

Mechanism for Si Poisoning of Al-Ti-B Grain Refiners in Al-Alloys

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Abstract

Al-5Ti-1B is the most widely used grain refiner for Al-alloys. However, it is not effective for grain refining Al-alloys containing more than 3 wt.% Si. This adverse effect of Si is referred to as Si poisoning. In spite of extensive experimental and theoretical investigations in the past decades, the exact mechanism for Si poisoning is still not clear. In this work, the state-of-the-art electron microscopy was performed to investigate the mechanism for Si poisoning. Our experimental results suggest that Si segregates preferably to the TiB₂/Al-Si melt interface and the pre-existing Al₃Ti 2-dimensional compound (2DC) layer on TiB₂ surface dissolves into the Al-Si melt. Based on the experimental results, we have postulated a new mechanism for Si poisoning: interfacial segregation of Si leads to enrichment of Si at the TiB₂/Al-Si melt interface, and this in turn makes the pre-existing Al₃Ti 2DC on the TiB₂ surface unstable and dissolve gradually in the melt, resulting in a loss of TiB₂ nucleation potency and hence a decreased total number of potent TiB₂ particles available for heterogeneous nucleation and grain initiation and consequently an increased grain size. This mechanism for Si poisoning can explain consistently the experimentally observed phenomenon reported in the literature.

Keywords: Solidification; Heterogeneous nucleation; Grain refinement; Si poisoning.

1. Introduction

A grain refined microstructure is usually desirable for Al-alloy castings, since it not only facilitates the casting processes, but also improves mechanical performance of the alloys through reduced cast defects, such as macro-segregation, hot tearing and porosity. In the Al industry, a common foundry practice for grain refinement is addition of grain refiner prior to casting processes, with Al-5Ti-1B (all the alloy compositions are in wt.% unless stated otherwise) being the most widely used commercial grain refiner. Since the introduction of Al-Ti-B based grain refiners in early 1950s, [1] extensive experimental investigations and theoretical studies have been carried out to understand the underpinning mechanisms for grain refinement. [2-7] It is now generally accepted that promoting heterogeneous nucleation of numerous α Al grains on TiB₂ particles is responsible for grain refinement. Various hypotheses have been proposed to explain the mechanisms of heterogeneous nucleation in the Al-TiB₂ system. [3-7] It is only until very recently to realize that the formation of an atomic layer of Al₃Ti 2-dimensional compound (2DC) on the (0 0 0 1) TiB₂ surface is responsible for the high potency of the TiB₂ particles for nucleation of α Al grains. [8]

The presence of alloying elements has long been recognized as one of the important factors for grain refinement by providing growth restriction. However, this may not be true for all the elements. For instance, Al-5Ti-1B becomes ineffective for grain refinement when certain elements are present in the alloy melt, such as Zr, [9-14] Li, [15-16] Cr, [17-18] and high levels of Si. [19-34] The negative effect of solute elements on grain refinement is referred to as “poisoning” in the literature. One of the main explanations to the poisoning effect is that the

58 interaction between solute elements and TiB_2 particles leads to the decrease in nucleation
59 potency of the TiB_2 particles. [35] Our recent research work on Zr poisoning disclosed that the
60 presence of Zr in the melt results in the dissolution of the pre-existing Al_3Ti 2DC layer (formed
61 during the grain refiner production process) and the formation of a Ti_2Zr 2DC atomic layer on
62 TiB_2 surface, which is responsible for the reduced potency of TiB_2 for heterogeneous
63 nucleation of αAl . [36]

64 The phenomenon of Si poisoning has been observed in Al-Si alloys containing more than 3%
65 Si inoculated with Al-5Ti-1B grain refiner. [19-23, 30-32] Sigworth and Guzewski [20] and
66 Johnsson *et al* [21-22] showed that, with inoculation by Al-5Ti-1B, the grain size of Al-Si
67 alloys first decreased slightly and then increased with increasing Si content with a minimum
68 value at ~3% Si. A number of studies subsequently confirmed the poisoning effect of Si. [23-
69 34] In addition, it was found that at a given processing temperature and a given Si
70 concentration (> 3%), the grain size increases with increasing holding time of the melt prior
71 casting. [32] Furthermore, Si poisoning has also been reported in Al-Si alloys without the
72 addition of Al-5Ti-1B grain refiner. It was found that the grain size of un-inoculated Al-Si
73 alloys began to increase after reaching to a minimum value at ~3% Si. [26, 29-31, 34]

74 Overcoming Si poisoning has been a significant research topic in the past decades. The major
75 approaches include: (i) higher addition level of hyper-stoichiometric (the stoichiometric weight
76 ratio of Ti:B = 2.2:1) Al-Ti-B master alloys; [32-33, 37] (ii) modification of grain refiner
77 composition, such as Al-2.2Ti-1B, Al-3Ti-3B and Al-1Ti-3B; [37-41] and (iii) development of
78 new grain refiners based on the other alloy systems, such as Al-Ti-C, [37, 42-43] Al-Ti-B-C,
79 [44] Al-B [37,40,45-47] and Al-Nb-B. [48-50] For instance, addition level of as high as 0.6%
80 (typically 0.1% for a standard practice in industry) of Al-5Ti-1B grain refiner was shown to
81 result in a fully refined structure for Al-7Si alloys. [32, 33] In addition, some newly developed
82 alternatives, such as Al-3Ti-3B and Al-1Ti-3B (sub-stoichiometric), have been reported to
83 provide a better grain refinement performance than the conventional Al-5Ti-B refiner. [37-40]
84 Furthermore, binary Al-B system without Ti involved, Al-3B for instance, was shown to offer a
85 better refining performance than Al-5Ti-1B. [33, 45-47] More recently, Al-2Nb-2B based grain
86 refiner were claimed to offer good performance in grain refinement of Al-Si alloys with
87 poisoning resistance. [48-50] Effect of trace elements on refining effectiveness of Al-Ti-B
88 based refiner has also been investigated. It was noted that some elements, such as Mg and Sr
89 etc., were shown to counteract Si poisoning. [32, 41, 51]

90 A number of hypotheses were proposed to explain the mechanism for Si poisoning, although
91 no consensus has been reached so far. One school of thoughts is the formation of Ti-Si or Ti-
92 Si-Al compounds on the TiB_2 surface. It was postulated that formation of the silicides by
93 interaction between TiB_2 and solute Si made the nucleant particles less potent, [20, 21, 35, 52-
94 54] although there was little direct experimental evidence for this mechanism. For instance,
95 formation of Ti-Si compounds at the $\text{TiB}_2/\alpha\text{Al}$ interface was reported only in metallic glass
96 ($\text{Al}_{80}\text{Ni}_{10}\text{Cu}_8\text{Si}_2$ alloy containing up to 0.09% Ti), [52-54] but not in Al melt containing high Si
97 content. Thermodynamic analysis for formation of various silicides was carried out. [35, 55] It
98 was reported that, with increasing Si content, the Ti level required for TiSi_2 formation is
99 reduced. [55] In addition, based on thermodynamics and lattice matching, [35] it was suggested
100 that, among all the possible Ti-Si or Ti-Si-Al compounds, Ti_5Si_3 was the likely one to form on
101 TiB_2 surface causing poisoning effect. Another school of thoughts involves the increased

102 growth velocity of α Al. Due to a reduced growth restriction caused by formation of titanium
 103 silicides, [56] the growth velocity of α Al would increase. Thermodynamic calculations also
 104 showed that, with high level of Si and excess Ti in Al-Si melt, the growth restriction parameter
 105 Q would be greatly affected by strong exothermic interaction between the solutes Si and Ti.
 106 [57] “Coincidentally” at ~3% Si, a morphological transition from globular (cellular) to dendritic
 107 for α Al was observed. [29] It was thus suggested that highly branched dendrites, which grew
 108 more rapidly, had a smaller dendrite tip radius and were thus able to disperse solute sideways
 109 as opposed to globular tips which pushed solute ahead of the solid/liquid interface. Arguably Si
 110 poisoning was attributed to the increase in the growth velocity of the dendrite arms due to a
 111 decreased tip radius with increasing Si content, [22, 23, 58] although the similar morphological
 112 transition was observed in Al-Cu alloys. [30, 59] Other hypotheses involve the change of
 113 solid/liquid interfacial energy, [29, 32, 60] solidification range [24, 30, 31] despite limited
 114 understanding, [61] and reduced peritectic temperature for the formation of a ternary aluminide
 115 (Al-Ti-Si) layer. [37]

116 Si poisoning has been a well-known phenomenon observed in various Al-Si alloys for decades.
 117 Although a number of explanations have been proposed, the exact cause remains elusive. In
 118 this work, based on the confirmation of Si poisoning in Al-Si binary alloys solidified at a
 119 constant cooling rate, extensive electron microscopy was carried out on the collected TiB_2
 120 particles from Al-Si melts, focusing on TiB_2/α Al interfaces to reveal any possible structural
 121 and chemical modification of the TiB_2 particles caused by interactions between solute Si or
 122 impurity elements and the introduced TiB_2 particles. Composition profiles of Si and relevant
 123 impurities were established at local areas across the TiB_2/α Al interface by high resolution
 124 STEM and high resolution Super-X EDS analysis. Based on the experimental findings of Si
 125 segregation at TiB_2/α Al (liquid) interface and the subsequent influence on the potency of TiB_2
 126 particles for heterogeneous nucleation of α Al, we aim to identify the operating mechanism for
 127 Si poisoning of Al-Ti-B based grain refiners, providing elucidation of experimental
 128 observations. Understanding of mechanism for the poisoning effect provides the basis for
 129 developments of effective methods and alternative grain refiners to alleviate and overcome
 130 eventually the negative poisoning effect.

