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Mechanism for Zr Poisoning of Al-Ti-B Based Grain Refiners

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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 refiner production 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.

Keywords: Heterogeneous nucleation; Grain refinement; Aluminium alloys; Zirconium poisoning.

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%), Al₃Zr 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 [5, 25].

However, Zr-containing Al-alloys are usually difficult to grain refine using the Al-Ti-B grain refiners. Jones and Pearson [9] observed that it was not possible for the grain size of an Al-5Zn-1.5Mg-0.2Zr 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 minutes, and a considerably larger grain size was observed in samples with prolonged holding time [9]. Birch and Fishers [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 Ahmady *et al.* [11] and Kearns and Cooper [12] in 7050 Al-alloy containing 0.10-0.13% Zr. Results of Birch and Cowell [13] and Abdel-Hamid [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 [16].

Impurities were found to affect Zr poisoning. Spittle and Sadli [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 [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.* [19] proposed a co-poisoning mechanism by Zr and Ti when a certain amount of Fe impurity was present in terms of crystallographic analysis. Johnsson [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 aluminide phase, (Ti_{1-x}Zr_x)Al₃. It was speculated that the formation of the ternary aluminide 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 [9] attributed the poisoning effect of Zr to the formation of ZrB₂ coatings on the TiB₂ surface, because ZrB₂ is thermodynamically more stable than TiB₂. They believed that ZrB₂ coatings prevent TiB₂ from acting as a nucleating site for the α-Al due to its larger lattice parameters than TiB₂, although no evidence of the formation of ZrB₂ was presented. Trying to explain the poisoning effect of Zr and Cr, Abdel-Hamid [14] proposed that some of the Ti atoms in Al₃Ti and TiB₂ 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 [5, 21, 22] shared this point of view in their explanation of the poisoning effect of Cr and

1 Zr. The mechanism involving the formation of ternary aluminides was also supported by Johnsson
2 [20] who suggested that the poisoning effect of Zr was associated with the reduced potency of Al₃Ti
3 through the formation of (Ti_{1-x}Zr_x)Al₃. Bunn *et al.* [31] observed the presence of Zr in Al₃Ti and
4 attributed the poisoning effect to the modification of both Al₃Ti and TiB₂ by Zr. In addition, the
5 formation of (Ti_{1-x}Zr_x)Al₃ would reduce the Ti concentration in the melt and thus the growth
6 restriction, which is also believed to be an important factor for grain refinement. However, Bunn *et al.*
7 [31] realized that reduction in growth restriction arising from reduced solute concentrations in
8 the melt was not the dominant factor in Zr poisoning and that the poisoning was mainly attributed to
9 the interaction between Zr and the nucleating substrates. Another explanation for the poisoning
10 effect of Zr and Cr was proposed by Jones in his hyper-nucleation theory [32], which involves the
11 atomic size mismatch between Zr or Cr and the solvent Al.

12
13 Although the exact mechanism for the poisoning effect is so far unclear, it is generally accepted that
14 poisoning is mainly due to the interaction of these alloying elements, Zr, Cr, Si and Li, with the
15 nucleating particles, such as Al₃Ti and TiB₂ [9, 14, 31, 33]. It is anticipated that such interaction
16 may give rise to the formation of complex aluminides, borides and silicides, which have a poor
17 potency for nucleating α -Al grains, on the surface of nucleating particles.

18
19 The loss of nucleation potency through poisoning is known to be time dependent; i.e., grain size
20 increases with holding time after addition of grain refiner. Experimental work [9, 31] showed that
21 the poisoning effect increases with holding time after the addition of Zr, being consistent with
22 progressive substitution of Ti atoms with Zr atoms. In general, loss of nucleation potency by
23 poisoning is non-recoverable, unlike gravity-induced fading (i.e., settling of nucleant particles),
24 which can be recovered by stirring the melt prior to casting.

25
26 Zr is an important trace alloying element in some 2xxx and 7xxx series Al-alloys due to its
27 contribution to dispersion strengthening and impedance of dynamic recrystallization. For example,
28 typical 7xxx series alloys contain about 0.12% Zr for dispersion strengthening. Problems can be
29 encountered during direct chill (DC) casting of such alloys, where the performance of Al-Ti-B grain
30 refiner is significantly reduced due to the Zr poisoning effect. Considerable work has been carried
31 out to reduce or eliminate such poisoning. Increasing the addition level of Al-5Ti-1B master alloy
32 has been shown to be a way to improve the grain refining response [9, 33], although the
33 accumulation of non-active TiB₂ particles in the alloy causes serious concern. Another approach to
34 overcome the problem is to use alternative grain refiners, such as Al-Ti-C based master alloys [34-
35 38]. As a promising grain refiner, Al-Ti-C master alloy has been reported to be resistant to Zr
36 poisoning to a certain extent, although there are some controversies between different investigators
37 [38]. In a 7xxx Al-alloy containing 0.06% Zr, addition of Al-3Ti-0.15C master alloy has been
38 shown to result in a very fine grain structure without twin columnar growth [34]. Schneider *et al.*
39 [35] also found that the grain refining effect of Al-5Ti-0.25C grain refiner was better than that of Al-
40 5Ti-0.2B in a Zr-containing 7050 alloy at the same addition level. However, experimental study [37]
41 has demonstrated that Al-Ti-C master alloy may be poisoned in the presence of Zr. The grain
42 refining ability of Al-5Ti-0.4C master alloy (0.2% addition) was reported to diminish when 0.12%
43 Zr was added to the melt [38]. It was suggested that Zr interacted with both TiAl₃ and TiC phases.

44
45 In the present work, extensive electron microscopy has been carried out focusing on the Al/TiB₂
46 interface, in order to reveal any possible modification caused by interaction between Zr and TiB₂ at
47 the interface. An *ab initio* molecule dynamics method is employed to simulate the structure and
48 stability of the segregation layer at the interface at temperature above the liquidus of Al in
49 accordance with the experimental observation. Mechanism underlying Zr poisoning is discussed in
50 the context of Zr segregation at the Al(liquid)/TiB₂ interface and its consequence on the potency of
51 TiB₂ 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. TiB₂ 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 hours 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 of the TP-1 sample. 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 field (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

1 generation) at the SuperSTEM Centre (Daresbury, UK). This microscope was equipped with a field
2 emission gun operated at 100 kV, and a Nion spherical aberration (Cs) corrector and electron
3 energy loss spectroscopy (EELS) system. Super-X EDS mapping and atomic resolution EELS
4 mapping were conducted to obtain compositional profiles across Al/TiB₂ interface.

5 Simulation of STEM-HAADF images was conducted using the QSTEM multislice simulation
6 package developed by Koch [42], and the simulated results were compared to the STEM HAADF
7 images obtained experimentally using Cs-corrected high resolution STEM.
8

9 **2.4 *Ab initio* molecular dynamics simulations**

10 *Ab initio* molecular dynamics (MD) simulations were carried out using the code VASP (Vienna *ab*
11 *initio* Simulation Package) [43, 44], which employs the *ab initio* density functional theory (DFT)
12 within the projector-augmented wave (PAW) framework [45, 46]. The exchange and correlation
13 terms were described using the generalized gradient approximation (GGA-PBE) [47]. A cut off
14 energy of 320 eV and only Γ -point in the BZ [48] were used. The liquid Al was generated by
15 equilibrating for about 10 picoseconds (ps) at 3000 K, followed by cooling down to and equilibrated
16 at a designated temperature for 10ps. The liquid Al obtained in this way was brought in contact with
17 the TiB₂ substrate and then equilibrated at the same temperature for 10ps to ensure equilibrium. The
18 time-averaged method was employed to take samples with over several ps (2000 to 3000 steps,
19 1.5fs/step) to satisfy the statistics. The substrate and liquid atoms were fully relaxed during the
20 simulations.
21

22 **3. Results**

23 **3.1 Confirmation of Zr poisoning**

24 Prior to investigation of the poisoning mechanism, it is important to confirm the Zr poisoning effect
25 through designed solidification experiments. Figs. 1a and 1d show the macrostructure of CP-Al
26 solidified under TP-1 conditions. Both the transverse and longitudinal sections show a coarse
27 columnar grain structure. Addition of 0.1% commercial Al-5Ti-1B grain refiner to the CP-Al melt
28 resulted in a fine and fully equiaxed grain structure (Figs. 1b and 1e), with the average grain size
29 being 175±25 μm . This suggests that the commercial Al-5Ti-1B grain refiner used in this
30 experiment is effective for grain refinement of CP-Al. However, the macrostructure of Al-0.058Zr
31 alloy inoculated with 0.1% Al-5Ti-1B grain refiner has a coarse columnar grain structure (Figs. 1c
32 and 1f). This indicates that the effectiveness of the grain refiner was reduced dramatically due to the
33 presence of 580 ppm Zr in the melt, confirming the poisoning effect of Zr. With further increase of
34 Zr concentration up to 0.45%, the macrostructures of Al-Zr alloys inoculated with 0.1% Al-5Ti-1B
35 grain refiner remain coarse and columnar, and the width of the columnar grains increases with
36 increasing Zr concentration (Fig. 2). This suggests that the effect of Zr poisoning increases with
37 increasing Zr concentration.
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39 **3.2 Segregation of Zr atoms on TiB₂ surface in dilute Al-Zr alloys**

