Fig. 8a that the Zr atoms in the Ti$_2$Zr 2DC are protruded into the liquid Al. This protrusion of Zr atoms is quantified by the atomic density profile (Fig. 8b) where the atomic density peak for Ti$_2$Zr 2DC is separated into two sub-peaks marked as Ti and Zr. The central positions of the Zr atoms are 0.45 Å away from that of the Ti atoms, which represents 19% of Al (1 1 1) d-spacing (0.2338 nm). Therefore, it can be concluded that the Ti$_2$Zr 2DC formed on the (0 0 0 1) TiB$_2$ surface has a 19% surface roughness at atomic level. Consequently, the atomic ordering in the liquid Al adjacent to the liquid/substrate interface is significantly weakened; only two clear
peaks are shown in the atomic density profile (Fig. 8b) compared with 6 peaks with an atomically flat substrate surface [50]. Furthermore, Fig. 8b suggests that the atomically rough Ti2Zr 2DC is highly stable over a broad range of temperatures, 900–1200 K.

4. Discussion

4.1. Zr segregation on TiB2 surface

Our previous work [8] revealed that a Ti segregation layer on the (0 0 0 1) TiB2 surface in Zr-free CP-Al melts inoculated by Al-5Ti-1B grain refiner is an Al3Ti 2DC. Compared with the Ti segregation layer, the Zr segregation layer observed in this work is substantially different. The Al3Ti 2DC is situated on top of the Ti-terminated (0 0 0 1) TiB2 surface with a smaller plane spacing of 0.25 ± 0.01 nm. In contrast, the Ti2Zr 2DC forms a new terminating surface of the TiB2 particle with an enlarged atomic plane spacing of 0.34 nm compared with the Ti-layer spacing (0.32 nm) in the TiB2 structure. This larger spacing (by 0.2 Å) observed experimentally at room temperature is in qualitative agreement with the results (by 0.45 Å) obtained by ab initio MD simulations at 1000 K (Fig. 5). This larger spacing can be attributed to the larger atomic size of Zr than that of Ti and stronger chemical attraction between Zr and Al atoms compared with that between Ti and Al atoms.

Crystal structures of various binary and ternary Ti-Zr intermetallic compounds have been investigated previously, with ω-Ti2Zr intermetallic phase being particularly relevant to this work [51–54]. The experimental investigations [51–53] and first-principles DFT study [54] have confirmed that, as a metastable phase, ω-Ti2Zr phase has a hexagonal structure (AlB2 type) with the lattice parameters: a = 0.4795 nm and c = 0.3020 nm [51], which may vary slightly in different work. As shown in Fig. 9a, the unit cell of the ω-Ti2Zr phase contains one Zr atom at {0, 0, 0} position forming the (0 0 0 1) Zr plane and two Ti atoms at {1/3, 2/3, 1/2} and {2/3, 1/3, 1/2} positions forming the (0 0 0 1) Ti plane. Fig. 9b and c shows the arrangement of Zr atoms and Ti atoms in the (0 0 0 1) Zr and (0 0 0 1) Ti planes of ω-Ti2Zr phase, respectively. In fact, the structure of the Ti2Zr 2DC on the TiB2 surface based on our HRTEM observations (Fig. 6b) can be constructed by superimposition of a (0 0 0 1) Ti plane and two Ti atoms at (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2) positions forming the (0 0 0 1) Ti plane. The simulation of STEM HAADF images was carried out using the QSTEM multislice simulation package developed by Koch [42], according to the constructed super-lattice structure of Ti2Zr 2DC on the (0 0 0 1) surface of TiB2 as shown schematically in Fig. 6b, c and 6d.
TiB₂ lattice parameters. However, this discrepancy may become smaller when thermal expansion of both Ti₂Zr 2DC and TiB₂ and structural relaxation of the Ti₂Zr 2DC at the interface at the nucleation temperature are taken into full consideration. More importantly, the experimentally observed “lattice parameter” for the Ti₂Zr 2DC in this work equals to the a-value 0.3020 nm of the lattice parameters of TiB₂, because the 2DC is totally coherent with the (0 0 0 1) Ti plane of TiB₂.