131

132 2. Experimental

133 2.1. Raw Materials

134 Commercial purity aluminum (CP-Al) and Al-50Si master alloy were used in this work. Al-Si
 135 alloys containing up to 10% Si were prepared using the CP-Al and Al-50Si master alloy in a
 136 resistance furnace at 750°C with isothermal holding for an hour after melting. TiB_2 particles
 137 were introduced by addition of 0.2% commercial Al-5Ti-1B grain refiner rods, supplied by
 138 LSM (Rotherham, UK). The chemical compositions and impurity levels of the materials used
 139 in this work are given in Table 1.

140

141 Table 1 Compositions (wt.%) of materials used in this work.

Alloy	Si	Ti	B	Fe	V	Zn	Ni	Cu	Cr	Al	Supplier
-------	----	----	---	----	---	----	----	----	----	----	----------

CP-Al	0.03	0.006	--	0.08	--	0.003	0.005	0.001	0.001	Bal.	Norton
Al-50Si	49.90	0.02	--	0.60	--	0.02	0.01	0.03	0.01	Bal.	Avon Metals
Al-5Ti-B	0.08	4.8	0.85	0.09	0.04	--	--	--	--	Bal.	LSM

142

143 2.2. Casting and grain size assessment

144 The grain size of the Al-Si alloys was assessed using the standard TP-1 test [62] which
 145 provides a consistent cooling rate of ~3.5 K/s at the central region of the transverse section 38
 146 mm from the bottom of the TP-1 cast ingot. After the addition of 0.2% Al-5Ti-1B grain refiner,
 147 the Al-Si melt was holding for further 30 min. at 750 °C and stirred in every 10 minutes, and
 148 then poured into the pre-heated TP-1 mold (350 °C) which was then cooled by water spray
 149 with a flow rate of 3.8 l/min. For comparison, TP-1 tests were also conducted for CP-Al with
 150 and without inoculation with the commercial Al-5Ti-1B grain refiner.

151 Examination of grain structure and quantification of grain size of the solidified TP-1 samples
 152 were carried out at the transverse section 38 mm from the base, and the longitudinal section of
 153 the lower part of the TP-1 ingots. The specimens for the quantitative metallography were
 154 prepared following the standard procedures, subjected to a final polishing before anodizing
 155 using Barker's reagent (5 ml HBF₄ + 200 ml distilled water). A Zeiss optical microscope fitted
 156 with the Axio Vision 4.3 image analysis system was used for the grain size measurement. For
 157 each of the measurement by the mean linear intercept technique, the average of at least 500
 158 grains from areas covering the whole transverse section of the TP-1 ingot was taken for the
 159 quantification of the grain size under the given casting conditions.

160

161 2.3. SEM and high resolution TEM/STEM

162 In order to facilitate examinations of TiB₂ particles and their interfaces with α Al by electron
 163 microscopy, a pressurized melt filtration technique was used to collect the TiB₂ particles in the
 164 Al-Si melts inoculated with Al-5Ti-1B grain refiner. In this process, the prepared CP-Al or Al-
 165 Si alloy melt containing TiB₂ particles was transferred into the crucible in the pressure chamber
 166 of the melt filtration unit. Argon was introduced to force the melt to flow through a porous
 167 ceramic filter attached to the bottom of the crucible. TiB₂ particles were thus collected
 168 immediate above the filter. The solidified material above the filter, which contained the locally
 169 concentrated TiB₂ particles, was subjected to sampling. A detailed description of melt filtration
 170 for collection of particles can be found elsewhere. [63, 64]

171 The collected TiB₂ particles, their surface and interface with α Al in particular, were examined.
 172 Scanning electron microscopy (SEM) was performed using a Carl Zeiss Crossbeam 340
 173 microscope equipped with energy dispersive x-ray spectroscopy (EDS). Thin foil specimens for
 174 transmission electron microscopy (TEM) and scanning transmission electron microscopy
 175 (STEM) were prepared from 3 mm diameter discs sliced from the filtered residue material. The
 176 discs were manually ground to a thickness less than 60 μ m before further thinning by argon ion
 177 beam milling using a Gatan precision ion polishing system (PIPS) under a voltage of 1.0-5.0

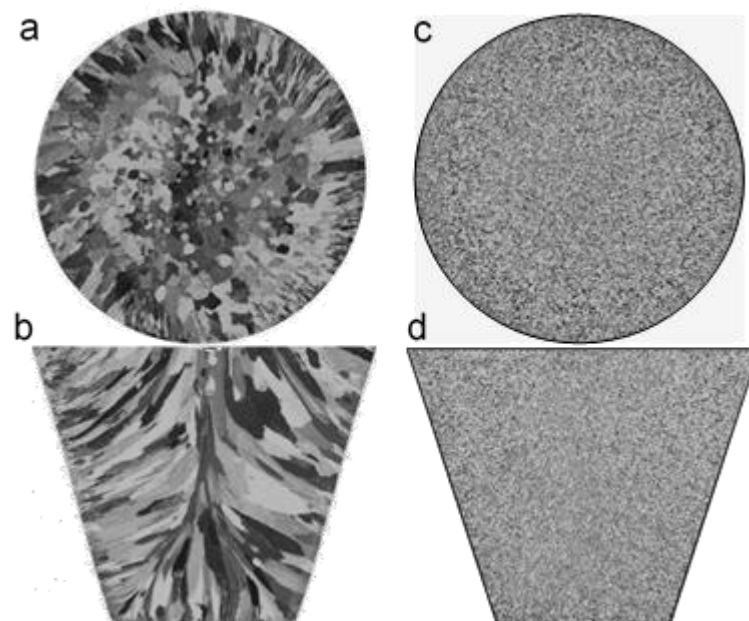
178 kV and an incident beam angle of 3-5°. High resolution TEM examination was conducted on a
179 JEOL 2100F microscope operated with an accelerating voltage of 200 kV. Atomic resolution
180 STEM with Z contrast high-angle annular dark field (HAADF) imaging was carried out on an
181 aberration (Cs)-corrected FEI Titan 80-200 instrument equipped with Super-X energy
182 dispersive x-ray spectroscopy (Super-X EDS) system, operated with an accelerating voltage of
183 200 kV. High resolution elemental mapping by STEM/Super-X EDS was conducted to obtain
184 compositional profiles across TiB₂/αAl interface.

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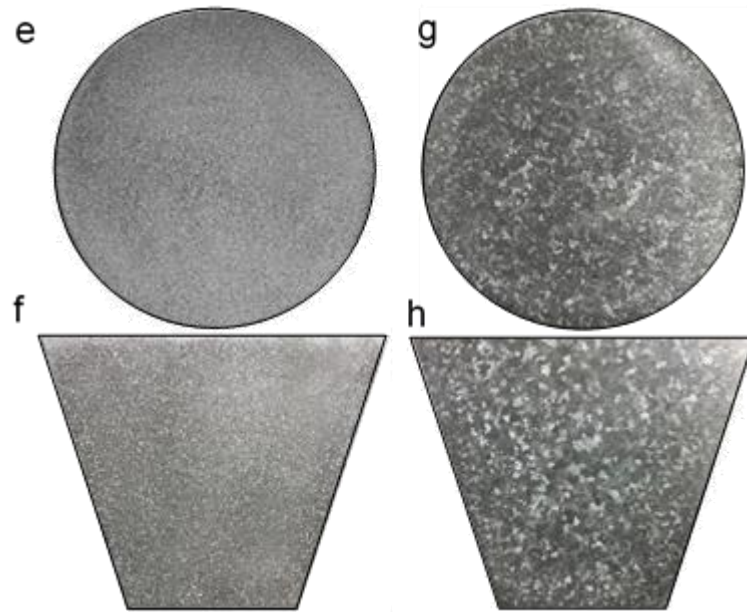
186 3. Results

187 3.1. Si poisoning of Al-5Ti-1B grain refiner

188 Figure 1 shows the typical macrostructures of CP-Al, Al-2.0Si and Al-8.4Si alloys solidified
189 under the TP-1 test conditions. As expected, the addition of 0.2% Al-5Ti-1B grain refiner
190 resulted in a significant grain refinement of CP-Al, transforming the coarse columnar grain
191 structure (Figures 1a and 1b) into a fine and fully equiaxed one (Figures 1c and 1d). Similarly,
192 a considerably refined and fully equiaxed grain structure was obtained for Al-2.0Si alloy
193 inoculated with the grain refiner, as shown in Figures 1e and 1f. However, Al-8.4Si alloy
194 inoculated with the same amount of the grain refiner showed a coarse and equiaxed grain
195 structure (Figures 1g and 1h). The optical micrographs in Figure 2 show the microstructures of
196 Al-2.0Si and Al-8.4Si alloys inoculated with the Al-5Ti-1B grain refiner. The average grain
197 size of the primary αAl phase for Al-2.0Si alloy is 195±22 μm, being comparable to 202±26
198 μm for the refined CP-Al. However, the grain size is 686±73 μm for the inoculated Al-8.4Si
199 alloy, which is considerably larger than that for the inoculated Al-2.0Si alloy. In addition, there
200 is also clear difference in grain morphology between Al-2.0Si and Al-8.4Si alloys. The primary
201 αAl has a typical rosette morphology for the inoculated Al-2.0Si alloy (Figure 2c), but a well-
202 developed dendritic morphology for the inoculated Al-8.4Si alloy (Figure 2d).