40 The reference point for our investigation is the TiB₂ particles brought into the Al melt by the
41 commercial Al-5Ti-1B grain refiner. It was confirmed in our previous work [8] that the TiB₂
42 particles in such grain refiner are extremely potent for heterogeneous nucleation of α -Al due to the
43 presence of Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface. High temperature, high concentration of Ti and
44 prolonged reaction time in the fabrication processing of the grain refiner ensures the formation of
45 the Al₃Ti 2DC. A well-defined orientation relationship (OR): (0 0 0 1)[1 1 -2 0] TiB₂// (1 1 1) [0 -1
46 1] Al was observed readily in the CP-Al sample inoculated by the Al-5Ti-1B grain refiner.
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1 In order to examine any possible modification of the TiB_2 surface due to the presence of Zr in the
2 alloy melt, TiB_2 particles in the Al-Zr alloy were collected and examined in detail by SEM and
3 TEM/STEM, focusing on their faceted surfaces. It was confirmed that the terminating facets of the
4 TiB_2 particles are $\{0\ 0\ 0\ 1\}$ basal and $\{1\ 0\ -1\ 0\}$ prismatic planes. Their average size is 0.2~3.2 μm
5 in diameter, which is the typical size range observed in a commercial Al-5Ti-1B grain refiner [49].
6 No obvious change in size and morphology was observed before and after the Zr addition by SEM
7 examination. However, TEM/STEM examination has revealed several interesting facts: (i) the well-
8 defined OR between TiB_2 and Al was not observed in the Al-Zr alloy inoculated by Al-5Ti-1B
9 refiner, although as many as 100 TiB_2 particles in total were examined in multiple thin foil TEM
10 specimens; (ii) the original Al_3Ti 2DC was not observed on $(0\ 0\ 0\ 1)$ TiB_2 surface; and (3) the
11 original Ti-terminated $(0\ 0\ 0\ 1)$ TiB_2 surface is replaced by a new segregation layer.
12

13 Atomic scale examination of this new segregation layer (STEM HAADF images in Fig. 3) reveals
14 that it is an atomic monolayer of chemical segregation on the $(0\ 0\ 0\ 1)$ TiB_2 surface, as evidenced
15 by the atomic columns having a brighter contrast than that of the Ti columns in TiB_2 when the TiB_2
16 is viewed along both $[1\ 1\ -2\ 0]$ (Fig. 3a) and $[1\ 0\ -1\ 0]$ (Fig. 3c) directions. The α -Al is oriented
17 away from any low index zone direction in both Figs. 3a and 3c, suggesting that this particular TiB_2
18 particle did not participate in grain initiation during solidification. The higher brightness of atom
19 columns in the segregation layer indicates that heavier (than Ti) atoms exist in these columns (large
20 green spheres represent heavier atom X in Figs. 3b and 3e). Particularly, on tilting the specimen by
21 30° from $[1\ 1\ -2\ 0]$ to $[1\ 0\ -1\ 0]$ TiB_2 , the brightness of the segregation layer is no longer uniform as
22 shown more clearly by the SuperSTEM HAADF image in Fig. 3d. Instead, it has a periodic
23 variation with two darker atomic columns between the two brighter atomic columns as illustrated
24 schematically in Fig. 3e. The periodic variation in brightness in the HAADF image indicates that
25 there are at least two types of atoms in the segregation layer, with their arrangement being ordered
26 in 2D. In addition, experimental measurement shows that the spacing between the segregation layer
27 and its closest Ti layer in TiB_2 was slightly larger than the spacing between two Ti layers in TiB_2 ,
28 i.e., 0.34 ± 0.01 nm compared with 0.32 nm. These results suggest that the surface segregation layer
29 is an ordered 2DC, in which the atoms are arranged in a hexagonal configuration, following that of
30 Ti atoms in the $(0\ 0\ 0\ 1)$ TiB_2 terminating plane.
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36 High resolution Super-X EDS analysis using aberration (Cs)-corrected STEM instrument was
37 performed to identify the chemical nature of the segregation layer on the TiB_2 surface. An example
38 of such analysis is given in Fig. 4. The elemental mapping across the Al/ TiB_2 interface shows the
39 segregation of Zr atoms (Fig. 4b) at the interface, corresponding to the brighter contrast of the
40 segregation layer in the HAADF image (Fig. 4a). No Zr segregation was observed on $\{1\ 0\ -1\ 0\}$
41 prismatic planes of the TiB_2 particles in this work, suggesting that segregation of Zr atoms is
42 selective, depending on atomic configuration of the terminating surfaces of TiB_2 . In addition, the
43 presence of Al and Ti atoms in the segregation layer cannot be conclusive due to the existence of Al
44 in the Al matrix and Ti in the TiB_2 substrate (Figs. 4c and 4d). Furthermore, particular attention was
45 paid to the potential segregation of the main impurity elements in the alloy, such as Fe and Si. The
46 EDS mapping results in Figs. 4e and 4f do not suggest any existence of either Fe or Si in the
47 segregation layer.
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52 Intuitively, one would not expect that the basal surface of all the TiB_2 particles to be entirely
53 covered by the Zr-containing segregation layer. Indeed, it was occasionally found that some of TiB_2
54 particles were covered only partially by the segregation layer on their $(0\ 0\ 0\ 1)$ surface. For instance,
55 Fig. 5 shows that Zr segregation occurs on the left hand side of the $(0\ 0\ 0\ 1)$ TiB_2 surface, confirmed
56 by the specific periodic pattern of brightness in the HAADF image in Fig. 5a and the corresponding
57 Zr elemental map from Super-X EDS analysis in Fig. 5b. Again Figs. 5c and 5d show no existence
58 of Fe or Si in the segregation layer.
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3.3 Chemistry and structure of Zr segregation layer

1 From the above experimental findings by the direct STEM observation and EDS analysis (Figs. 3-5),
2 the segregation layer has the following unique characteristics: (i) it is an atomic monolayer; (ii) it is
3 a 2-dimensional compound (2DC) in which the atoms have a hexagonal arrangement; and (iii) it
4 contains Zr and one or more other elements. Based on the compositions of CP-Al and the master
5 alloys used in this work (Table 1), other possible elements in the segregation layer may include Ti,
6 Al, Fe and Si. However, Fe and Si are ruled out by the EDS results (Figs. 4 and 5). The possibility
7 of Al can also be eliminated by the fact that Al atoms do not substitute Ti atoms in the Ti-terminated
8 (0 0 0 1) TiB₂ surface as presented in our previous work [8], and this is consistent with the
9 thermodynamic analysis that TiB₂ is more stable than AlB₂ (ZrB₂ is thermodynamically more stable
10 than TiB₂ [9]). Therefore, the only possibility left is that the segregation layer contains 2 elements:
11 Zr and Ti, with the atomic ratio of Zr/Ti being 1:2 according to the brightness pattern in the
12 HAADF images (Figs. 3a, 3c and 3d). Based on the above analysis, it can be concluded that the
13 segregation layer is Ti₂Zr 2DC.
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18 The atomic arrangement in the Ti₂Zr 2DC can therefore be constructed, as shown in Fig. 6. Figs. 6a
19 and 6b show the atomic arrangement of (0 0 0 1) TiB₂ plane and Ti₂Zr 2DC, respectively, whilst
20 Figs. 6c and 6d show the side view of the Ti₂Zr 2DC on the top of TiB₂ viewed along [1 1 -2 0]TiB₂
21 and [1 0 -1 0]TiB₂ directions, respectively. It is seen in Fig. 6b that, in the Ti₂Zr 2DC, every atomic
22 column along direction A has the same Ti:Zr ratio (2:1), whilst there are two Ti atomic columns
23 between the Zr ones along direction B (directions A and B are paralleled to [1 1 -2 0]TiB₂ and [1 0 -
24 1 0]TiB₂ directions, respectively). Such atomic configuration produces the uniform and periodic Z-
25 contrast brightness pattern as shown in Figs. 6c and 6d, which are consistent with those observed
26 experimentally along these two directions (Figs. 3a, 3c and 3d). Fig. 6e presents a 3D construction
27 of the Ti₂Zr 2DC on the (0 0 0 1) TiB₂ surface. The full coherency between Ti₂Zr 2DC and the Ti-
28 terminated (0 0 0 1) TiB₂ surface suggest that the “lattice parameters”, i.e., the inter-atomic spacing,
29 for the Ti₂Zr 2DC equals to the a-value (a = 0.3030 nm) of the lattice constants of TiB₂.
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34 Using the QSTEM multi-slice simulation package developed by Koch [42], simulation of STEM
35 HAADF images was performed in order to validate the established characteristics of the segregation
36 layer. A hybrid lattice structure composing of the Ti₂Zr 2DC on the (0 0 0 1) TiB₂ surface was
37 established according to the analysis above, as shown schematically in Fig. 6. The parameters used
38 for the simulation were Cs = -0.1 mm, Cc = 1.4 mm, Defocus-convergent angle = 20 mrad,
39 specimen thickness = 50 nm. Fig. 7 compares the simulated STEM HAADF images with the
40 experimental ones, along both [1 1 -2 0] and [1 0 -1 0] directions of TiB₂. The good agreement
41 between the simulated images and the STEM HAADF images in Fig. 7 confirmed that the
42 segregation layer is Ti₂Zr 2DC with an atomic configuration as shown in Fig. 6b.
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3.4 The nature of Ti₂Zr 2DC

