

1

2 **Formation of θ -Al₁₃Fe₄ and the multi-step phase transformations** 3 **to α -Al₈Fe₂Si, β -Al₅FeSi and δ -Al₄FeSi₂ in Al-20Si-0.7Fe alloy**

4 **Zhongping Que***, Chamini L. Mendis

5 Brunel Centre for Advanced Solidification Technology (BCAST), Brunel University London,
6 Uxbridge, Middlesex UB8 3PH, UK

7 *Corresponding author E-mail address: Zhongping.Que@brunel.ac.uk

8

9 **Abstract**

10 Formation of Al₁₃Fe₄ and the phase transformations on these particles between numbers of
11 different types of Fe-containing intermetallic compounds (FIMCs) were observed in Al-20Si-
12 0.7Fe alloy when solidified at a slow cooling rate (0.01K/s). The experimental results show
13 that the Al₁₃Fe₄ phase (monoclinic) solidified initially and transformed into an intermediate α -
14 Al₈Fe₂Si (hexagonal) and nano-scaled α -Al grains via a quasi-peritectic reaction.
15 Subsequently, the intermediate α -Al₈Fe₂Si transformed into β -Al₅FeSi (monoclinic). The
16 transformed β -Al₅FeSi phase contained many defects, and with heat treatment (530°C for 30
17 minutes) transformed into δ -Al₄FeSi₂ (tetragonal). The variation in the composition and the
18 lattice parameters of these FIMCs was examined with TEM which shows that the phase
19 transformation among FIMCs starts from FIMCs with lower Si content and process to FIMCs
20 with higher Si content. The interfaces between each of these phases were examined to
21 determine the orientation relationships between various FIMCs. The phase transformation
22 mechanism and the FIMCs transformation sequence have been proposed based on the
23 experimental investigation.

24 **Keywords:** θ -Al₁₃Fe₄; α -Al₈Fe₂Si; β -Al₅FeSi; δ -Al₄FeSi₂; phase transformation; diffusion

25

26 **1. Introduction**

27 Fe is an unavoidable impurity which deteriorates the mechanical properties of Al alloys,
28 especially in the recycled Al alloys by forming different types of Fe-containing intermetallic
29 compounds (FIMCs) [1-2]. More than 20 different types of FIMCs were reported in the
30 literature, including α -Al₁₅(Fe, Mn)₃Si₂, β -Al₅FeSi, δ -Al₄FeSi₂, θ -Al₁₃Fe₄, Al₆(Fe, Mn) [3-7].
31 They have different crystal structures, compositions and morphologies. Due to the difficulties
32 associated with nucleation [8], the phase selection can easily be changed during the initial
33 nucleation stage [9], which affects the subsequent phase transformation [10]. The equilibrium
34 phase diagrams calculated to date using experimental results and thermodynamic modelling
35 cannot accurately predict the formation of FIMCs, as there is a gap in the understanding of the
36 nucleation, the composition-lattice relationship, and the phase transformation of these FIMCs.

37 It remains unclear as to which of the FIMCs are stable at elevated temperatures and
38 subsequently undergo phase transformations as the temperature is reduced, and if subsequent
39 phase transformations occur but not to completion due to kinetic constraints such as diffusion
40 of elements.

41 The mechanical properties of the alloys containing these FIMCs are influenced by their
42 morphologies. As reported, the primary β -Al₅FeSi and θ -Al₁₃Fe₄ which have monoclinic
43 crystal structures have plate-like morphologies [11-13]. The primary Al₆(Fe, Mn) phase that
44 has an orthorhombic crystal structure forms with a hollow needle-like morphology, and the
45 eutectic structure has a Chinese script morphology [14-15]. The α -Al₁₅(Fe, Mn)₃Si₂ which has
46 a body centred cubic structure has a compacted morphology as the primary phase [9, 16-17].
47 The plate-like and needle-like morphologies are extremely harmful to the mechanical
48 properties. Small plate-like FIMCs such as β -Al₅FeSi can be subsequently refined following
49 heat treatment, but heat treatment may only be used with limited success to achieve an ideal
50 distribution and morphology of FIMCs. Heat treatments cannot refine other types of FIMCs
51 such as α -Al₈Fe₂Si with a Chinese script morphology. Some research show that deformation
52 can result in limited refinement on these FIMCs, which is limited to the wrought alloys [18].
53 Our recent research found that during solidification, the phase selection of core-shell structured
54 of FIMCs depends on the heterogeneous nucleation process [10]. The initially nucleated FIMCs
55 will nucleate subsequent binary and or ternary eutectic structures [19]. The compounds will act
56 as a nucleus for not only FIMCs in the eutectic structure but also the other intermetallic phases
57 in Al alloys such as Mg₂Si, which could easily nucleate on the primary FIMCs [19].
58 Additionally, the eutectic structures nucleated on the selected intermetallic compounds easily
59 grown into large size compared when α -Al was selected as the leading phase [19].