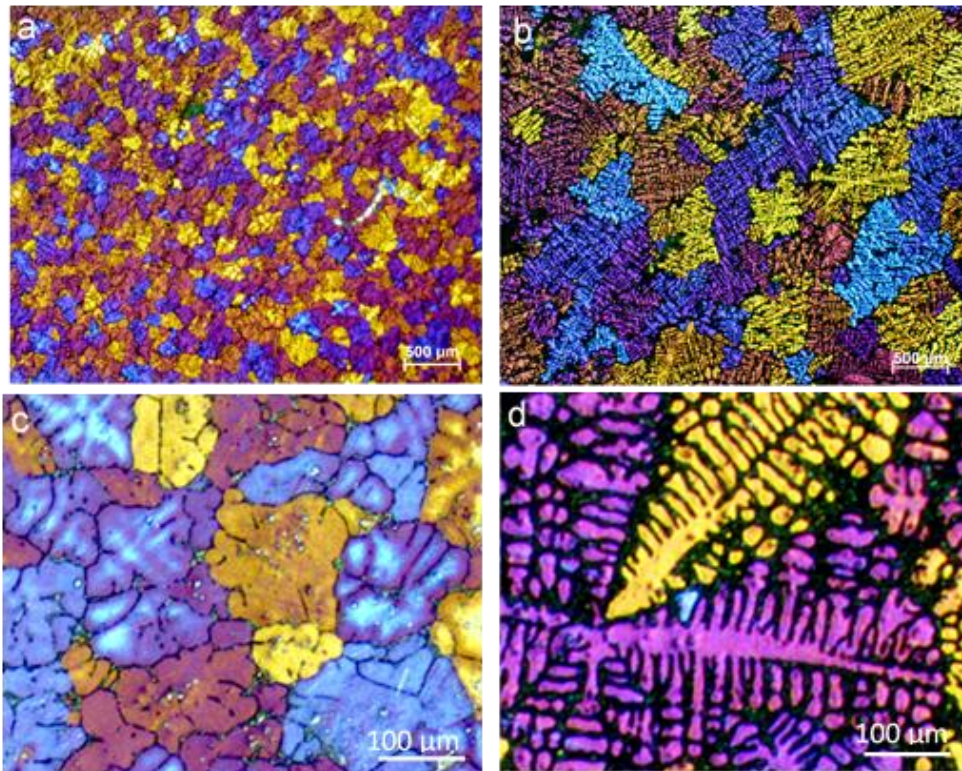


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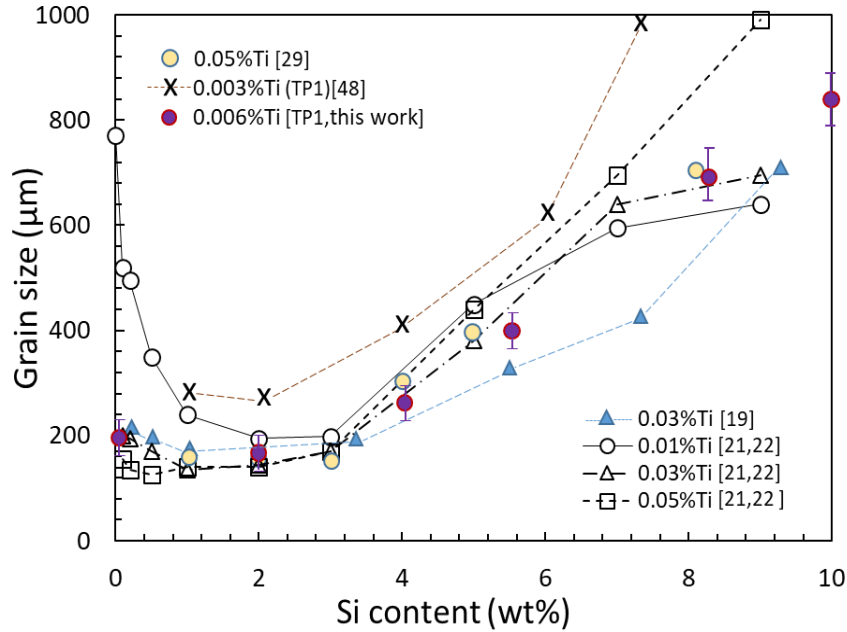
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205 Fig. 1 Macrographs showing grain structures of TP-1 test samples on (a, c, e, g) transverse and
 206 (b, d, f, h) longitudinal sections of (a, b) CP-Al with no addition of grain refiner, (c, d) CP-Al,
 207 (e, f) Al-2.0Si and (g, h) Al-8.4Si alloys with addition of 0.2wt% commercial Al-5Ti-1B grain
 208 refiner.



209

210 Fig. 2 Optical micrographs showing (a, b) general view of grain structures of TP-1 test samples
 211 of (a) Al-2.0Si and (b) Al-8.4Si alloy inoculated with 0.2 wt% Al-5Ti-1B, and (c, d)
 212 morphological transition from cellular to dendritic for the primary α Al with Si concentration
 213 increasing from (c) 2.0 wt% to (d) 8.4 wt%. The average grain size of α Al is measured to be
 214 $195 \pm 22 \mu\text{m}$ and $686 \pm 73 \mu\text{m}$ for Al-2.0Si and Al-8.4Si, respectively.



215

216 Fig. 3 Experimentally measured grain size of the primary α Al of hypoeutectic Al-Si alloys
 217 inoculated with Al-5Ti-1B grain refiner as a function of Si concentration, together with the
 218 representative data found in the literature.

219

220 The experimentally measured grain size is plotted in Figure 3 as a function of Si concentration,
 221 being compared with the representative experimental data found in the literature. In agreement
 222 with previous studies, the present work confirms the variation in grain size of Al-Si alloys with
 223 changing Si content, although the absolute values of grain size vary, probably due to the
 224 differences in the addition level of grain refiner, alloy composition, impurity level and
 225 solidification conditions in the different studies. All the experimental observations show in
 226 general that, when inoculated with Al-5Ti-1B grain refiners, grain size of hypoeutectic Al-Si
 227 alloys decreases slightly until \sim 3% Si and then increases with further increase of Si content.

228

229 3.2 TiB₂ particles added to Al-Si alloy melts

230 TiB₂ particles collected from the Al-Si alloy melt were subjected to extensive examinations by
 231 various microscopic techniques. The reference point for this study is the original state of the
 232 TiB₂ particles from the commercial grain refiner. Such TiB₂ particles are potent substrates for
 233 heterogeneous nucleation of α Al due to the presence of Al₃Ti 2DC layer on their (0 0 0 1)
 234 surface. [8, 36] There exists a well-defined orientation relationship (OR) between TiB₂ and α Al:
 235 [8, 36]

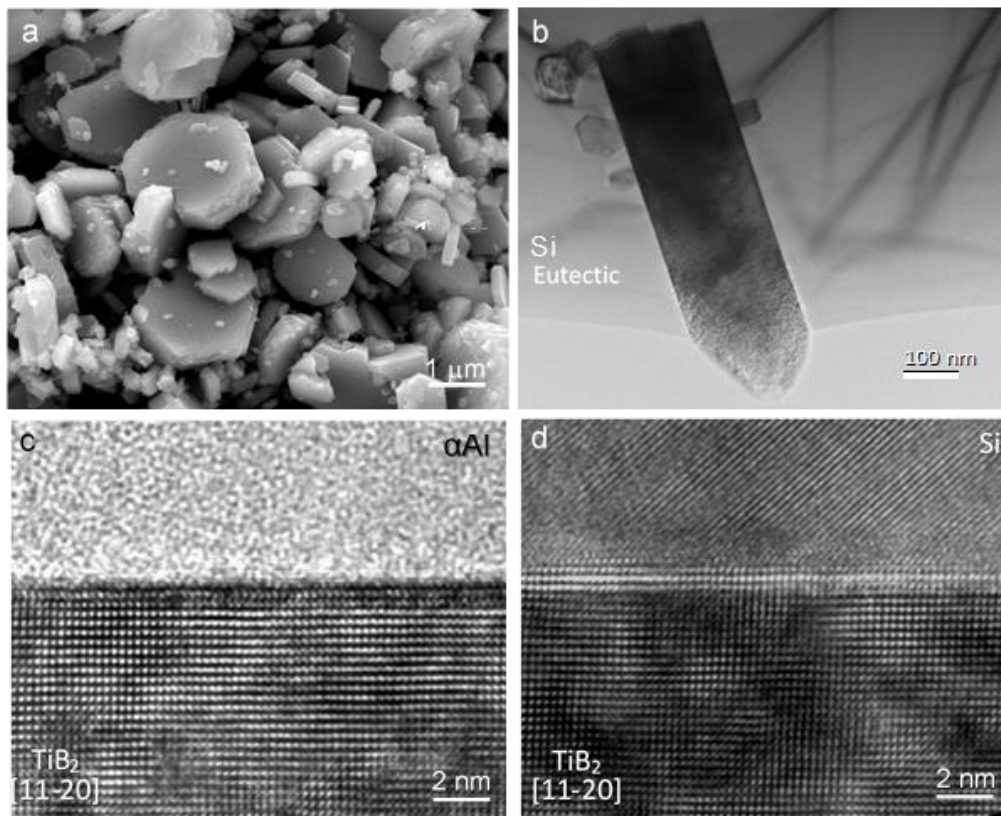
$$236 \quad (0\ 0\ 0\ 1) [1\ 1\ -2\ 0] \text{TiB}_2 // (1\ 1\ 1) [0\ -1\ 1] \alpha\text{Al} \quad (\text{OR1})$$

237 which serves as hard evidence for the nucleation of α Al on TiB₂ substrate.