46 To understand the influence of TiB₂ substrate with Ti₂Zr 2DC on heterogeneous nucleation of α-Al,
47 knowledge of the atomic ordering in the liquid Al adjacent to the TiB₂ substrate at a temperature
48 close to the alloy liquidus is important. Therefore, *ab initio* MD simulations were performed for the
49 Al(liquid)/TiB₂ (Ti₂Zr 2DC) system at 900 K, 1000 K and 1200 K, respectively. A snapshot of the
50 system equilibrated at 1000 K viewed along the [1 0 -1 0] TiB₂ direction is shown in Fig. 8a. Fig. 8b
51 shows the atomic density profiles of the liquid Al adjacent to the Al(liquid)/TiB₂ (Ti₂Zr 2DC)
52 interface equilibrated at the three different temperatures. It is seen from Fig. 8a that the Zr atoms in
53 the Ti₂Zr 2DC are protruded into the liquid Al. This protrusion of Zr atoms is quantified by the
54 atomic density profile (Fig. 8b) where the atomic density peak for Ti₂Zr 2DC is separated into two
55 sub-peaks marked as Ti and Zr. The central positions of the Zr atoms are 0.45 Å away from that of
56 the Ti atoms, which represents 19% of Al (1 1 1) d-spacing (0.2338 nm). Therefore, it can be
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1 concluded that the Ti_2Zr 2DC formed on the (0 0 0 1) TiB_2 surface has a 19% surface roughness at
2 atomic level. Consequently, the atomic ordering in the liquid Al adjacent to the liquid/substrate
3 interface is significantly weakened; only two clear peaks are shown in the atomic density profile
4 (Fig. 8b) compared with 6 peaks with an atomically flat substrate surface [50]. Furthermore, Fig. 8b
5 suggests that the atomically rough Ti_2Zr 2DC is highly stable over a broad range of temperatures,
6 900~1200 K.

7 4. Discussion

8 4.1 Zr segregation on TiB_2 surface

9 Our previous work [8] revealed that a Ti segregation layer on the (0 0 0 1) TiB_2 surface in Zr-free
10 CP-Al melts inoculated by Al-5Ti-1B grain refiner is an Al_3Ti 2DC. Compared with the Ti
11 segregation layer, the Zr segregation layer observed in this work is substantially different. The Al_3Ti
12 2DC is situated on top of the Ti-terminated (0 0 0 1) TiB_2 surface with a smaller plane spacing of
13 0.25 ± 0.01 nm. In contrast, the Ti_2Zr 2DC forms a new terminating surface of the TiB_2 particle with
14 an enlarged atomic plane spacing of 0.34 nm compared with the Ti-layer spacing (0.32 nm) in the
15 TiB_2 structure. This larger spacing (by 0.2 Å) observed experimentally at room temperature is in
16 qualitative agreement with the results (by 0.45 Å) obtained by *ab initio* MD simulations at 1000 K
17 (Fig. 8). This larger spacing can be attributed to the larger atomic size of Zr than that of Ti and
18 stronger chemical attraction between Zr and Al atoms compared with that between Ti and Al atoms.
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20 Crystal structures of various binary and ternary Ti-Zr intermetallic compounds have been
21 investigated previously, with ω - Ti_2Zr intermetallic phase being particularly relevant to this work
22 [51-54]. The experimental investigations [51-53] and first-principles DFT study [54] have confirmed
23 that, as a metastable phase, ω - Ti_2Zr phase has a hexagonal structure (AlB_2 type) with the lattice
24 parameters: $a=0.4795$ nm and $c=0.3020$ nm [51], which may vary slightly in different work. As
25 shown in Fig. 9a, the unit cell of the ω - Ti_2Zr phase contains one Zr atom at $\{0, 0, 0\}$ position
26 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
27 forming the (0 0 0 1) Ti plane. Figs. 9b and 9c show the arrangement of Zr atoms and Ti atoms in
28 the (0 0 0 1) Zr and (0 0 0 1) Ti planes of ω - Ti_2Zr phase, respectively. In fact, the structure of the
29 Ti_2Zr 2DC on the TiB_2 surface based on our HRTEM observations (Fig. 6b) can be constructed by
30 superimposition of a (0 0 0 1) Ti plane and its neighbouring (0 0 0 1) Zr plane to form a 2D
31 superstructure, as schematically shown in Fig. 9d. The superimposition of the two atomic layers is
32 feasible because neither Zr nor Ti atoms in ω - Ti_2Zr phase are closely packed in their respective
33 crystal planes. It should be pointed out that the Ti_2Zr 2DC does not necessarily need to be an actual
34 plane of the 3D (bulk) ω - Ti_2Zr phase. The “lattice parameter” of the Ti_2Zr 2DC structure constructed
35 according to the ω - Ti_2Zr phase is $a = 0.277$ nm at room temperature [51], which is smaller than the
36 a -value 0.3020 nm of TiB_2 lattice parameters. However, this discrepancy may become smaller when
37 thermal expansion of both Ti_2Zr 2DC and TiB_2 and structural relaxation of the Ti_2Zr 2DC at the
38 interface at the nucleation temperature are taken into full consideration. More importantly, the
39 experimentally observed “lattice parameter” for the Ti_2Zr 2DC in this work equals to the a -value
40 0.3020 nm of the lattice parameters of TiB_2 , because the 2DC is totally coherent with the (0 0 0 1) Ti
41 plane of TiB_2 .
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53 Formation of the 2DC through chemical segregation in a dilute Al-Zr solution is expected to be time
54 dependent, giving rise to the partial formation of the Ti_2Zr 2DC on the TiB_2 surface (Fig. 5). Further
55 penetration of Zr atoms into the TiB_2 crystal structure beyond the (0 0 0 1) Ti-terminated surface is
56 difficult due to the presence of the layer of B atoms beneath the Ti_2Zr 2DC, which have strong
57 covalent bonds between the B atoms and the Ti atoms below them. This means that the formation of
58 both bulk (3D) ZrB_2 and $(\text{Zr}_x\text{Ti}_{1-x})\text{B}_2$ are kinetically unfavourable even if they are
59 thermodynamically feasible as suggested in the literature [9, 55, 56].
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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) TiB_2 surface (Figs.4 and 5). In fact, Fe segregation was observed on {1 0 -1 0} prismatic planes of TiB_2 , although Si segregation was not observed on either basal or prismatic surfaces of TiB_2 particles. Fig. 10 is an example of STEM/EDS analysis across the Al/(1 0 -1 0) TiB_2 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 $\text{Al}_8\text{Fe}_4\text{Zr}$ intermetallic coating on the surface of Al_3Ti particles was responsible for Zr poisoning by decreasing the potency of the Al_3Ti substrate. However, it is well documented in the literature that, in commercial Al-5Ti-1B grain refiner, Al_3Ti is not the nucleant particle responsible for grain refinement of Al-alloys since Al_3Ti 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 TiB_2 particles with a clean surface (no elemental segregation) are not potent for heterogeneous nucleation of α -Al and that the formation of the Al_3Ti 2DC on (0 0 0 1) TiB_2 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 TiB_2 particles with the Al_3Ti 2DC on their (0 0 0 1) TiB_2 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 TiB_2 particles are fully coated with the Al_3Ti 2DC. From a lattice matching point of view, the formation of such Al_3Ti 2DC on the (0 0 0 1) TiB_2 surface results in a significant reduction of the absolute lattice misfit with α -Al from 4.22% for the TiB_2 without the segregation layer to 0.09% for the TiB_2 with the segregation layer. Consequently, this makes the TiB_2 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 Al_3Ti 2DC on the (0 0 0 1) TiB_2 surface becomes thermodynamically unstable in the presence of Zr in the Al melt, since Al_3Zr has lower free energy of formation than Al_3Ti [58]. In Zr-containing Al-alloy melts, Al_3Ti 2DC dissolves quickly, making the Ti-terminated TiB_2 surface exposed directly to the Zr-containing Al melt. Due to the higher thermodynamic stability of ZrB_2 than that of TiB_2 [9, 55], Zr atoms from the liquid will substitute gradually for some of the Ti atoms in the exposed (0 0 0 1) TiB_2 surface. The substitution process of Zr for Ti atoms on the terminating surface of TiB_2 continues until an ordered Ti_2Zr 2DC structure is established, provided that there are sufficient Zr atoms in the melt and sufficient time for the segregation to take place. Therefore, the Ti_2Zr 2DC forms the new terminating surface of the TiB_2 particle.