60 Our previous work [8] showed that different types of FIMCs require different nucleation
61 undercooling in based on the composition of the alloys. This caused the competition among
62 multiple types of FIMCs which start at the very early nucleation stage. Therefore, the phase
63 selection is difficult to control. However, the morphology of the FIMCs does not only depends
64 on the initially nucleated FIMCs, but also affected by the subsequent phase transformations
65 among FIMCs. Our recent investigations [10] showed that although the initially nucleated
66 FIMC is plate-like Al₁₃Fe₄, after phase transformation into α -AlFeSi, the FIMC particles have
67 a compacted morphology which is less harmful for the mechanism properties. Thus,
68 understanding the competition between the heterogeneous nucleation of FIMCs is not
69 sufficient, as the subsequent phase transformations can be critical to the microstructure control
70 through changes in the FIMCs morphology.

71 These FIMCs have a range of compositions and lattice parameters. Many alloying elements
72 such as Si, Mn, Ni, Cr etc. can incorporate into many types of the FIMCs [20-25], which not
73 only causes the compositional variations but also modifies the lattice parameters, and in some
74 circumstances, modifies or changes the crystal structure. Especially, the Si incorporation in
75 the FIMCs cause complicated phase reactions among different types of FIMCs. As reported,

76 the Si content in the alloys affect the formation of the FIMCs [26]. Only a limited number of
77 reports has been published on the phase transformation phenomena between different FIMCs
78 [27-29]. In this study, further investigation on two aspects: the compositions variation and the
79 crystal structure transition among these FIMCs are reported. A number of well-defined
80 orientation relationships between phases will be elucidated.

81 Al-Si eutectic alloys have been widely investigated due to range of excellent properties,
82 including excellent wear and corrosion resistance, elevated temperature strength, low
83 coefficient of thermal expansion, good casting performance, and high specific strength.
84 Therefore, the hypereutectic Al-Si alloys are widely used in aeronautic and automotive
85 industries. Some transitional elements such as Fe and Ni etc. are added to improve the elevated
86 temperature mechanical properties by forming the thermally stable intermetallic compounds
87 [26, 30-33]. It is reported that [32] an Al-13 wt% Si casting alloy containing 0.5~1.20 wt.% Fe
88 forms needle-like β -AlFeSi which dramatically deteriorates the mechanical properties,
89 particularly the elongation. Therefore, to overcome these negative effects, it is very important
90 to investigate the formation of FIMCs and the phase transformations that occur during
91 solidification which affect the final morphology of FIMCs. Based on our current understanding
92 of the heterogeneous nucleation of FIMCs, the phase relationship and phase transformation
93 mechanism are very important to control the microstructure in both primary and secondary Al
94 alloys. The authors propose that the FIMCs structure should be controlled during the
95 solidification rather than through subsequent heat treatments.

96 In this study, the phase transformations among different types of FIMCs, in a hypereutectic Al-
97 20Si-0.7Fe alloy, with different crystal structures will be discussed. According established
98 phase diagrams the initial FIMC expected in this alloy is β -AlFeSi in the eutectic structure.
99 However, experimental observations with very slow cooling rates does not show the formation
100 of this phase but a different primary FIMC which undergoes number of phase transformations
101 that culminate in δ -AlFeSi. The phase transformations between different types of FIMCs were
102 investigated. The phase relationship and phase transformation mechanisms were examined
103 with SEM, SEM-EBSD and TEM.