238 Figure 4a shows the typical hexagonal morphology of the TiB₂ particles collected from the Al-
 239 8.4Si alloy melt inoculated with 0.2% Al-5Ti-1B. Compared with the original TiB₂ particles
 240 from the commercial grain refiner, [65] there was no visible change in morphology and size

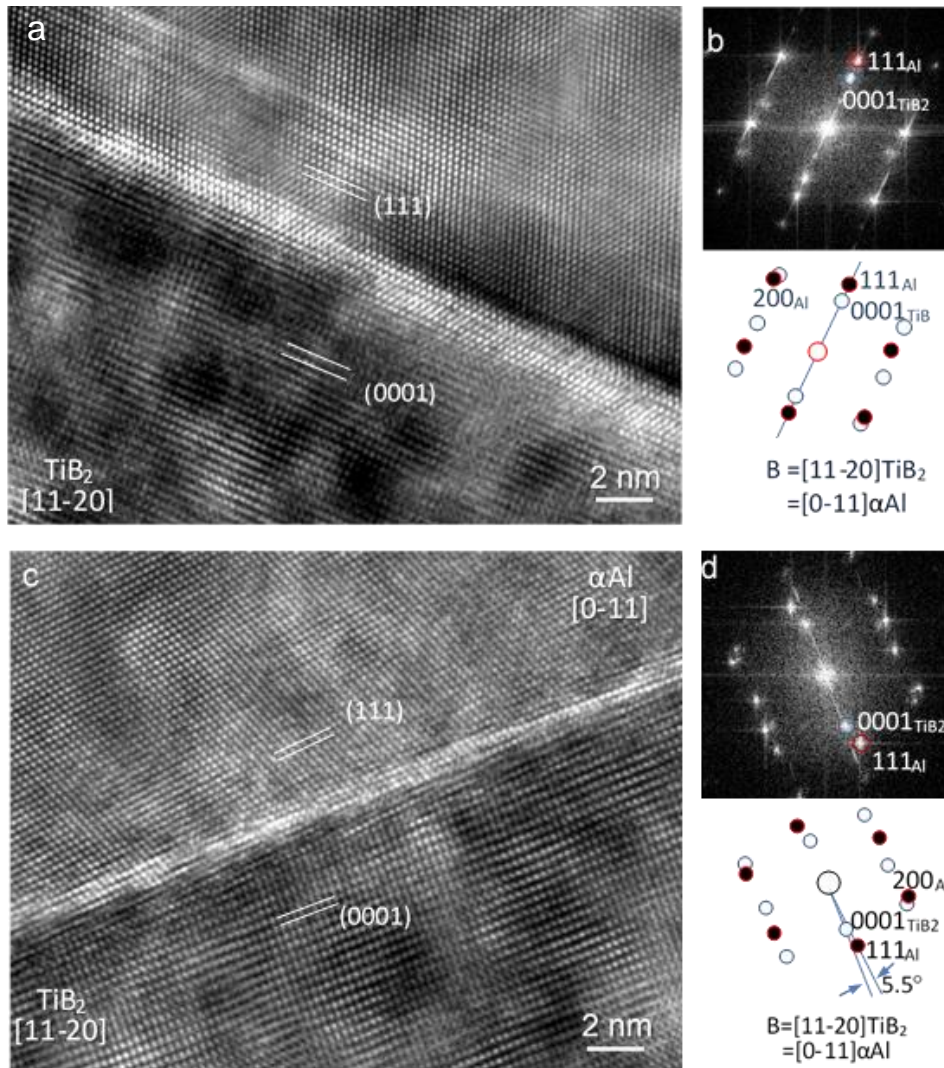
241 after they were added to the melt and isothermally hold at 750°C. Figure 4b is a TEM bright
 242 field image showing the sharp TiB₂/Si interfaces at a higher magnification. Extensive high
 243 resolution TEM examination of multiple TiB₂ particles focusing on both TiB₂/αAl and TiB₂/Si
 244 interfaces revealed no evidence for the formation of any 3D bulk phase at the interfaces.
 245 Examples are given in Figures 4c and 4d, where sharp and smooth TiB₂/αAl (Figure 4c) and
 246 TiB₂/Si (Figure 4d) interfaces are evident at atomic scale.

247



248
 249 Fig. 4 (a) SEM and (b) TEM bright field image showing the morphology of TiB₂ particles
 250 collected from Al-8.4Si alloy melt inoculated with 0.2 wt% Al-5Ti-1B grain refiner, indicating
 251 the typical hexagonal shape of TiB₂ and its sharp surface; and (c, d) high resolution TEM
 252 images showing sharp and smooth (c) TiB₂/αAl and (d) TiB₂/Si (eutectic) interfaces at atomic
 253 scale.

254
 255 TEM/STEM examinations showed that the majority of TiB₂ particles in Al-2.0Si and Al-8.4Si
 256 alloys were not in any defined OR with the adjacent αAl, indicating that the majority of the
 257 added TiB₂ particles did not participate in grain initiation of αAl during solidification. This is
 258 consistent with the conclusion derived from the free growth model that only less than 1% of the
 259 added TiB₂ particles are active for grain initiation. [65] TEM/STEM examination of multiple
 260 TiB₂ particles showed that the well-defined OR1 between TiB₂ and αAl was readily observed
 261 in the Al-2.0Si sample, as shown in Figures 5a and 5b. Occasionally, OR1 is not followed, e.g.,
 262 {1 1 1} planes of αAl being a few degrees away from being parallel to {0 0 0 1} planes of TiB₂,
 263 although [1 1 -2 0]TiB₂ and [0 -1 1]αAl zone directions remain to be parallel to each other. As
 264 shown in Figures 5c and 5d, it is found by careful measurement through the fast Fourier



265
 266 Fig. 5 (a, c) High resolution TEM images showing TiB₂/αAl interfaces in Al-2.0Si alloy sample
 267 where the TiB₂ particle and αAl are viewed along [1 1 -2 0]TiB₂ and [0 -1 1]αAl zone
 268 directions respectively; and (b, d) the corresponding fast Fourier transformation (FFT) patterns
 269 and their index showing that (1 1 1) αAl plane has a 5.5 degrees angle from (0 0 0 1)TiB₂ plane
 270 in (c, d).

271
 272 transformation (FFT) patterns that (1 1 1)αAl plane is ~5.5° away from being parallel to (0 0 0
 273 1) TiB₂ plane. This gives:

274 $(0\ 0\ 0\ 1)\text{TiB}_2 \sim 5.5^\circ (1\ 1\ 1)\ \alpha\text{Al}$, and $[1\ 1\ -2\ 0]\text{TiB}_2 // [0\ -1\ 1]\alpha\text{Al}$. (OR2)

275 OR2 is actually equivalent to:

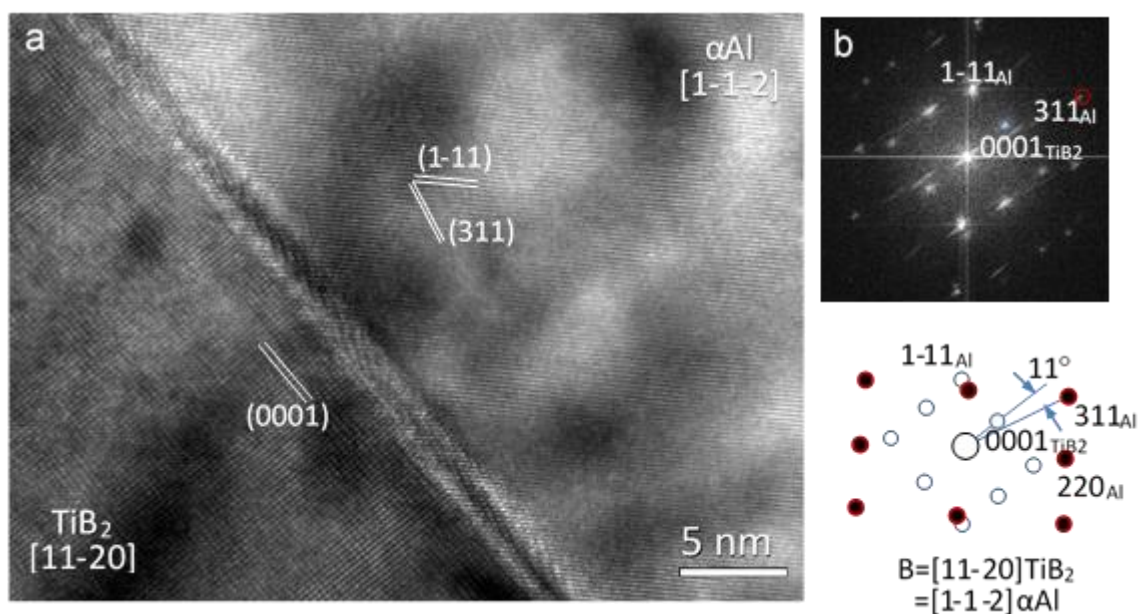
276 $(0\ 0\ 0\ 1)\ [1\ 1\ -2\ 0]\text{TiB}_2 // (5\ 5\ 4)\ [0\ -1\ 1]\alpha\text{Al}$ (OR2a)

277 In this case, the actual crystal plane of αAl which is parallel to (0 0 0 1)TiB₂ is (5 5 4), a
 278 relatively high index crystal plane of αAl.

279 However, TEM/STEM examinations of the TiB₂ particles collected from Al-8.4Si alloy melt
 280 inoculated with 0.2% Al-5Ti-1B grain refiner failed to find any well-defined OR between TiB₂
 281 and αAl, although as many as 80 TiB₂ particles in total were examined in multiple thin foil

282 TEM specimens. TiB_2 and adjacent Al were occasionally found to be in some sort of
 283 orientations considerably deviated from OR1. For example, Figure 6 shows that, in one
 284 occasion, $(1\ 1\ 1)$ αAl plane is far away from being paralleled to $(0\ 0\ 0\ 1)$ TiB_2 , and $[1\ 1\ 0]$ αAl
 285 zone is not parallel to $[1\ 1\ -2\ 0]$ TiB_2 zone either. Instead, $[1\ -1\ -2]$ αAl direction is parallel to
 286 $[1\ 1\ -2\ 0]$ TiB_2 direction, with a relatively high index $(3\ 1\ 1)$ plane of αAl being about 11
 287 degrees away from being parallel to $(0\ 0\ 0\ 1)$ surface of TiB_2 . Obviously this does not give a
 288 defined OR.