The consequence of the formation of the Ti_2Zr 2DC on the (0 0 0 1) TiB_2 surface is that the original potent TiB_2 particles in the commercial Al-Ti-B grain refiners lose their potency for heterogeneous nucleation of α -Al. Since the Ti_2Zr 2DC is completely coherent with (0 0 0 1) TiB_2 , the lattice misfit between the Ti_2Zr 2DC and Al will be the same as that between TiB_2 and Al. This means that due to the dissolution of Al_3Ti 2DC and the formation of the Ti_2Zr 2DC as the new terminating surface, the original small lattice misfit 0.09% between Al_3Ti 2DC and (1 1 1) Al is reversed back to the large value 4.22%. This makes the TiB_2 particles with Ti_2Zr 2DC impotent for heterogeneous nucleation of α -Al.

1 More importantly, the *ab initio* MD simulations in this work show that, at the nucleation
2 temperature, the Zr atoms in the Ti₂Zr 2DC protrude about 0.45 Å from the Ti atom plane towards
3 the liquid Al, resulting in an atomically rough surface (Fig. 8). This atomic roughness on the TiB₂
4 substrate surface decreases atomic ordering in the liquid adjacent to the liquid/substrate interface
5 and hence impedes heterogeneous nucleation [59], as discussed below.

6 Prenucleation phenomenon caused by a crystal substrate in an alloy melt at a temperature above the
7 nucleation temperature has been investigated recently by molecular dynamics simulations [50, 59,
8 60]. It was found that there exists significant atomic ordering in the liquid adjacent to the
9 liquid/substrate interface, which can be taken as a precursor for the subsequent heterogeneous
10 nucleation [50]. Such atomic ordering can be either enhanced by decreasing the lattice misfit
11 between the substrate and the solid [50] and/or increasing the attractive chemical interaction
12 (measured by the heat of mixing) between the substrate and the liquid [60], or impeded by an
13 atomically rough surface of the substrate [59]. Based on the understandings, Zr poisoning can be
14 attributed to the impeding of pre-nucleation on the TiB₂ particles. The formation of the Ti₂Zr 2DC
15 on the (0 0 0 1) TiB₂ surface to replace the original Al₃Ti 2DC results in not only an increase in
16 lattice misfit from 0.09% to 4.22%, but also the roughening of the (0 0 0 1) TiB₂ surface, both of
17 which impede pre-nucleation and lead to poisoning of the originally potent TiB₂ particles for
18 heterogeneous nucleation.
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23 Therefore, the mechanism for Zr poisoning can be summed up as dissolution of the Al₃Ti 2DC on
24 the (0 0 0 1) TiB₂ surface in the commercial TiB₂ based grain refiners and the formation of the Ti₂Zr
25 2DC in the Al-Zr melt, which renders TiB₂ particles impotent for heterogeneous nucleation of α-Al.
26 This mechanism for Zr poisoning is consistent with the our experimental observations in this work:
27 (i) the absence of the well-defined OR between TiB₂ and α-Al: (0 0 0 1) [1 1 -2 0] TiB₂ // (1 1 1) [0
28 -1 1] Al, when Zr is present in Al melt; (ii) only a ppm level of Zr is required even if the Ti₂Zr 2DC
29 is formed on the entire TiB₂ surface; and (iii) Zr poisoning is time dependent [9, 31] and the partial
30 formation of Ti₂Zr 2DC on (0 0 0 1) TiB₂ surface (Fig. 5) due to its slow kinetics of formation in a
31 dilute Al-Zr liquid solution.
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35 The mechanism is consistent with the experimental observations present in this work (Figs. 2 and 5)
36 and in the previous studies in the literature [e.g., 9, 29-31.]. Thermodynamically, a ppm level of Zr
37 addition is sufficient for the formation of the Ti₂Zr 2D layer on the basal surface of all the added
38 TiB₂ particles. Kinetically, the dissolution of the pre-existing Al₃Ti 2DC layer and the formation of
39 the Ti₂Zr 2DC layer will take time to complete, depending upon the temperature and Zr
40 concentration of the melt. It is not expected that all the TiB₂ particles are completely poisoned in a
41 limited period of time. It has been shown in the previous study that the Zr poisoning effect is still
42 increasing with the melt being held at 800°C for over 6 hours [31]. Indeed, our experimental
43 observation shown in Fig. 5 provides the evidence that not all the surface of TiB₂ particles have
44 been covered by Ti₂Zr 2DC layer. It is understandable that a higher concentration of Zr promotes
45 the poisoning, as shown in Fig. 2.
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49 When the addition level of Zr is more than the peritectic composition (0.11%), Al₃Zr particles can
50 possibly act as heterogeneous nucleation sites for α-Al, and may potentially result in grain
51 refinement [29, 30]. In this work, apart from oxides, poisoned TiB₂ and Al₃Zr particles co-exist in
52 the melt with higher Zr contents (>0.11%). In such cases there is an inevitable competition for
53 nucleation between those particles. The lattice misfit with α-Al is 1.34% for Al₃Zr, 3.4% for γ-
54 Al₂O₃ and -4.2% for TiB₂. Although Al₃Zr has the highest potency among these particles, it would
55 not lead to grain refinement due to the large particle size (~115 μm in diameter [30]) and thus low
56 particle number density. In cases of Zr poisoning, γ-Al₂O₃ particles are more likely to be
57 responsible for the grain size observed.
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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 misfit 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 Al₃Ti 2DC 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 Al₃Ti 2DC on the (0 0 0 1) TiB₂ surface and the formation of the Ti₂Zr 2DC 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 the α -Al and they are more potent than TiB₂ particles with a clean basal surface (no chemical segregation). Formation of the Al₃Ti 2DC 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 Ti₂Zr 2DC 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-5Ti-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 Al₃Ti 2-dimntional compound (2DC) formed on the (0 0 0 1) TiB₂ surface during the grain refiner production process; and (ii) the formation of an atomic monolayer of Ti₂Zr (Ti₂Zr 2DC) 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 α -Al and TiB₂ with Al₃Ti 2DC) to 4.22% (between α -Al and TiB₂ with Ti₂Zr 2DC), rendering TiB₂ particles in Al-Zr melts impotent for heterogeneous nucleation of α -Al.

1 *Ab initio* MD simulations have confirmed that the Ti₂Zr 2DC formed on the (0 0 0 1) TiB₂ surface
2 is atomically rough. This atomic roughness can be attributed to the facts that Zr atoms have a larger
3 atomic size and a stronger attractive chemical interaction with liquid Al in comparison with Ti
4 atoms in the Ti₂Zr 2DC. According to the recent MD simulation results [59], this atomically rough
5 surface weakens atomic ordering in the liquid adjacent to the liquid/substrate interface and
6 consequently hinders heterogeneous nucleation.

7 The mechanism for Zr poisoning can, therefore, be summed up as dissolution of the Al₃Ti 2DC on
8 the (0 0 0 1) TiB₂ surface in the commercial Al-Ti-B based grain refiner and the formation of the
9 Ti₂Zr 2DC on TiB₂ basal surface in the Al-Zr melt, which renders TiB₂ particles impotent for
10 heterogeneous nucleation of α -Al due to the increased lattice misfit and surface roughness at atomic
11 level.