Formation of the 2DC through chemical segregation in a dilute Al-Zr solution is expected to be time dependent, giving rise to the partial formation of the Ti₂Zr 2DC on the TiB₂ surface (Fig. 5). Further penetration of Zr atoms into the TiB₂ crystal structure beyond the (0 0 0 1) Ti-terminated surface is difficult due to the presence of the layer of B atoms beneath the Ti₂Zr 2DC, which have strong covalent bonds between the B atoms and the Ti atoms below them. This means that the formation of both bulk (3D) ZrB₂ and (ZrₓTi₁₋ₓ)B₂ are kinetically unfavourable even if they are thermodynamically feasible as suggested in the literature \[9,55,56\].

4.2. Effect of impurities (Fe and Si) on poisoning

Spittle and Sadli [17] suggested the possible involvement of Fe and Si in delivering the poisoning effect of Zr. However, the main impurities Fe and Si in the CP-Al used in this study does not show any evidence of their segregation on the (0 0 0 1) TiB₂ surface (Figs. 4 and 5). In fact, Fe segregation was observed on the (1 0 -1 0) prismatic planes of TiB₂, although Si segregation was not observed on either basal or prismatic surfaces of TiB₂ particles. Fig. 10 is an example of STEM/EDS analysis across the Al/(1 0 -1 0)TiB₂ interface, showing Fe segregation, but no segregation of Zr and Si. As the heterogeneous nucleation of α-Al takes place only on (0 0 0 1) basal plane surface [8,57], any involvement of Fe or Si in Zr poisoning can be ruled out.

Based on crystallographic matching, Qiu et al. [19] proposed a mechanism of Zr poisoning, in which the formation of Al₈Fe₄Zr intermetallic coating on the surface of Al₃Ti particles was responsible for Zr poisoning by decreasing the potency of the Al₃Ti substrate. However, it is well documented in the literature that, in commercial Al-5Ti-1B grain refiner, Al₃Ti is not the nucleant particle responsible for grain refinement of Al-alloys since Al₃Ti dissolves quickly when the grain refiner is added to Al melts with a low concentration of Ti (see reviews in Refs. [4,5]).

4.3. Mechanism for Zr poisoning

In our previous work [8], we have demonstrated that TiB₂ particles with a clean surface (no elemental segregation) are not potent for heterogeneous nucleation of α-Al and that the formation of the Al₃Ti 2DC on (0 0 0 1) TiB₂ surface is responsible for the enhanced heterogeneous nucleation, leading to significant grain refinement. Enhanced heterogeneous nucleation and thus effective grain refinement can only be achieved by those TiB₂ particles with the Al₃Ti 2DC on their (0 0 0 1) TiB₂ surface. The production process for commercial Al-Ti-B grain refiners is characterized by high concentration of Ti, high temperature and long reaction time [4,5].
which ensures that the TiB₂ particles are fully coated with the Al₃Ti 2DC. From a lattice matching point of view, the formation of such Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface results in a significant reduction of the absolute lattice misfit with α-Al from 4.22% for the TiB₂ without the segregation layer to 0.09% for the TiB₂ with the segregation layer. Consequently, this makes the TiB₂ particles in commercial Al-Ti-B based grain refiners extremely potent for heterogeneous nucleation and thus effective for grain refinement of Al-alloys.

However, the Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface becomes thermodynamically unstable in the presence of Zr in the Al melt, since Al₃Zr has lower free energy of formation than Al₃Ti [58]. In Zr-containing Al-alloy melts, Al₃Ti 2DC dissolves quickly, making the TiB₂ particle on the (0 0 0 1) TiB₂ surface results in a significant ordering in the liquid adjacent to the liquid/substrate interface, which can be taken as a precursor for the subsequent heterogeneous nucleation [50]. Such atomic ordering can be either enhanced by decreasing the lattice misfit between the substrate and the solid [50] and/or increasing the attractive chemical interaction (measured by the heat of mixing) between the substrate and the liquid [60], or impeded by an atomically rough surface of the substrate [59]. Based on the understandings, Zr poisoning can be attributed to the impeding of pre-nucleation on the TiB₂ particles. The formation of the Ti₂Zr 2DC on the (0 0 0 1) TiB₂ surface to replace the original Al₃Ti 2DC results in not only an increase in lattice misfit from 0.09% to 4.22%, but also the roughening of the (0 0 1) TiB₂ surface, both of which impede prenucleation and lead to poisoning of the originally potent TiB₂ particles for heterogeneous nucleation.