104

105 **2. Experimental**

106 The Al-20Si-0.7Fe alloy investigated in this work had a composition of 20.5 ± 0.5 Si and
107 0.65 ± 0.05 Fe (compositions are in wt.% unless specified otherwise). Commercially pure Al
108 (>99.86 %), Al-50 Si were used to prepare the alloy. Fe was added as impurity in CP Al and
109 Al-Si master alloy. The pure Al and Al-Si alloys were heated in the electric resistance furnace
110 to 800°C and held there until molten. The molten pure Al was stirred to accelerate the melting
111 of Al-Si master alloy. After fully molten, the alloy was held for further 30 minutes. Before
112 each casting, the slag on the surface of the melt was removed and melt stirred to ensure
113 homogeneity. The melt was cast into a “mushroom” steel mould. The mushroom sample was

114 manually ground for the composition test. The composition measurement was carried on
115 foundry master Spark chemical analyser. Finally, the melt was cast into a preheated TP-1
116 mould [34] at a pouring temperature of 760°C. The remaining melt was solidified in the
117 furnace. The sample solidified in the furnace has a very slow cooling rate with the average
118 cooling rate from pouring temperature to solidified sample was calculated as 0.01K/s according
119 to the cooling curve.

120 The TP-1 sample was cut in the cross section which has a cooling rate of 3.5K/s at 38mm height
121 from the bottom. The slowly solidified sample was sectioned from top to bottom. The primary
122 Si particles were observed at the top due to the lower density of Si (2.32g/cm^3 [35]) compared
123 with Al (2.70g/cm^3 [36]). The Fe-containing intermetallic compounds (FIMCs) settled to the
124 bottom of the casting. The phase formation and transformation of these FIMCs were analysed
125 with optical microscopy (OM), scanning electron microscopy (SEM), electron backscatter
126 diffraction (EBSD) and transmission electron microscopy (TEM). Specimens for
127 metallography were prepared using standard procedures. The solidification characteristics of
128 the samples were examined with a Zeiss optical microscope fitted with the Axio Vision 4.3
129 image analysis system. The detailed features of phases were examined with a Zeiss Supra 35
130 scanning electron microscope (SEM), operated at an accelerating voltage of 20 kV. The EBSD
131 measurements were made on a Zeiss Cross beam 340 FIB-SEM, operated at an accelerating
132 voltage of 20kV. The scanning step size was 0.1-0.2 μm . Thin foils for high resolution
133 transmission electron microscopy (HRTEM) examinations were prepared from slowly cooled
134 sample (0.01 K/s) which were mechanically ground and cut into 3 mm diameter discs. The
135 discs were then hand ground to a thickness of less than 60 μm , followed by ion-beam-thinning
136 using a Gatan precision ion polishing system (PIPS) at ion beam energy of 3.0-5.0kV and an
137 incident angle of 4-6°. TEM examination was performed on a JEOL 2100F transmission
138 electron microscope equipped with EDX (Energy Dispersive X-ray) Spectroscopy facility
139 operated at an accelerating voltage of 200 kV.

140

141 3. Results

142

143 3.1 As-cast microstructure

144

145 Fig.1 shows the as-cast microstructure of the Al-20Si-0.7Fe alloy solidified at different cooling
146 rates. Fig.1a shows that when solidified at 3.5K/s, the microstructure of Al-20Si-07Fe consisted
147 of large size primary Si particles and surrounding eutectic structures. The FIMCs in this sample
148 have a plate-like morphology, and these FIMCs phases can only be observed in the eutectic
149 structures. No primary FIMCs phases can be observed. However, when the Al-20Si-0.7Fe alloy
150 solidified at 0.01K/s, the primary Si particles floated to the top of the sample, and some large
151 FIMCs particles settled to the bottom and observed, Fig.1b. These settled FIMCs particles have
152 a long plate-like morphology. The details of these particles were further examined.