12 In addition, we have found that there is no segregation of Fe or Si at the basal surface of TiB₂,
13 although Fe was found to segregate on the {1 0 -1 0} TiB₂ prismatic surface. This confirms that
14 neither Fe nor Si (as impurity elements) played any role in Zr poisoning of TiB₂ particles in the Zr-
15 containing Al melt.
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17 Furthermore, this work, in combination of our previous work [8], demonstrates that heterogeneous
18 nucleation can be effectively manipulated, either enhanced or impeded, by chemical segregation of
19 selected alloying/ impurity elements at the liquid/substrate interface.
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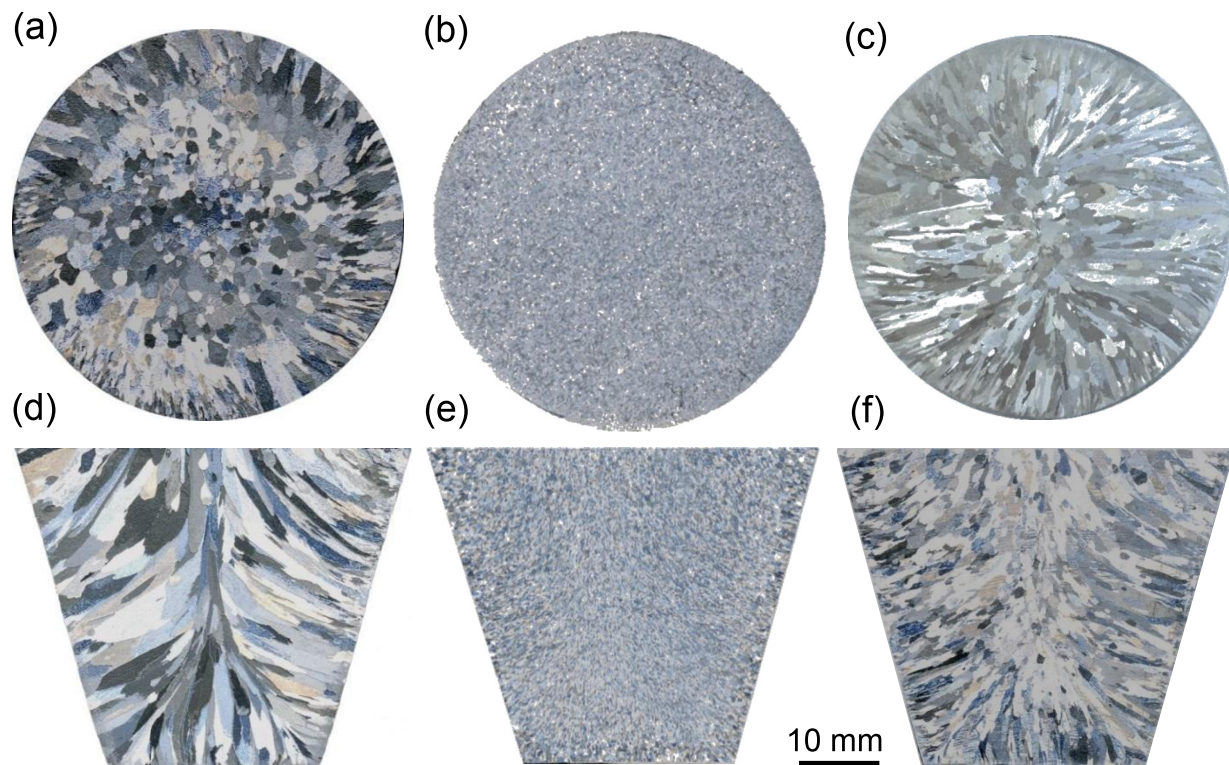


Fig. 1 Macrographs showing grain structure on (a-c) transverse and (d-f) longitudinal sections of CP-Al samples solidified in the TP-1 mould, with (a, d) no addition, (b, e) addition of 0.1% commercial Al-5Ti-1B grain refiner, and (c, f) additions of both 0.1% of the grain refiner and 0.058% (558 ppm) Zr, showing that the grain refiner has no ability to refine the CP-Al when the small amount of Zr is present.

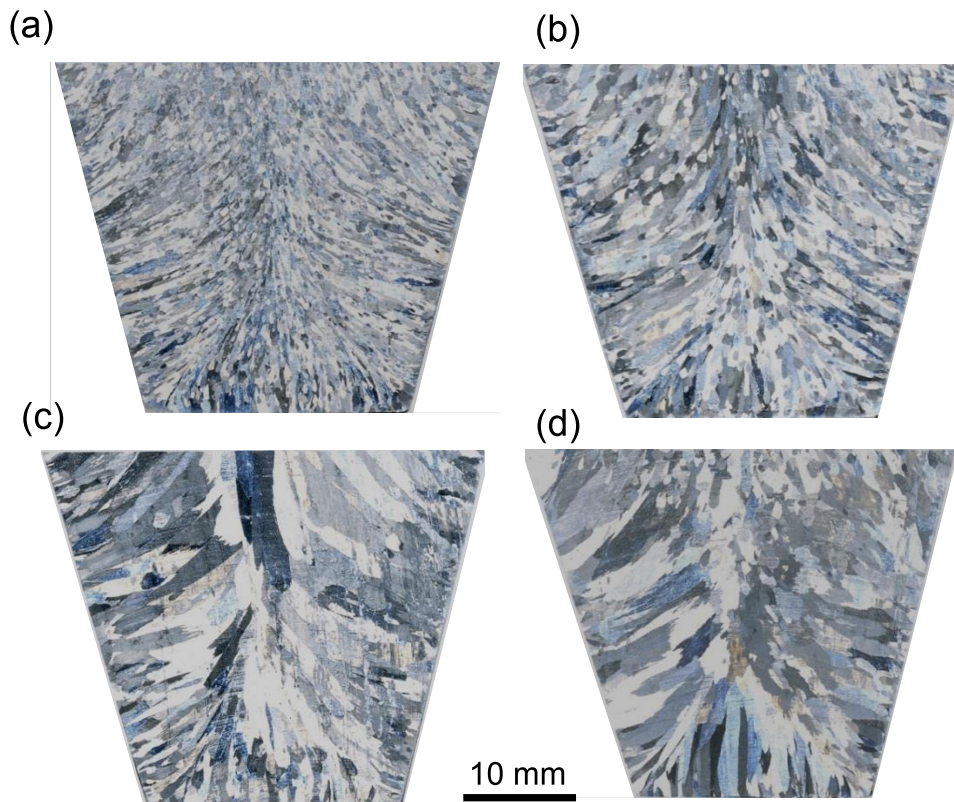


Fig. 2 Macrographs showing the grain structure on longitudinal sections of Al-Zr alloy samples solidified in the TP-1 mould, containing 0.1% commercial Al-5Ti-1B grain refiner and with increasing additions of Zr: (a) 0.088%, (b) 0.206%, (c) 0.310%, and (d) 0.450%. The grain structure remains columnar and the width of the columnar grains increases with increasing Zr concentration.

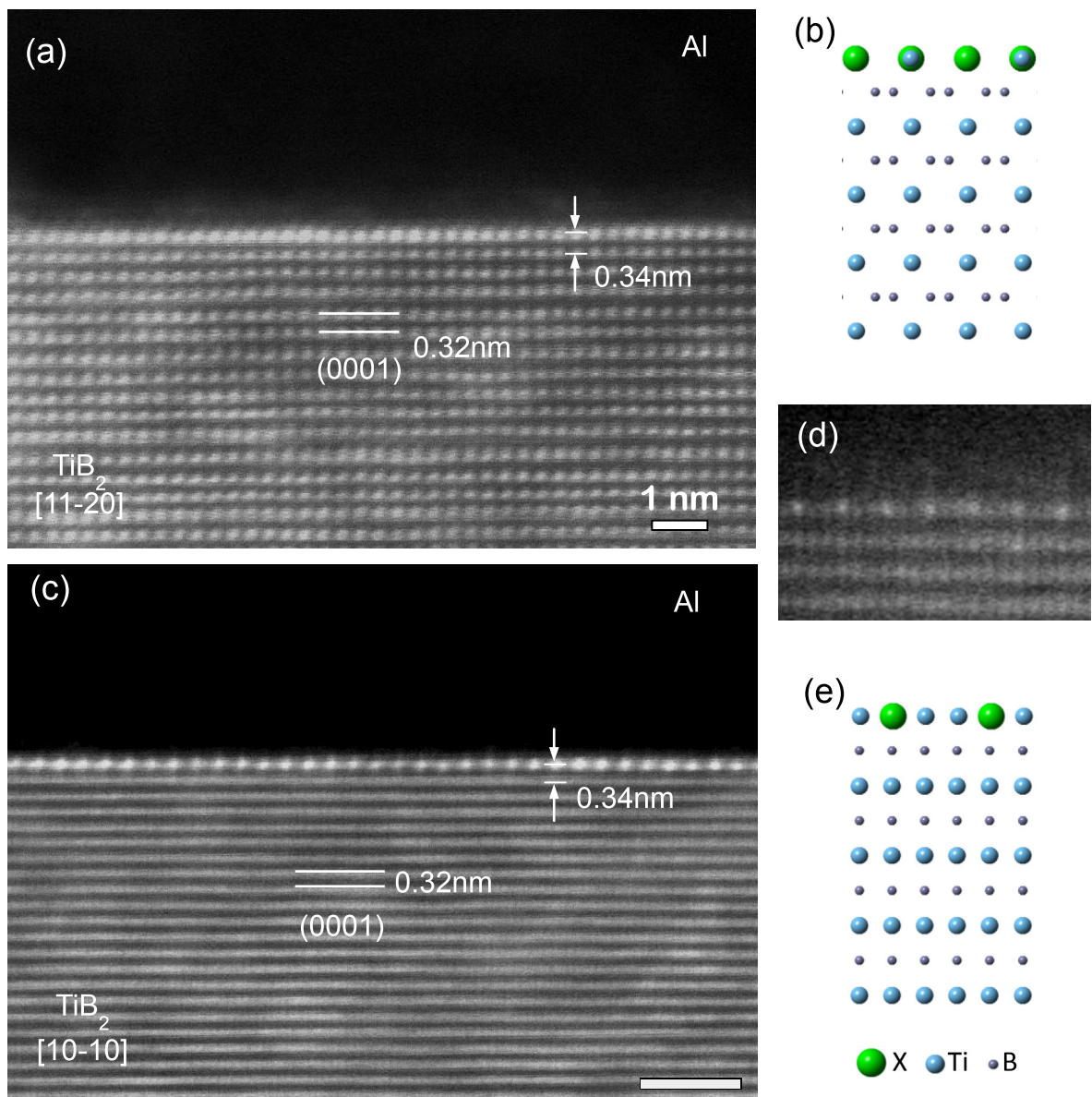


Fig. 3 (a, c) High resolution STEM Z-contrast HAADF images showing an atomic monolayer containing heavier atoms X (brighter contrast than Ti) on the (0 0 0 1) surface of TiB_2 particle being viewed along (a) $[1\ 1\ -2\ 0]$ and (c) $[1\ 0\ -1\ 0]$ directions respectively, (d) SuperSTEM HAADF image at higher resolution showing the periodic variation in brightness of the atomic columns of the segregation monolayer. The corresponding schematics in (b, e) show the possible atomic arrangement across the Al/ TiB_2 interface along the two directions (the large green spheres represent the heavier atoms X).