289



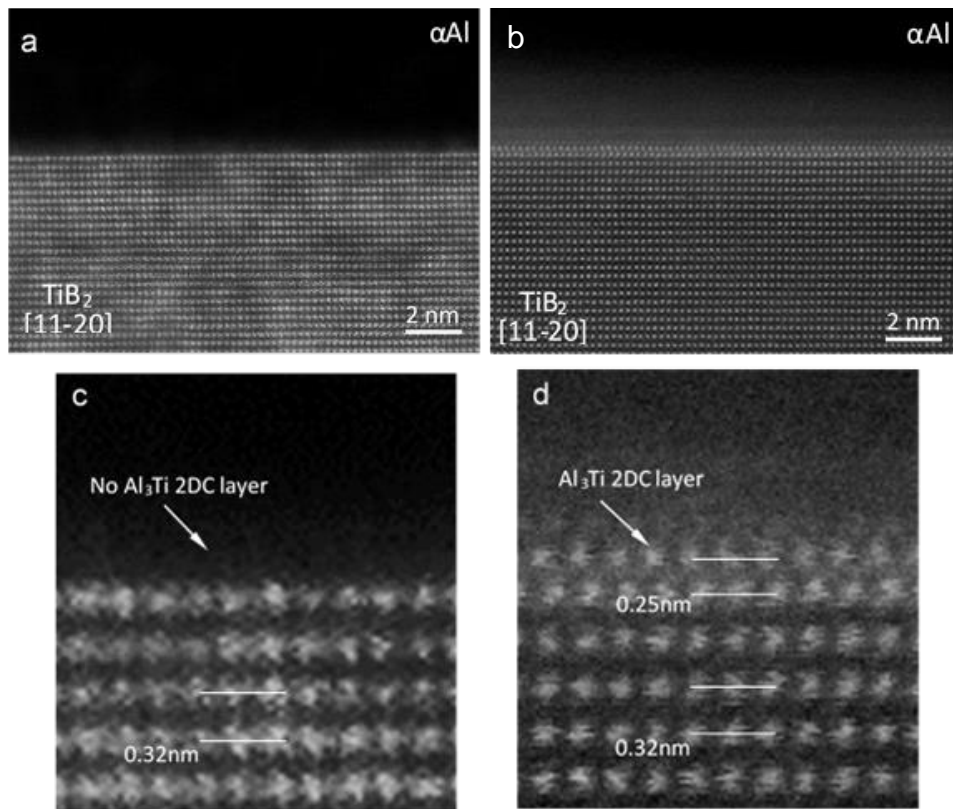
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291 Fig. 6 (a) High resolution TEM image showing $\text{TiB}_2/\alpha\text{Al}$ interface of a TiB_2 particle in Al-8.4Si
 292 alloy sample where the TiB_2 particle and αAl grain are viewed along $[1\ 1\ -2\ 0]$ TiB_2 and $[1\ -1\ -$
 293 $2]$ αAl zone directions, respectively, and (b) the corresponding fast Fourier transformation
 294 (FFT) pattern and its index.

295

296 Figures 7a and 7c are the high resolution STEM Z-contrast HAADF images showing the
 297 $\text{TiB}_2/\alpha\text{Al}$ interface of a TiB_2 particle in Al-8.4Si alloy, which suggest that there exists no bulk
 298 phase at the interface, verifying the above result from traditional high resolution TEM in Figure
 299 4. Again, atomically sharp and smooth $\text{TiB}_2/\alpha\text{Al}$ interfaces were observed. In comparison with
 300 the TiB_2 in CP-Al sample where the Al_3Ti 2DC atomic layer is reserved (Figures 7b and 7d), [8]
 301 it is found that the pre-existing Al_3Ti 2DC layer is missing on the $(0\ 0\ 0\ 1)$ TiB_2 surface for the
 302 TiB_2 particle collected from the Al-8.4Si sample (Figures 7a and 7c). High resolution STEM
 303 examination of multiple TiB_2 particles collected from the Al-8.4Si melt confirmed consistently
 304 the disappearance of Al_3Ti 2DC layer from TiB_2 surface.

305 However, a different situation was revealed for the TiB_2 particles collected from Al-2.0Si melt.
 306 Figure 8a is the high resolution STEM HAADF image across $\text{TiB}_2/\alpha\text{Al}$ interface with the TiB_2
 307 particle being viewed along its $[1\ 1\ -2\ 0]$ zone direction. It is noted in Figure 8b, which is the
 308 enlargement of the rectangular region marked in Fig 8a, that the Al_3Ti 2DC remains on the left
 309 hand side of the $(0\ 0\ 0\ 1)$ TiB_2 surface but is absent on the right hand side. As shown at higher
 310 magnification in Figure 8b, the brightness of the atomic columns of the Al_3Ti 2DC layer in the



311

312 Fig. 7 High resolution STEM Z-contrast HAADF images of $\text{TiB}_2/\alpha\text{Al}$ interface showing (0 0 0
 313 1) surface of TiB_2 viewed along $[1\ 1\ -2\ 0]\text{TiB}_2$ zone direction in (a, c) Al-8.4Si alloy and (b, d)
 314 CP-Al. It is clear from (c, d) the HAADF images at higher magnifications that the Al_3Ti 2DC
 315 layer [8, 36] is missing on the (0 0 0 1) TiB_2 surface in (c) Al-8.4Si sample but present in (d)
 316 CP-Al sample.

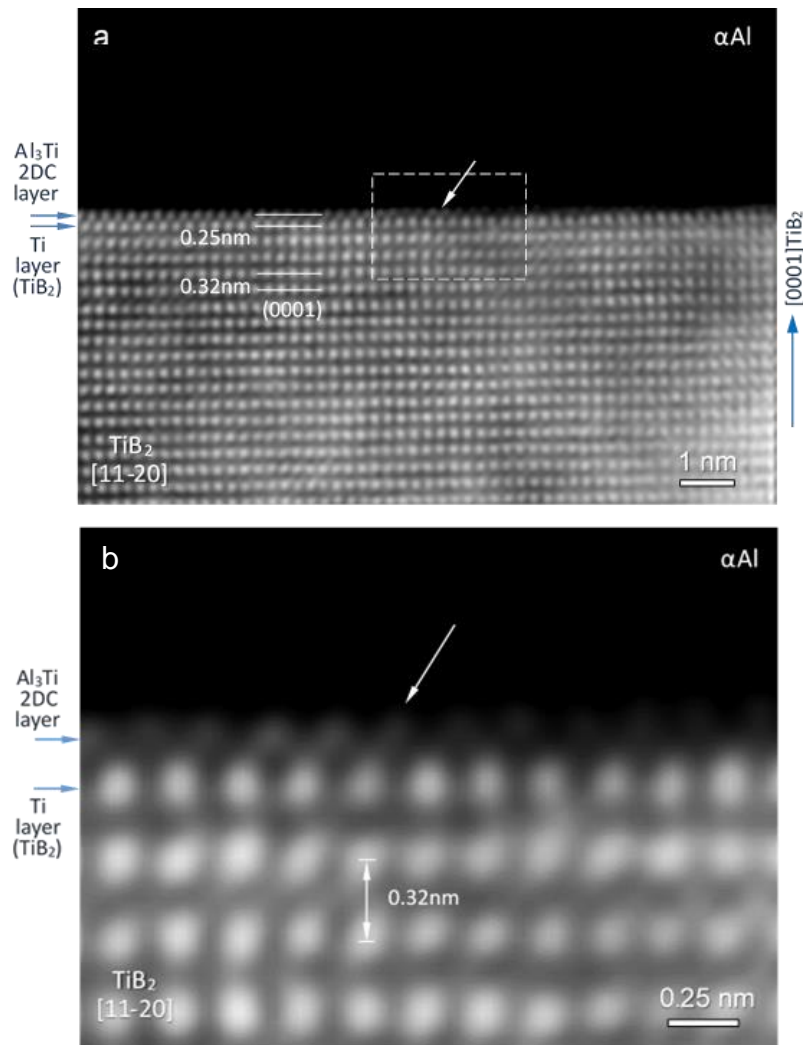
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318 STEM HAADF image is seen to start weakening at the position marked by the arrow and the
 319 atomic columns disappear completely towards the right hand side of the interface. This
 320 suggests that it is of significance that the Al_3Ti 2DC layer is not stable and tends to dissolve in
 321 the Al-Si melt. Figure 8 shows the on-going dissolution process of the 2DC layer, which occurs
 322 gradually after the TiB_2 particles were added to the Al-Si melt and holding at the processing
 323 temperature. In this work, Al_3Ti 2DC, which was formed on the surface of TiB_2 particles
 324 during production process of the commercial Al-5Ti-1B grain refiner, [8] was readily observed
 325 to remain on the surface of TiB_2 particles collected from the Al-2.0Si melt. This is in contrast
 326 to the situation in Al-8.4Si sample where the Al_3Ti 2DC layer was not at all observed, although
 327 multiple number of TiB_2 particles have been examined by high resolution STEM. That the
 328 possibility to observe the remaining Al_3Ti 2DC layer is considerably smaller in Al-8.4Si
 329 sample than that in Al-2.0Si indicates a faster dissolution rate for the 2DC layer in Al-Si melt
 330 with a higher Si content.