Therefore, the mechanism for Zr poisoning can be summed up as dissolution of the Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface in the commercial TiB₂ based grain refiners and the formation of the Ti₂Zr 2DC in the Al-Zr melt, which renders TiB₂ particles impotent for heterogeneous nucleation of α-Al. This mechanism for Zr poisoning is consistent with the our experimental observations in this work: (i) the absence of the well-defined OR between TiB₂ and α-Al: (0 0 0 1)[1 1 - 2 0] TiB₂/[0 - 1 1] Al, when Zr is present in Al melt; (ii) only a ppm level of Zr is required even if the Ti₂Zr 2DC is formed on the entire TiB₂ surface; and (iii) Zr poisoning is time dependent [9,31] and the partial formation of Ti₂Zr 2DC on (0 0 0 1) TiB₂ surface (Fig. 5) due to its slow kinetics of formation in a dilute Al-Zr liquid solution.

The mechanism is consistent with the experimental observations present in this work (Figs. 2 and 5) and in the previous studies in the literature [e.g., 9, 29–31]. Thermodynamically, a ppm level of Zr addition is sufficient for the formation of the Ti₂Zr 2DC layer on the basal surface of all the added TiB₂ particles. Kinetically, the dissolution of the pre-existing Al₃Ti 2DC layer and the formation of the Ti₂Zr 2DC layer will take time to complete, depending upon the temperature and Zr concentration of the melt. It is not expected

![Fig. 10. (a) STEM HAADF image of Al/(1 0 -1 0)TiB₂ interface and (b–d) STEM SuperX-EDS elemental mapping (from the marked area) of (b) Zr, (c) Fe and (d) Si across the interface, showing Fe segregation but no Zr or Si segregation at the interface between Al and the prismatic surface of TiB₂.](image)
that all the TiB₂ particles are completely poisoned in a limited period of time. It has been shown in the previous study that the Zr poisoning effect is still increasing with the melt being held at 800 °C for over 6 h [31]. Indeed, our experimental observation shown in Fig. 5 provides the evidence that not all the surface of TiB₂ particles have been covered by TiZr₂DC layer. It is understandable that a higher concentration of Zr promotes the poisoning, as shown in Fig. 2.

When the addition level of Zr is more than the peritectic composition (0.11%), Al₃Zr particles can possibly act as heterogeneous nucleation sites for α-Al, and may potentially result in grain refinement [25,30]. In this work, apart from oxides, poisoned TiB₂ and Al₃Zr particles co-exist in the melt with higher Zr contents (>0.11%). In such cases there is an inevitable competition for nucleation between those particles. The lattice misfit with α-Al is 1.34% for Al₃Zr, 3.4% for γ-Al₂O₃ and −4.2% for TiB₂. Although Al₃Zr has the highest potency among these particles, it would not lead to grain refinement due to the large particle size (5–115 μm in diameter [30]) and thus low particle number density. In cases of Zr poisoning, γ-Al₂O₃ particles are more likely to be responsible for the grain size observed.

4.4. Nucleation control by elemental segregation at the liquid/substrate interface

The epitaxial nucleation model [61] suggests that heterogeneous nucleation precedes layer-by-layer through a structural templating mechanism. It predicts that the nucleation undercooling increases with increasing lattice mismatch between the solid and the substrate. This means that heterogeneous nucleation can be controlled by manipulation of the liquid/substrate interface through chemical segregation of the alloying or impurity elements at the interface to either enhance or impede the structural templating. In our previous work, we have demonstrated that segregation of Ti atoms at the interface between the liquid and TiB₂ substrate leads to the formation of Al₃Ti₂DC on the (0 0 0 1) TiB₂ surface, resulting in a substantial reduction of lattice misfit from 4.22% to 0.09%. This makes the TiB₂ particles in the commercial Al-Ti-B grain refiners extremely potent for heterogeneous nucleation of α-Al. In this work, we have demonstrated that segregation of Zr at the liquid/TiB₂ interface leads to the dissolution of the Al₃Ti₂DC on the (0 0 0 1) TiB₂ surface and the formation of the Ti₃Zr₂DC as the new terminating surface of TiB₂, which in turn leads to a significant increase in lattice misfit from the original 0.09% for the TiB₂ particle in the grain refiner to 4.22% for the TiB₂ particle in Al-Zr alloys. Consequently, segregation of Zr atoms onto the TiB₂ surface renders the TiB₂ particles in the Al-Zr melt impotent for heterogeneous nucleation of α-Al, i.e., poisoning the TiB₂ particle by Zr.