Fig 4

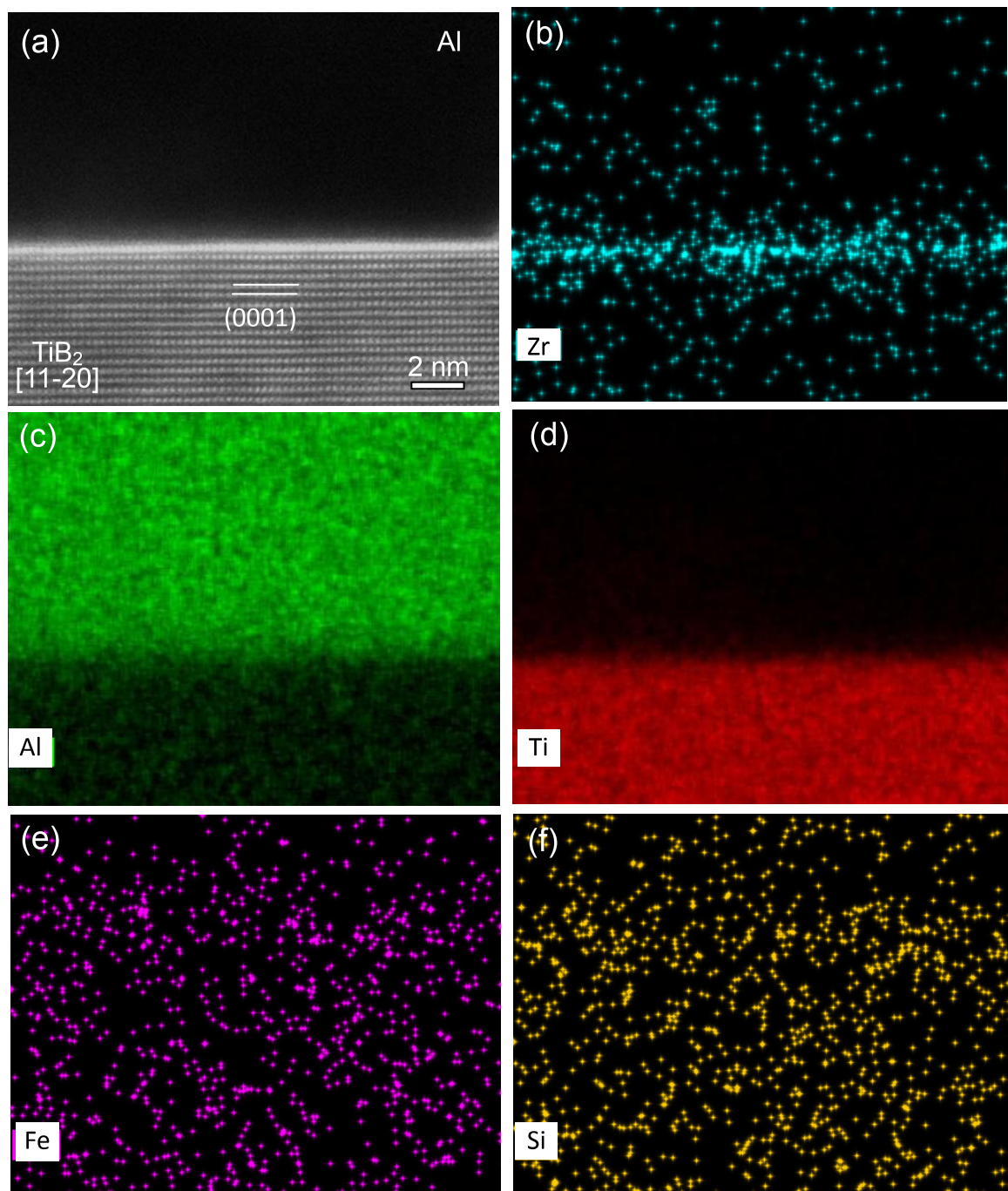


Fig. 4 (a) High resolution STEM HAADF image across Al/TiB₂ interface viewed along [1 1 - 2 0]TiB₂ direction, and (b-f) Super-X EDS elemental mapping of (b) Zr (cyan), (c) Al (green), (d) Ti (red), (e) Fe (purple) and (f) Si (yellow) across the interface, showing Zr segregation but no segregation of Fe and Si at the interface between Al and (0 0 0 1) basal plane surface of TiB₂.

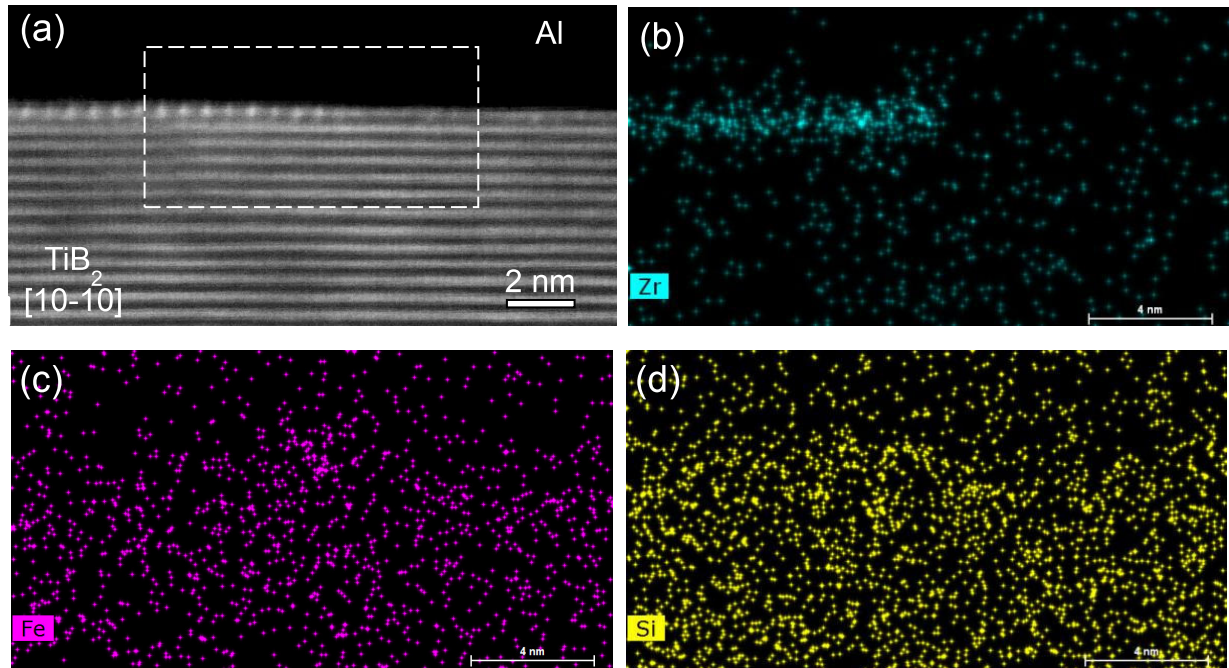


Fig. 5 (a) High resolution STEM HAADF image across Al/TiB₂ interface viewed along [1 0 - 1 0] TiB₂ direction, and (b-d) Super-X EDS elemental mapping (from the marked area in (a)) of (b) Zr (cyan), (c) Fe (purple) and (d) Si (yellow) across the interface, showing the on-going Zr segregation process on 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.