331

332 3.3 Si Segregation at $\text{TiB}_2/\alpha\text{Al}$ interface

333 Apparently Si concentration plays an important role in determining the dissolution kinetics of
 334 the Al_3Ti 2DC layer. It is therefore essential to study the chemical profiles across $\text{TiB}_2/\alpha\text{Al}$

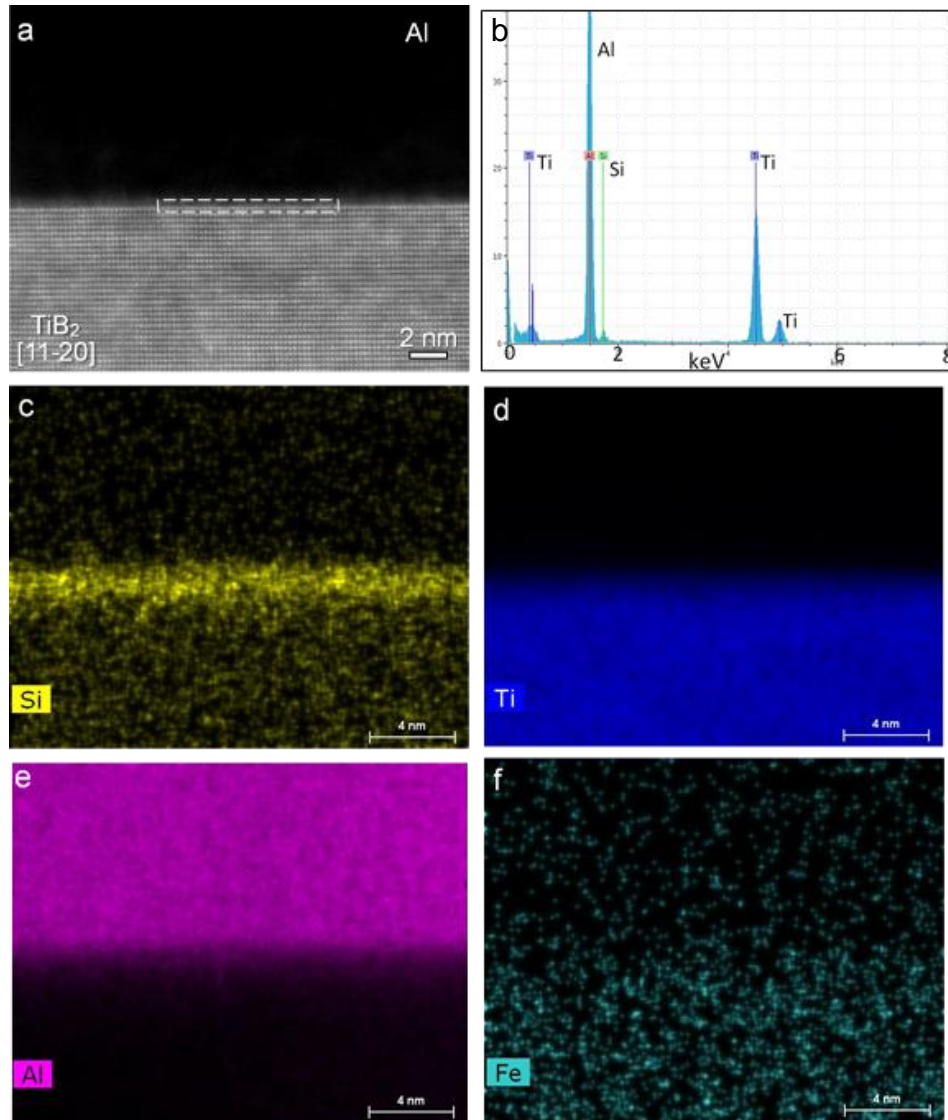


335
 336 Fig. 8 High resolution STEM HAADF images across $\text{TiB}_2/\alpha\text{Al}$ interface viewed along $[1\ 1\ -2\ 0]$
 337 TiB_2 zone direction showing (a) on-going dissolution (starting at the point marked by the arrow)
 338 of Al_3Ti 2DC layer on $(0\ 0\ 0\ 1)$ surface of TiB_2 particle collected from Al-2.0Si alloy melt, and
 339 (b) enlargement of the marked rectangular region in (a).

340
 341 interface. Figure 9 presents the EDS results obtained from Al-8.4Si sample. The STEM
 342 HAADF image in Figure 9a shows the $\text{TiB}_2/\alpha\text{Al}$ interface with no Al_3Ti 2DC layer covering
 343 the TiB_2 surface, and the corresponding Super-X EDS spectrum in Figure 9b taken from the
 344 local interface region marked in Figure 9a shows a major peak at energy 1.74 keV, i.e., the
 345 characteristic K_α peak of Si. More evidence of Si segregation at the $\text{TiB}_2/\alpha\text{Al}$ interface is
 346 provided by the elemental mapping of Si (Figure 9c), accompanied by those of Ti, Al and Fe,
 347 one of the main impurities in CP-Al (Table 1), as shown in Figures 9d-9f, respectively. It
 348 should be pointed out that Si segregation at $\text{TiB}_2/\alpha\text{Al}$ interface is hardly visible in terms of the
 349 brightness contrast in HAADF image due to the small difference of atomic number of Si (14)
 350 from that of Al (13). The EDS mapping did not suggest segregation of Fe at $(0\ 0\ 0\ 1)\text{TiB}_2/\alpha\text{Al}$
 351 interface (Figure 9f). Further SuperX EDS analysis of other Al-Si alloys revealed that Si
 352 segregation at the $\text{TiB}_2/\alpha\text{Al}$ interface is common to all the Al-Si alloys. The elemental mapping
 353 in Figure 10, where the Al_3Ti 2DC layer was survived partially on the left-hand side of $(0\ 0\ 0\ 1)$

354 TiB_2 surface found in a TiB_2 particle collected from Al-2.0Si melt, indicates a similar Si
355 segregation (Figure 10b) at the interface with and without the Al_3Ti 2DC.

356 Besides at $\{0\ 0\ 0\ 1\}\text{TiB}_2/\alpha\text{Al}$ interface, Si was found to segregate also to $\{1\ 0\ -1\ 0\}\text{TiB}_2/\alpha\text{Al}$
357 interfaces, as shown by the EDS mapping in Figure 11. As a result, the TiB_2 particles added to
358 Al-Si melt are actually coated by a Si-enriched layer of Al-Si melt where the Si concentration
359 is higher than that in the bulk melt away from the $\text{TiB}_2/\alpha\text{Al}$ interface.

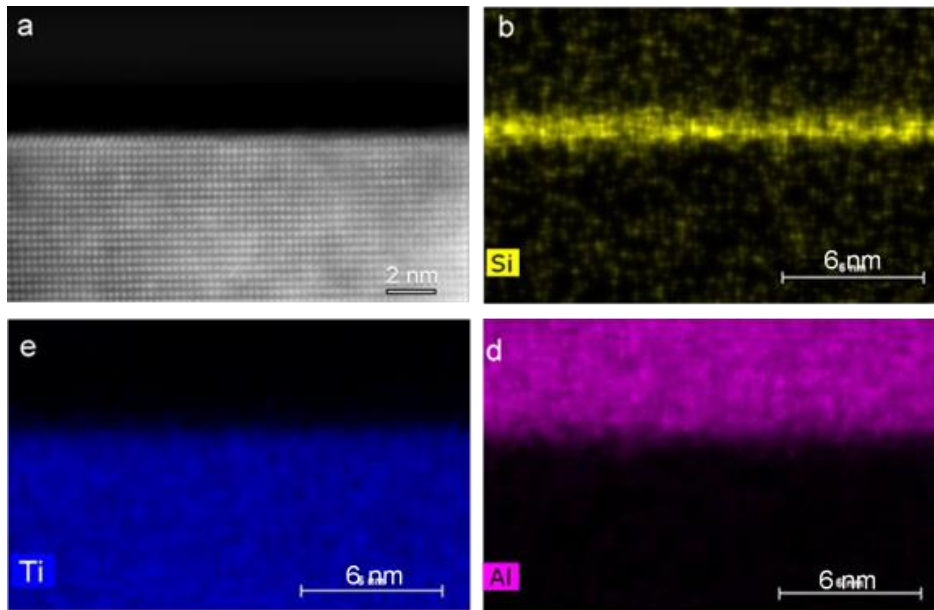


360
361 Fig. 9 (a) STEM Z-contrast HAADF image of TiB_2/Al interface in Al-8.4Si alloy sample
362 inoculated with 0.2 wt% Al-5Ti-1B grain refiner; (b) Super-X EDS spectrum taken from the
363 local region marked in (a) at the interface, and (c-f) Super-X EDS elemental mapping of (c) Si
364 (yellow), (d) Ti (blue), (e) Al (purple) and (f) Fe (cyan) showing Si segregation at the interface.
365

366 4. Discussion

367 4.1 Facilitating TEM examination of nucleants by melt filtration

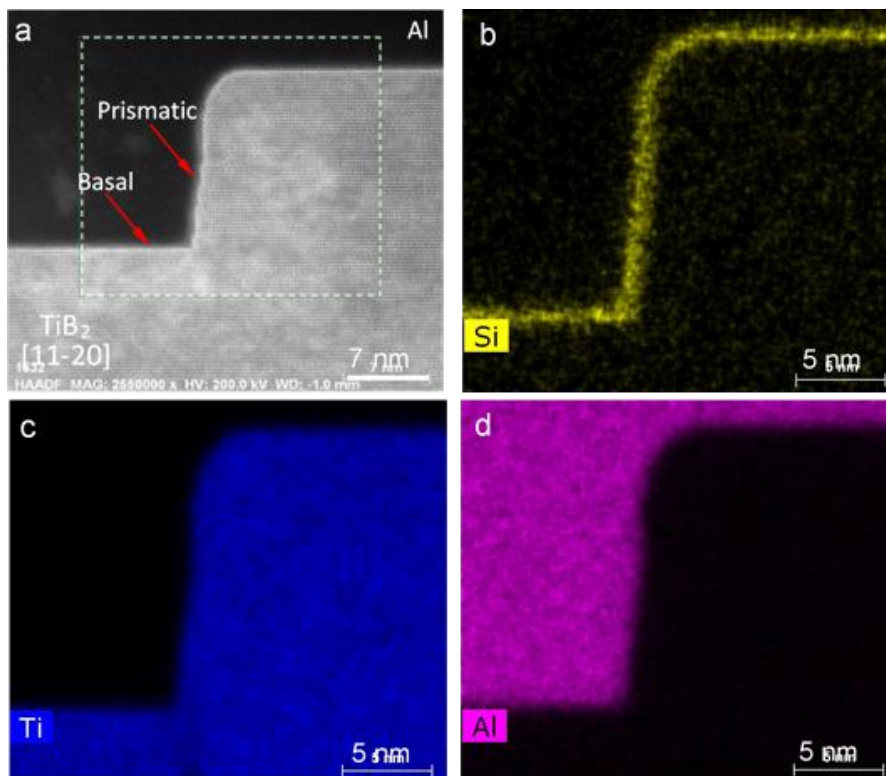
368 It is well accepted by the community that a well-defined OR observed by TEM is a direct
369 evidence of nucleation of a solid on a nucleant. However, the difficulty comes from the