153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192

Fig.2 shows the microstructure of the Fe-containing intermetallic compounds in Al-20Si-0.7Fe alloy solidified at 0.01K/s (Fig. 2a). These particles were later identified as $\text{Al}_{13}\text{Fe}_4$ with SEM, EBSD and TEM analysis. Within the yellow rectangle in Fig 2a two different grey contrast was observed and details of this region is show in Figs.2b-c. The $\text{Al}_{13}\text{Fe}_4$ was considered to be the parent phase and two different structures were observed on the surface of these parent $\theta\text{-Al}_{13}\text{Fe}_4$ particles. They are identified as ($\alpha\text{-Al}_8\text{Fe}_2\text{Si} + \alpha\text{-Al}$) two-phase region and $\beta\text{-Al}_5\text{FeSi}$ single phase. Fig.2c shows the very edge of a $\theta\text{-Al}_{13}\text{Fe}_4$ particle, which showed that the particles transformed into $\beta\text{-Al}_5\text{FeSi}$ before the end of the solidification process. This as-cast sample was heat treated at 530°C for 30 minutes. The microstructure in the sample was directly observed again with SEM-BSD without re-polishing. The SEM-EDX spectra shown in Fig.2d demonstrates that the Si content in the edge of the particle is much higher than that of the centre of the parent FIMC. The SEM-EDX results are summarised in Table 1 indicated this trend clearly, while there is a significantly large variation in the absolute values of composition. The compositions measured with SEM-EDX spectra are similar to those of TEM-EDX spectra data discussed below. The surface FIMC was identified subsequently with TEM as $\delta\text{-Al}_4\text{FeSi}_2$ which has the tetragonal structure. These results suggested that the phase formation sequence from the parent $\theta\text{-Al}_{13}\text{Fe}_4$ may be observed and it is: $\theta\text{-Al}_{13}\text{Fe}_4 \rightarrow$ the two-phase structure ($\alpha\text{-Al}_8\text{Fe}_2\text{Si} + \alpha\text{-Al}$) $\rightarrow \beta\text{-Al}_5\text{FeSi} \rightarrow$ (heat treatment) $\delta\text{-Al}_4\text{FeSi}_2$.

Initially, various phases present in the FIMCs observed in Fig. 2 were characterised with EBSD, Fig.3. Fig.3a shows the SEM image of the area investigated and the EBSD phase mapping is shown in Fig.3b. The EBSD mapping indicates that the parent phase, $\theta\text{-Al}_{13}\text{Fe}_4$ (green, left) is associated with the $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$ phase (blue, middle). Microstructure also contained $\beta\text{-Al}_5\text{FeSi}$ (orange) and $\alpha\text{-Al}$ (yellow) regions observed on the top right of the image. The interfaces between these phases were analysed with TEM in detail and presented in the following sections.

The composition and the corresponding lattice parameters of these FIMCs were listed in Table 1 and 2. The compositions of FIMCs in this study (Table 1) show that a 2.7at.% Si was contained in $\theta\text{-Al}_{13}\text{Fe}_4$. Additionally, the Si content in FIMCs from centre ($\text{Al}_{13}\text{Fe}_4$) to edge ($\beta\text{-Al}_5\text{FeSi}$) then to ($\delta\text{-Al}_4\text{FeSi}_2$) increased continuously. The lattice parameter and crystal structure information in Table 2 shows that these FIMCs have crystal structure as reported [4, 6, 38, 39], such as $\theta\text{-Al}_{13}\text{Fe}_4$ (monoclinic), $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$ (hexagonal), $\beta\text{-Al}_5\text{FeSi}$ (monoclinic). Some difference in lattice parameters of these FIMCs between this study and the previously reported were observed, which is likely due to the compositional difference between this study and those reported.

3.2 $\theta\text{-Al}_{13}\text{Fe}_4/\alpha\text{-Al}_8\text{Fe}_2\text{Si}$ interface

193 The interface between parent θ -Al₁₃Fe₄ phase and adjacent α -Al₈Fe₂Si was analysed with TEM.
 194 Both θ -Al₁₃Fe₄ and α -Al₈Fe₂Si were examined using more than 8 TEM EDX spectra and using
 195 more than 3 zone directions in TEM to identify the crystal structure. The interface between the
 196 θ -Al₁₃Fe₄ and α -Al₈Fe₂Si was examined with high resolution TEM (HRTEM) and shown in
 197 Fig.4. Fig.4a shows the interface between the θ -Al₁₃Fe₄ and α -Al₈Fe₂Si when the incident
 198 electron beam is parallel to $[\bar{1} \bar{3} \bar{4}]$ zone direction of θ -Al₁₃Fe₄ and $[\bar{3} 2 \bar{1}]$ of α -Al₈Fe₂Si. The
 199 interface is not sharp, and a transition area with 5-10 nm thick range can be observed at the
 200 interface. The fast Fourier transformation (FFT) patterns of θ -Al₁₃Fe₄ and α -Al₈Fe₂Si viewed
 201 along $[\bar{1} \bar{3} \bar{4}]$ zone direction of θ -Al₁₃Fe₄ and $[\bar{3} 2 \bar{1}]$ of α -Al₈Fe₂Si were presented in Fig.4 b
 202 and c, respectively. The FFT pattern which contains both sets of θ -Al₁₃Fe₄ and α -Al₈Fe₂Si is
 203 shown in Fig.3 d. The schematically indexed FFT of Fig.4d was shown in Fig.4e, which shows
 204 a well-defined orientation relationship (OR) between the θ -Al₁₃Fe₄ and α -Al₈Fe₂Si: $(\bar{1} 0 3)$
 205 Al₁₃Fe₄ // $(1 \bar{1} 1)$ α -Al₈Fe₂Si and $[\bar{1} \bar{3} \bar{4}]$ Al₁₃Fe₄ // $[\bar{3} 2 \bar{1}]$ α -Al₈Fe₂Si.