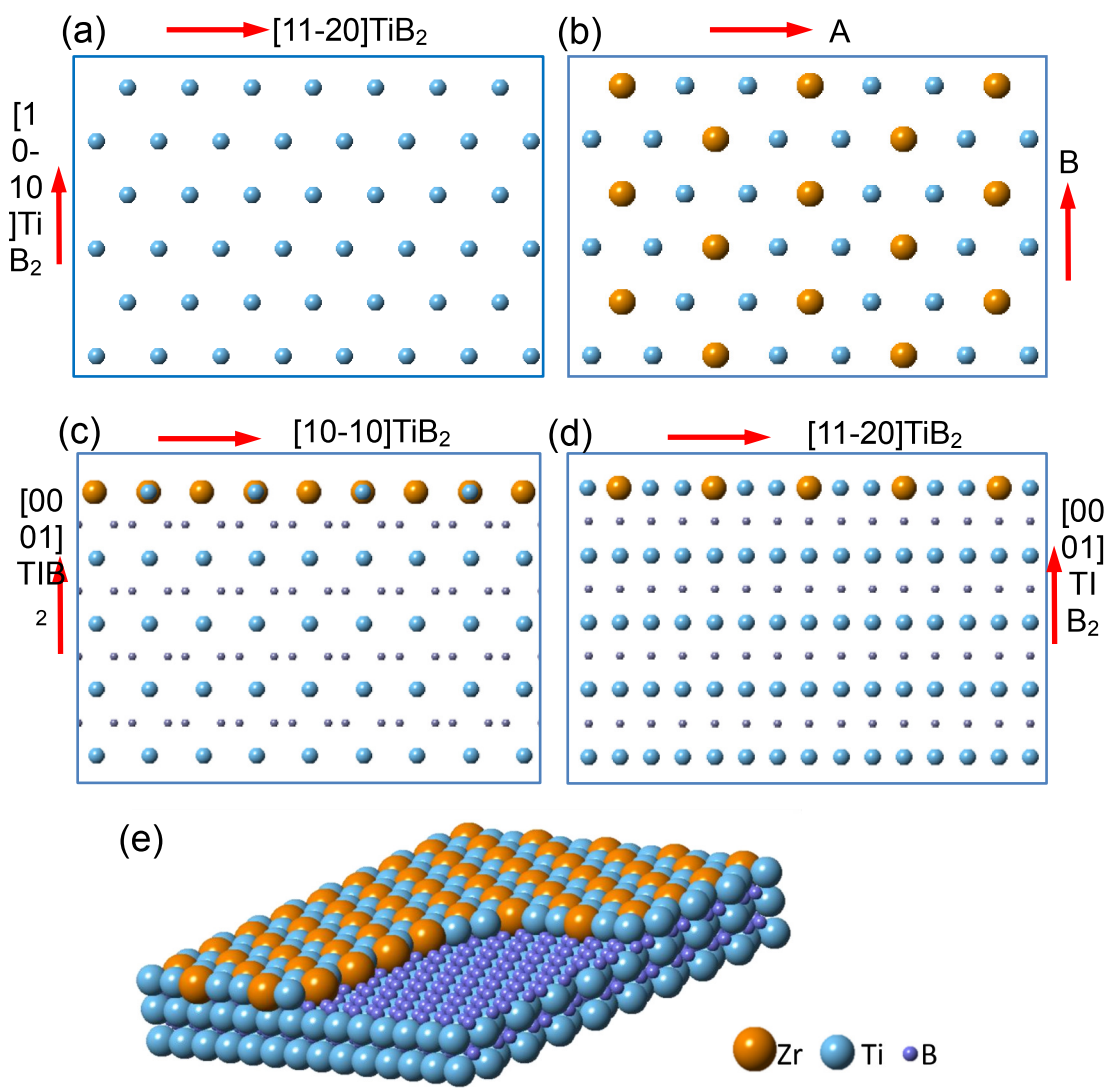


Fig. 6 Schematic illustrations showing (a, b) arrangement of (a) Ti atoms in (0 0 0 1)Ti planes of TiB₂ and (b) Ti and Zr atoms in the Ti₂Zr 2DC; (c, d) side view of TiB₂ (Ti₂Zr 2DC) along (c) [1 1 -2 0]TiB₂ and (d) [1 0 -1 0]TiB₂ direction, respectively; and (e) 3D construction of the Ti₂Zr 2DC on top of TiB₂.

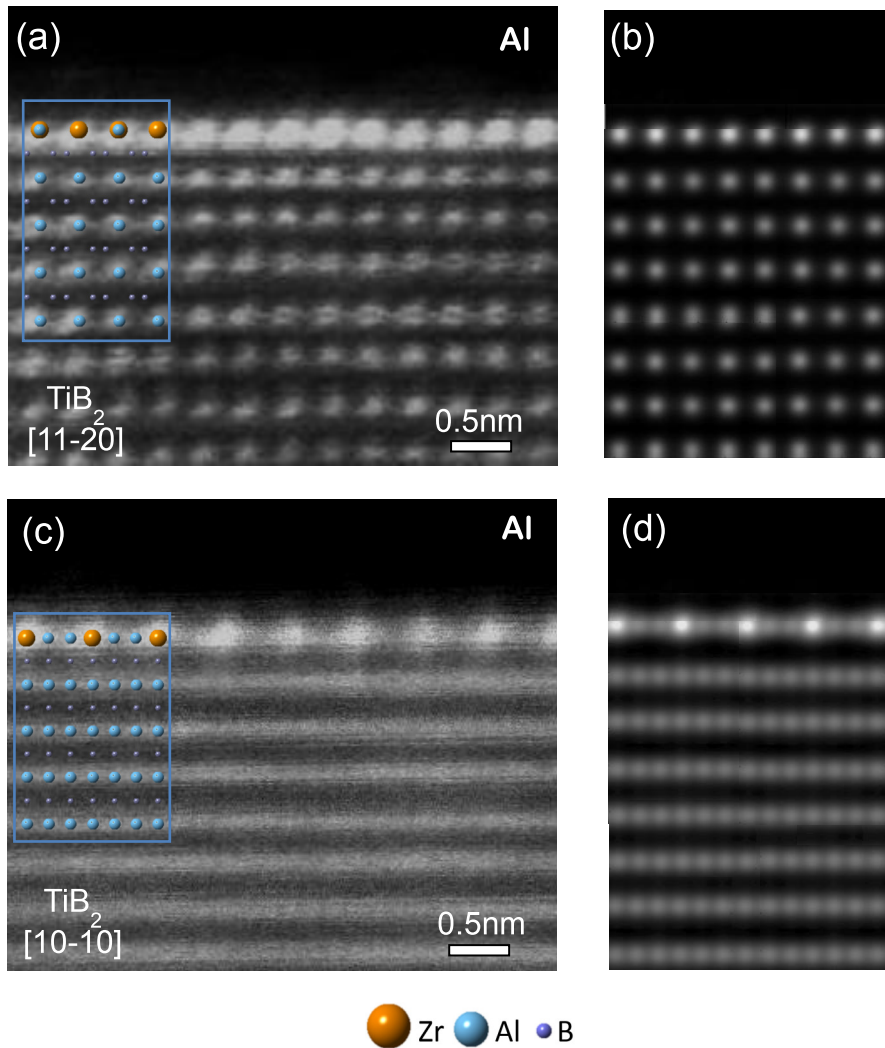


Fig. 7 (a, c) Experimental STEM HAADF images compared with (b, d) the simulated HAADF images along (a, b) $[1\ 1\ -2\ 0]$ and (c, d) $[1\ 0\ -1\ 0]$ TiB_2 direction, respectively. The simulation of STEM HAADF images was carried out using the QSTEM multislice simulation package developed by Koch [41], according to the constructed super-lattice structure of Ti_2Zr 2DC on the $(0\ 0\ 0\ 1)$ surface of TiB_2 as shown schematically in Figs. 6b, 6c and 6d.