370

371 Fig. 10 (a) High resolution STEM HAADF image across TiB₂/αAl interface viewed along [1 1
 372 -2 0] TiB₂ zone direction showing partially dissolved Al₃Ti 2DC layer on the (0 0 0 1) surface
 373 of the TiB₂ particle collected from Al-2.0Si melt, and (b-d) Super-X EDS elemental mapping
 374 of (b) Si (yellow), (c) Ti (blue) and (d) Al (purple) across the TiB₂/αAl interface showing that
 375 Si segregation is independent of the Al₃Ti 2DC.

376



377

378 Fig. 11 (a) STEM HAADF image of TiB₂/Al interface in Al-8.4Si alloy inoculated with 0.2 wt%
 379 Al-5Ti-1B grain refiner, and (b-d) Super-X EDS mapping of (b) Si (yellow), (c) Ti (blue) and
 380 (d) Al (purple) across the TiB₂/αAl interface, showing Si segregation on both {0 0 0 1} basal
 381 and {1 0 -1 0} prismatic surfaces of TiB₂.

382 preparation of thin foil specimens for TEM examination. We take TiB₂ particles in Al-alloys as
383 an example to demonstrate the challenge. If a TiB₂ particle (say 0.5 μm in size) has nucleated
384 an Al grain (say 200 μm in size), it would sit inside the Al grain. The probability to find this
385 TiB₂ particle on a 2D sectioning using the traditional metallography technique would be lower
386 than one in a million, even lower probability to find this TiB₂ particle in the limited electron-
387 transparent regions around the perforation of a φ3 mm disc for TEM examination. This
388 explains why there has been no success in obtaining such an OR by TEM to evidence
389 nucleation in the history of Al-Ti-B master alloys until the mid-1990s. Schumacher and Greer
390 used devitrification of an Al-based metallic glass containing a high density of TiB₂ particles as
391 an analogue to the nucleation of α-Al on TiB₂, and obtained successfully the first HRTEM
392 images of TiB₂/Al interface in this analogue alloy. [66, 67] Successful examination of TiB₂/Al
393 interface only became a routine when the melt filtration technique was used for TEM sample
394 preparation in 2015. [8]

395 Pressurized melt filtration, as described previously, allows a significant increase of TiB₂
396 particle number density in a localized region of the melt, but it does not change either the
397 particle potency or melt composition. According to the recent understanding of early stages of
398 solidification, [68] the heterogeneous nucleation processes of the melt before and after filtering
399 are exactly the same, although the increase in particle number density may leads to an increase
400 grain initiation events, thus a finer grain size. Both increase in TiB₂ particle number density
401 and decrease in grain size favor the promotion of the probability of successful TEM samples
402 containing TiB₂/Al interface. So far, this technique has been successfully deployed to study the
403 mechanisms of grain refinement, [8] Zr-poisoning [36] and Si-poisoning (this work), all related
404 to TiB₂ particles in Al-alloys.

405

406 4.2 Si interfacial segregation and its effect on nucleation

407 Interfacial segregation of Si at the TiB₂/Al-Si melt interface is both theoretically plausible and
408 practically feasible. Experimentally, Si segregation has been observed at TiB₂/melt interfaces
409 in the literature under various conditions. [37, 52-54, 69] Khalifa *et al* observed Si segregation
410 on surfaces of various inclusions in Al melt, including TiB₂ and Al₂O₃. [60] Even with a very
411 low concentration as an impurity in NiAl/TiB₂ composite, a Si segregation layer about ~0.6 nm
412 thick was detected at (0 0 0 1)/TiB₂/matrix interface. [69] McKay *et al* [52-53] and Schumacher
413 *et al* [54] also observed Si segregation on the surface of TiB₂ in amorphous Al-Si-Ni and Al-
414 Cu-Ni-Si alloys. It is confirmed in this work that Si segregates to both the basal and prismatic
415 surfaces of TiB₂ particles in Al-Si alloy melts (Figures 9, 10 and 11). Theoretically, interfacial
416 segregation is driven by reduction of interfacial energy and can be described by the Gibbs
417 adsorption isotherm. [70] Solute segregation at substrate/liquid interface has been demonstrated
418 to change both interfacial energies and the wetting behavior, and therefore affects
419 heterogeneous nucleation behavior. [71-73] Recently, Men and Fan [74] have applied the
420 Gibbs adsorption isotherm to analyze solute segregation at substrate/liquid interfaces and
421 showed that the interfacial solute segregation is governed by i) the difference in interfacial
422 energies between the pure solute/substrate and pure solvent/substrate interfaces, ii) the heat of
423 mixing of the solution, and iii) the difference in entropies of fusion between pure solute and
424 solvent. Due to the lack of relevant input data in the literature, an accurate prediction of Si

425 segregation at the $\text{TiB}_2/\text{Al-Si}$ melt interface is not possible. However, a qualitative analysis
426 using the above model [74] does suggest that a significant amount of excess Si can segregate at
427 the $\text{TiB}_2/\text{Al-Si}$ melt interface. The higher the Si concentration in the melt, the more enrichment
428 of Si at the interface is resulted.

429 Si segregation at the $\text{TiB}_2/\text{Al-Si}$ melt interface leads to the formation of a 2-dimensional solution
430 (2DS). Under the experimental conditions of this work, the high resolution TEM and STEM
431 examination has confirmed that there is no formation of either 2D compound (2DC) or 3D bulk
432 phase at the $\text{TiB}_2/\alpha\text{Al}$ interface (Figures 4 to 8), although Si segregation is clearly observed at
433 the interface. According to the Gibbs adsorption isotherm, solute segregation driven by
434 interfacial energy reduction occurs only in one or two atomic layers. It is therefore believed
435 that Si enrichment at the interface is a 2-dimensional solution (2DS). In addition, it seems that
436 the formation of Si-enriched 2DS occurs only in Al-Si melt containing sufficiently high Si
437 concentration, since notable Si segregation at the TiB_2/melt interface was not observed in CP-
438 Al which contains about 0.03% Si as one of the main impurities. [8, 36] This is different from
439 the cases of interfacial segregation of Ti or Zr, where ordered Al_3Ti 2DC [8] and Ti_2Zr 2DC
440 [36] were observed at the $\text{TiB}_2/\alpha\text{Al}$ interface at low concentrations of Ti or Zr in the melt,
441 respectively. The formation of Si-enriched 2DS at the $\text{TiB}_2/\text{Al-Si}$ melt interface is expected to
442 play an important role in modifying the surface of TiB_2 particles, and therefore their potency
443 for heterogeneous nucleation.

444 An important phenomenon revealed in this work is the dissolution of Al_3Ti 2DC layer which
445 was formed on the TiB_2 surface during the fabrication of the commercial Al-5Ti-1B grain
446 refiner. [8] The Al_3Ti 2DC layer is at least kinetically stable in CP-Al melt, with its dissolution
447 rate in CP-Al being so slow that a visible effect on grain refinement was observed only after
448 isothermal holding of the inoculated melt for a period of time up to 78 hours at 800°C . [8]
449 However, it is clear from this work that the stability of Al_3Ti 2DC layer is considerably
450 reduced when sufficiently high Si content is present in the Al melt. The Al_3Ti 2DC layer is
451 readily observed to remain on some TiB_2 particles collected from Al-2.0Si melt (Figures 8 and
452 10) but hardly found on the surface of those TiB_2 particles collected from Al-8.4Si melt
453 (Figures 7 and 9). This fact indicates that the Al_3Ti 2DC layer becomes thermodynamically
454 and/or kinetically unstable and dissolves faster in a higher Si melt than in a lower Si melt.
455 Furthermore, Figures 5 and 6 show that a well-defined OR1 and a slightly deviated OR2
456 between TiB_2 and αAl are found at low Si content (2.0%), but no defined OR is observed at
457 high Si contents (8.4%) in this study, suggesting that a fewer number of TiB_2 particles had
458 participated in grain initiation of αAl in the high Si melt, in comparison with that in the low Si
459 melt. As the Al_3Ti 2DC layer is on the Ti-terminated (0 0 0 1) TiB_2 surface, the dissolution rate
460 is actually dependent on the local Si content at the interface, which is expected to be much
461 higher than that in the bulk melt due to the Si interfacial segregation. With a given level of Al-
462 5Ti-1B addition and thus a fixed total number of the TiB_2 particles in the melt, more TiB_2
463 particles will lose their Al_3Ti 2DC layer when Si concentration is higher due to the
464 correspondingly faster dissolution rate, and then the number fraction of those unaffected TiB_2
465 particles decreases. In comparison with Zr effect on stability of the Al_3Ti 2DC, dissolution of
466 the Al_3Ti 2DC layer in Al-Si melt requires a much higher Si concentration and the dissolution
467 rate is dependent on Si content, whilst 580 ppm (0.058%) Zr in Al melt is sufficient to make
468 the Al_3Ti 2DC layer dissolve completely at a similar temperature. [36]

469 Dissolution of Al₃Ti 2DC layer results in a reduced potency of TiB₂ particles for heterogeneous
470 nucleation of αAl. Nucleation and subsequent grain initiation events are dependent on the exact
471 physical and chemical characteristics of the nucleant particles introduced to the alloy melt from
472 grain refiner, and their subsequent interactions with the melt. After dissolution of the pre-
473 existing Al₃Ti 2DC layer, heterogeneous nucleation of αAl takes place directly on the (0 0 0 1)
474 surface of TiB₂, and the crystallographic matching is between {0 0 0 1}TiB₂ and {1 1 1}αAl
475 according to OR1. The original small lattice misfit 0.09% at the interface between (1 1 1)αAl
476 and Al₃Ti 2DC now becomes much larger (-4.22%) between (0 0 0 1)TiB₂ and (1 1 1)αAl [8,
477 36]. The lattice misfit is even larger (more negative) between TiB₂ and Al-Si 2DS because the
478 lattice parameter of αAl will be reduced when Si is dissolved in it. For instance, the lattice
479 misfit is increased to -4.30% as the lattice parameter 0.4049 nm for pure Al decreases to 0.4047
480 nm for Al-0.97Si solid solution. [75] Consequently, the original TiB₂ particles in the grain
481 refiner lost their potency for heterogeneous nucleation of αAl in Al-Si melt with high enough
482 Si contents.