206

207 3.3 (α -Al₈Fe₂Si + α -Al) two-phase structure

208

209 Fig.2 also illustrates that a (α -Al₈Fe₂Si + α -Al) two-phase structure which contains nano-scaled
 210 α -Al cells is associated with the parent θ -Al₁₃Fe₄ and β -Al₅FeSi single phase. This structure
 211 appears to be similar to an eutectic structure and is considered to be an intermediate structure
 212 for the phase transformation from the parent θ -Al₁₃Fe₄ to the other types of FIMCs. Thus, a
 213 detailed understanding of this structure is very important to elucidate the microstructural
 214 evolution during phase transformation of FIMCs.

215

216 The detailed information on the α -Al₈Fe₂Si + α -Al structures were examined with TEM and
 217 shown in Fig.5 and Fig.6. The bright field image shown in Fig.5a demonstrates that the α -Al
 218 phase distributes uniformly in the α -Al₈Fe₂Si phase with a size distribution of approximately
 219 100-200 nm in diameter. The selected area electron diffraction (SAED) patterns of α -Al and α -
 220 Al₈Fe₂Si are shown in Fig.5b and c, respectively to illustrate the cells of α -Al and continuous
 221 α -Al₈Fe₂Si phase. The HRTEM shown in Fig.5d presents the interface between the α -Al (top
 222 right) and α -Al₈Fe₂Si (bottom left) and demonstrates that although the crystal structure of α -Al
 223 and α -Al₈Fe₂Si are very different, the interface between α -Al and α -Al₈Fe₂Si is not sharp. A
 224 transition region with a layer thickness of approximately 10-20 nm is clearly observed at the
 225 interface between the α -Al islands and the α -Al₈Fe₂Si phase, Fig 5d. This layer cannot be
 226 characterised according to known FIMCs.

227

228 The α -Al cells in the α -Al₈Fe₂Si phase were further examined with TEM, Fig 6, and show that
 229 the α -Al cells contained small scale precipitates, Fig. 6a. The bright field TEM image contains
 230 coffee bean like contrast observed due to lattice mismatch between the α -Al and the precipitate

231 phase which has a lath or plate like morphology, Fig 6a. The SAED patterns of α -Al with the
232 incident electron beam paralleled to $\langle 1\ 1\ 0 \rangle_{\text{Al}}$ and $\langle 2\ 1\ 1 \rangle_{\text{Al}}$ zone direction were shown in
233 Figs.6b-c. When the incident electron beam paralleled to $\langle 1\ 1\ 0 \rangle_{\text{Al}}$ zone there are no extra
234 reflection due to the precipitates but when the electron beam is parallel to $\langle 2\ 1\ 1 \rangle_{\text{Al}}$ zone,
235 number of extra diffraction spots are observed on the SAED that is attributed to the precipitates,
236 however the precipitate phase does not seem to be in low index zone in this orientation and
237 cannot be indexed accurately. The HRTEM image of a α -Al particle with the incident electron
238 beam paralleled to $\langle 1\ 1\ 0 \rangle_{\text{Al}}$ is shown in Fig.6d. A multi atomic layer structure with well-
239 defined orientation relationship with α -Al and a lath or plate like morphology. The HRTEM
240 image (Fig.6e) when the electron beam paralleled to $\langle 2\ 1\ 1 \rangle_{\text{Al}}$ zone did not show clear
241 precipitates but spherical regions which suggest that the precipitates have a plate like
242 morphology with $\langle 1\ 1\ 1 \rangle_{\text{Al}}$ type habit planes. The precipitates, however do not show clear
243 atomic planes when viewed along $\langle 2\ 1\ 1 \rangle_{\text{Al}}$. TEM-EDX analysis, Table 1, show the presence
244 of Fe and Si in the regions containing these precipitates and it is likely that these are β - Al_5FeSi
245 phase.