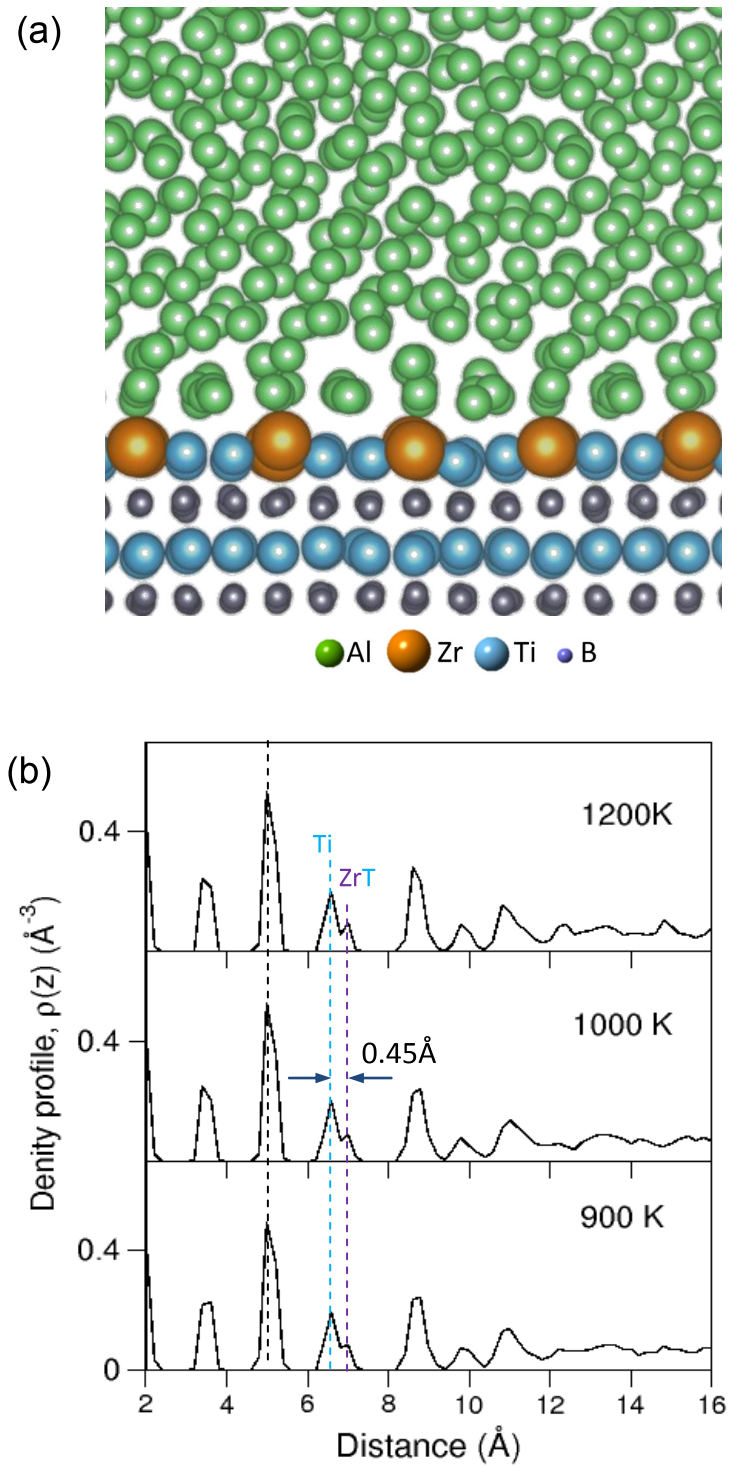


Fig. 8 (a) Snapshot of Al(liquid)/TiB₂(Ti₂Zr 2DC) interface along [1 0 -1 0] TiB₂(Ti₂Zr 2DC) direction simulated at 1000 K, and (b) atomic density profiles $\rho(z)$ across the Al(liquid)/TiB₂ (Ti₂Zr 2DC) interface simulated at 900 K, 1000 K and 1200 K, respectively. The dotted lines in (b) indicate the position of the Ti and Zr atoms in the Ti₂Zr 2DC.

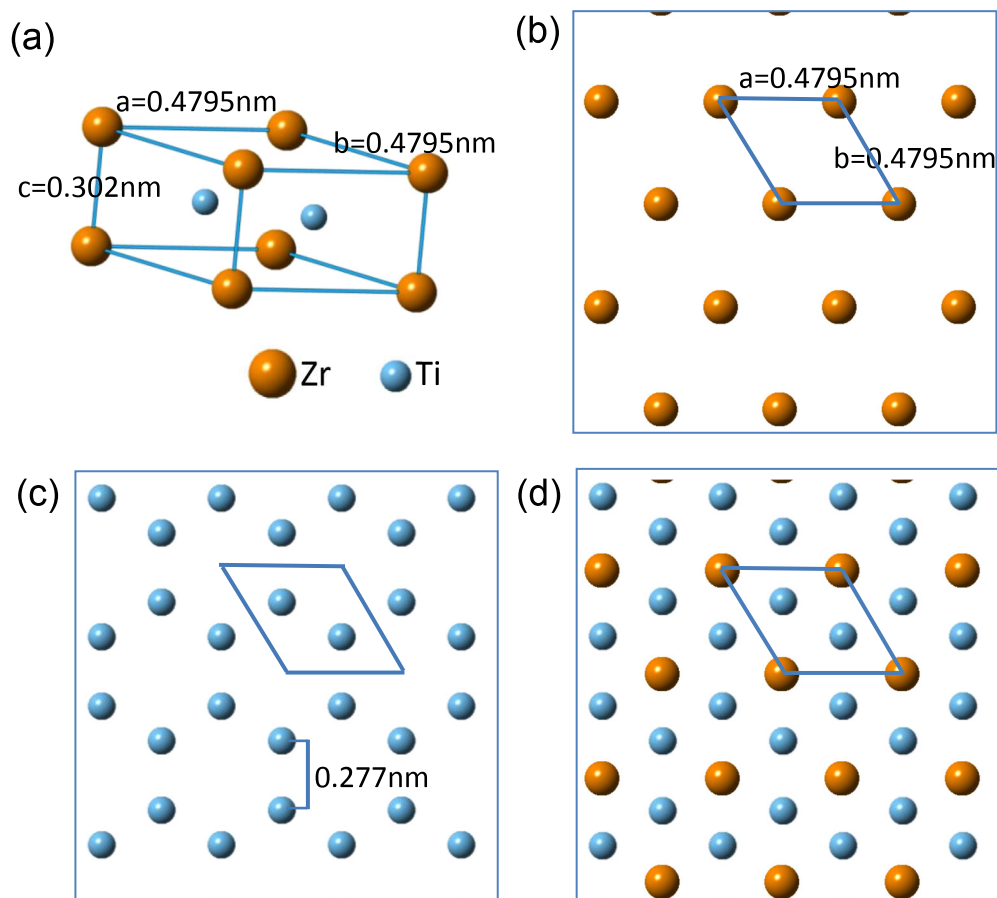


Fig. 9 Schematics showing (a) the unit cell of ω - Ti_2Zr phase [50] stacked by alternating Zr and Ti planes, (b, c) arrangement of Zr atoms in (0001) Zr plane and Ti atoms in (0001) Ti plane of ω - Ti_2Zr phase respectively, and (d) atomic configuration of a Ti_2Zr 2DC structure constructed by superimposition of the Zr and Ti planes of ω - Ti_2Zr phase.

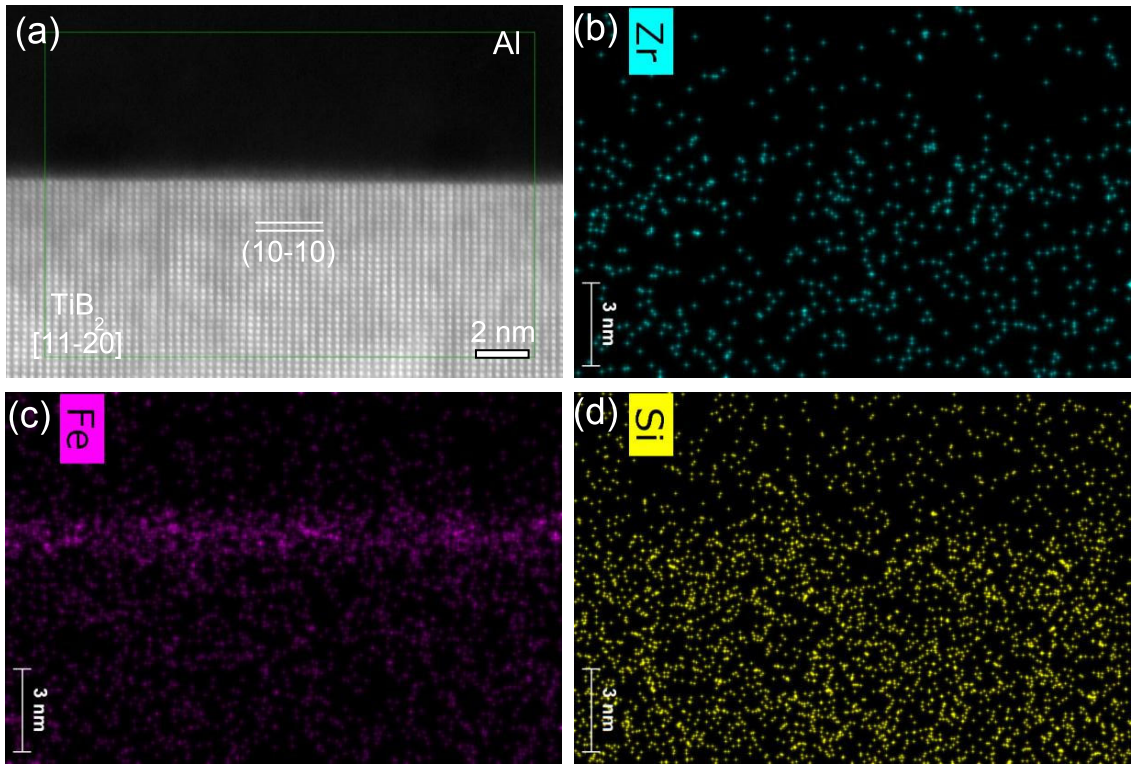


Fig. 10 (a) STEM HAADF image of Al/ (1 0 -1 0)TiB₂ interface and (b-d) STEM SuperX-EDS elemental mapping (from the marked area) of (b) Zr, (c) Fe and (d) Si across the interface, showing Fe segregation but no Zr or Si segregation at the interface between Al and the prismatic surface of TiB₂.

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	Ti	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.