In addition, the epitaxial nucleation model [61] predicts that particles with the highest potency will nucleate first since they require the lowest nucleation undercooling. This forms a general rule governing the competition for heterogeneous nucleation between co-existing particles of different potencies in the melt. In Al-alloys, for instance, there are always different types of in situ oxide particles in competition for heterogeneous nucleation with the ex situ TiB₂ particles from the grain refiner. Most of the oxides in Al-alloys have relatively high potency (small lattice misfit) for heterogeneous nucleation of α-Al and they are more potent than TiB₂ particles with a clean basal surface (no chemical segregation). Formation of the Al₃Ti₂DC on the (0 0 0 1) TiB₂ surface makes the TiB₂ particles in the Al-Ti-B grain refiner outperform all the in situ oxide particles and dominate the nucleation process. However, the formation of the Ti₃Zr₂DC on the TiB₂ surface makes the TiB₂ particles less potent than most of the oxide particles. It is likely that no TiB₂ particles from the Al-Ti-B grain refiner have a chance to participate in the nucleation process in the fully poisoned case.

5. Conclusions

In this work we investigated the mechanism for Zr poisoning through extensive examinations of the Al/TiB₂ interface using advanced electron microscopy and ab initio molecular dynamics (MD) simulations. We have confirmed that commercial Al-STi-1B grain refiner does not have the ability to refine Al-alloys when a small amount (a few hundred ppm) of Zr is present in the Al melt, resulting in a coarse and fully columnar grain structure after solidification. The well-defined orientation relationship between TiB₂ and Al: [0 0 0 1] // [1 1 - 2 0] TiB₂/(1 1 1) [0 -1 1] Al, was not observed after Zr addition, which indicates a reduced nucleation potency of TiB₂ particles in the Zr-containing Al melt.

The state-of-the-art electron microscopy and ab initio MD simulations were performed to investigate the mechanism for Zr poisoning. We found that the presence of Zr in Al melts leads to (i) the dissolution of the Al₃Ti₂DC (2-dimensional compound) on the (0 0 0 1) TiB₂ surface during the grain refiner production process; and (ii) the formation of an atomic monolayer of Ti₃Zr₂ (Ti₃Zr₂DC) on the (0 0 0 1) TiB₂ surface, which replaces the original Ti-terminated TiB₂ surface. This results in a significant increase in lattice misfit from the original 0.09% (between γ-Al and TiB₂ with Al₃Ti₂DC) to 4.22% (between α-Al and TiB₂ with Ti₃Zr₂DC), rendering TiB₂ particles in Al-Zr melts impotent for heterogeneous nucleation of α-Al.

Ab initio MD simulations have confirmed that the Ti₃Zr₂DC formed on the (0 0 0 1) TiB₂ surface is atomically rough. This atomic roughness can be attributed to the fact that Zr atoms have a larger atomic size and a stronger attractive chemical interaction with liquid Al in comparison with Ti atoms in the Ti₃Zr₂DC. According to the recent MD simulation results [59], this atomically rough surface weakens atomic ordering in the liquid adjacent to the liquid/substrate interface and consequently hinders heterogeneous nucleation.

The mechanism for Zr poisoning can, therefore, be summed up as dissolution of the Al₃Ti₂DC on the (0 0 0 1) TiB₂ surface in the commercial Al-Ti-B-based grain refiner and the formation of the Ti₃Zr₂DC on TiB₂ basal surface in the Al-Zr melt, which renders TiB₂ particles impotent for heterogeneous nucleation of α-Al due to the increased lattice misfit and surface roughness at atomic level.

In addition, we have found that there is no segregation of Fe or Si at the basal surface of TiB₂, although Fe was found to segregate on the (1 0 -1 0) TiB₂ prismatic surface. This confirms that neither Fe nor Si (as impurity elements) played any role in Zr poisoning of TiB₂ particles in the Zr-containing Al melt.

Furthermore, this work, in combination of our previous work [8], demonstrates that heterogeneous nucleation can be effectively manipulated, either enhanced or impeded, by chemical segregation of selected alloying/impurity elements at the liquid/substrate interface.

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