483

484 4.3 Mechanism of Si poisoning

485 Based on the previous analysis, a new mechanism for Si poisoning can be postulated here:

- 486 • Preferential interfacial segregation of Si leads to enrichment of Si at the TiB₂/Al-Si melt
487 interface. The higher the Si concentration in the melt, the more enrichment of Si at the
488 interface is;
- 489 • The pre-existing Al₃Ti 2DC layer on the TiB₂ surface dissolves gradually in the melt,
490 resulting in a loss of nucleation potency for the TiB₂ particles. The dissolution rate of
491 the 2DC layer increases with the increase of Si content at the interface;
- 492 • The overall effect is a reduced total number of potent (at original state) TiB₂ particles
493 available for heterogeneous nucleation and grain initiation of αAl, and hence an
494 increased grain size.

495 This mechanism for Si poisoning is consistent with the previous experimental observations
496 reported in the literature. Previous experiments and this work showed that, upon Si poisoning,
497 the minimum grain size of Al-Si alloys appeared at ~3% Si. This is in agreement with the
498 above mechanism. When Si content is less than 3%, the dissolution rate of Al₃Ti 2DC is slow
499 and the majority of the added TiB₂ particles are not affected or only partially affected.
500 Therefore, the number of TiB₂ particles reserving its original state is sufficient for grain
501 refinement. In this case, growth restriction will prevail over Si poisoning, giving rise to a
502 marginal decrease in grain size with increasing Si content until 3% Si. With further increase in
503 Si content, Si interfacial segregation increases and thus the dissolution of Al₃Ti 2DC layer
504 becomes faster, resulting in a rapid decrease in the number density of the potent TiB₂ particles,
505 and therefore Si poisoning effect prevails over the growth restriction, leading to an increase in
506 grain size.

507 The experimental observation of defined ORs between TiB₂ and Al (Figures 5 and 6) and
508 dissolution of Al₃Ti 2DC (Figures 7-8) in this work suggest that the number density of potent
509 nucleant particles decreases with increasing Si content beyond 3%. Khalifa *et al* [60] showed
510 that, in Al-Si alloys containing 0.3-0.9% Si, most of TiB₂ particles observed were located

511 within Al grains rather than the grain boundaries or the inter-dendritic regions. In contrast,
512 more TiB₂ particles in Al-6.4Si alloy were found to locate in inter-dendritic regions,
513 confirming that the TiB₂ particles were inactive nucleant particles in the high-Si alloys.
514 Recently, *in-situ* observation using synchrotron radiation technology showed directly that
515 nucleation events decreased with increasing Si content in TiB₂-inoculated Al-Si alloys. [34] In
516 Al-Si alloys inoculated with 0.33% Al-3Ti-1B, the nucleation frequency was found to be
517 reduced by two order of magnitude from 137 s⁻¹ to 1.1 s⁻¹ when Si content increased from 1.0%
518 to 9.0%. [34]

519 This mechanism also explains the dependence of Si poisoning on holding time and the addition
520 level of Al-Ti-B grain refiner. [28, 32] Abdel-Reihim *et al* found that, with 0.1% Al-5Ti-1B
521 addition, the grain size of Al-3.5Si alloy increased from about 240 μm to 320 μm when holding
522 time increases from 10 min. to 60 min.. [28] Kori *et al* [32] showed that, the higher the Si
523 content (>7%) and the longer the holding time, the larger the grain size was. For instance, the
524 grain size of Al-10Si alloy inoculated with 0.2% Al-5Ti-1B was about 260 μm and 650 μm for
525 holding times of 5 min. and 120 min., respectively. [32] In addition, they found that, with a
526 high level of grain refiner addition, for instance 0.6% (6 times of the standard 0.1%), [32] grain
527 refinement was achieved for high Si Al-Si alloys. The reason for stronger Si poisoning at a
528 longer holding time is because longer holding time leads to more impotent TiB₂ particles and
529 hence larger grain size. However, this decrease in number density of potent particles can be
530 compensated by increased level of grain refiner addition.

531 Si poisoning was also reported to occur in un-inoculated Al-Si alloys with the minimum grain
532 size occurring at a similar Si content (~3%) to that in the inoculated alloys. [26, 29-31, 34] Si
533 poisoning in un-inoculated Al-Si alloys is believed to be related to Si interfacial segregation,
534 despite different types of inoculants. As Prasad *et al* showed, [34] un-inoculated Al-Si alloys
535 also exhibited a significant number of nucleation events, suggesting that nucleation was
536 triggered by random oxide or impurity particles, in spite of their lower and different potencies
537 than that of TiB₂. Si could segregate to the interfaces between these oxide particles and Al-Si
538 melt, leading to reduction in their potency for nucleation and therefore poisoning.

539 Our previous work [8, 36] has shown that Ti and Zr atoms in Al melts segregate preferentially
540 to TiB₂/αAl interface, resulting in the formation of Al₃Ti 2DC or Ti₂Zr 2DC layer, respectively.
541 However, the effect of the two types of 2DC layer on heterogeneous nucleation is just opposite,
542 with Al₃Ti 2DC enhancing nucleation while Ti₂Zr 2DC impeding nucleation. In this work, Si
543 segregation at TiB₂/Al-Si melt interface results in dissolution of Al₃Ti 2DC, with the
544 dissolution rate being dependent on Si concentration at the interface. It is demonstrated that
545 interfacial segregation of solute elements can significantly alter the behavior of the substrate
546 during heterogeneous nucleation process. From nucleation point of view, segregation of solute
547 elements leads to either enhancement or impediment of heterogeneous nucleation. This makes
548 it possible to manipulate the nucleation process by modification of substrates through
549 deliberate segregation of certain elements.

550

551 5. Conclusions

552 1) Al-5Ti-1B grain refiner is not effective for grain refining Al-Si alloys with Si
553 concentration higher than 3%. Under the TP-1 solidification conditions of this work, the

- 554 grain size of α Al is increased from 195 ± 22 μm to 867 ± 78 μm as Si content is increased
555 from 2% to 10% in the hypoeutectic Al-Si alloys inoculated with 0.2% of Al-5Ti-1B
556 grain refiner. The increase in grain size with Si content was accompanied by a
557 morphological transition from cellular to dendritic for the primary α Al phase.
- 558 2) A well-defined orientation relationship (OR) between TiB_2 and α Al, $(0\ 0\ 0\ 1)\ [1\ 1\ -2\ 0]$
559 $\text{TiB}_2 // (1\ 1\ 1)\ [0\ -1\ 1]\ \alpha$ Al, is observed for the TiB_2 particles collected from Al-2.0Si
560 melt, but no defined OR is found for the TiB_2 particles in Al-8.4Si alloy melt.
- 561 3) Si segregates preferentially to the solid/liquid interface between TiB_2 and Al-Si melt on
562 both the $\{0\ 0\ 0\ 1\}$ basal and $\{1\ 0\ -1\ 0\}$ prismatic surfaces of TiB_2 particles.
- 563 4) The Al_3Ti 2DC layer formed on the TiB_2 surface during the grain refiner production
564 process becomes unstable in Al-Si melt and therefore dissolves into the melt with time.
565 The 2DC layer is readily found to remain on the surface of some of the TiB_2 particles in
566 low Si (2.0%) samples but not observed on the particles in high Si (8.4%) samples,
567 showing an increased dissolution rate at high Si contents.
- 568 5) There is no evidence of formation of 2D or 3D bulk phase at the TiB_2/α Al interface under
569 the experimental conditions of this work. Segregated Si atoms stay in a thin layer of Al-
570 Si melt at the interface as 2 dimensional solution (2DS).
- 571 6) A new mechanism for Si poisoning is proposed: Preferential interfacial segregation of Si
572 leads to enrichment of Si at the $\text{TiB}_2/\text{Al-Si}$ melt interface, and this in turn makes the pre-
573 existing Al_3Ti 2DC on the TiB_2 surface unstable and thus dissolve gradually in the melt
574 resulting in a loss of its nucleation potency. The overall effect is a reduced total number
575 of potent TiB_2 particles available for heterogeneous nucleation and grain initiation of α Al,
576 and hence an increased grain size.
- 577 7) This new mechanism is consistent with the experimental findings in the literature, such as
578 grain size minimum at 3% Si, dependence of grain size on holding time and levels of
579 grain refiner addition, Si poisoning of un-inoculated Al-Si melts, and so on.

580

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584

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