246

247 **3.4 α - $\text{Al}_8\text{Fe}_2\text{Si}/\beta$ - Al_5FeSi interface**

248 The β - Al_5FeSi phase is observed at the surface of the parent θ - $\text{Al}_{13}\text{Fe}_4$ particles in the as-cast
249 sample. This phase is associated with both the parent $\text{Al}_{13}\text{Fe}_4$ phase and the α - $\text{Al}_8\text{Fe}_2\text{Si}$ with an
250 irregular interface. Additionally, this phase has an interface with the α -Al cells which form in
251 the two-phase (α - $\text{Al}_8\text{Fe}_2\text{Si} + \alpha$ -Al) structure and the α -Al cells in β - Al_5FeSi itself. The interface
252 between the β - Al_5FeSi and the intermediated two-phase structure (α - $\text{Al}_8\text{Fe}_2\text{Si} + \alpha$ -Al) was
253 examined carefully with TEM, and shown in Fig.7.

254 The bright filed TEM image in Fig.7a shows the interface between the two-phase region and
255 the β - Al_5FeSi phase. The main interface between the two-phase (α - $\text{Al}_8\text{Fe}_2\text{Si} + \alpha$ -Al) structure
256 and β - Al_5FeSi is the α - $\text{Al}_8\text{Fe}_2\text{Si}/\beta$ - Al_5FeSi interface. High resolution TEM micrograph in
257 Fig.7b shows the interface between α - $\text{Al}_8\text{Fe}_2\text{Si}$ (bottom right) and β - Al_5FeSi (top left) viewed
258 along the zone direction of $[0\ 1\ 0]$ of β - Al_5FeSi , showing a faceted interface between α -
259 $\text{Al}_8\text{Fe}_2\text{Si}$ and β - Al_5FeSi . The selected area electron diffraction (SAED) pattern contains both
260 the β - Al_5FeSi with the incident electron beam paralleled to $[0\ 1\ 0]$ zone direction and α -
261 $\text{Al}_8\text{Fe}_2\text{Si}$ with the incident electron beam paralleled to $[1\ 2\ 3]$ zone direction is shown in Fig.7c.
262 The OR between α - $\text{Al}_8\text{Fe}_2\text{Si}$ and β - Al_5FeSi was identified: $(0\ 0\ 2)\ \beta$ - $\text{Al}_5\text{FeSi} // 10.2^\circ (1\ 0\ 0)\ \alpha$ -
263 $\text{Al}_8\text{Fe}_2\text{Si}$, $[0\ 1\ 0]\ \beta$ - $\text{Al}_5\text{FeSi} // [1\ 2\ 3]\ \alpha$ - $\text{Al}_8\text{Fe}_2\text{Si}$.

264

265 **3.5 β - $\text{Al}_5\text{FeSi}/\alpha$ -Al interface**

266 Fig.8a shows that the α -Al cells associated with β -Al₅FeSi not only from in the two-phase
267 region, but also from as some large regions of α -Al in β -Al₅FeSi. There is no evidence of an
268 orientation relationship between β -Al₅FeSi and the nano α -Al cells in the two-phases (α -
269 Al₈Fe₂Si + α -Al) structure. However, an orientation relationship between β -Al₅FeSi and the
270 larger regions of α -Al which associated each other were observed as shown in Fig.8. Fig.8a
271 shows the bright field TEM image of the interface of the β -Al₅FeSi and the large α -Al. The
272 SAED which contains both β -Al₅FeSi and α -Al is shown in Fig.8b. The corresponding
273 schematic representation of the two overlapped patterns from the interface of β -Al₅FeSi and
274 the large α -Al were shown in Fig.8c. The HRTEM image shown in Fig.8d illustrates the
275 interface between β -Al₅FeSi and the α -Al. It shows that the β -Al₅FeSi has a faceted interface
276 with the α -Al. The orientation relationship between the β -Al₅FeSi and the large α -Al as shown
277 in the yellow frame of Fig.8a is defined as $(0\ 0\ 1)\ [1\ 1\ 0]\ \beta\text{-Al}_5\text{FeSi} // 2.5^\circ\ \{\bar{3}\ 3\ \bar{1}\} \langle 1\ 1\ 0 \rangle\ \alpha\text{-}$
278 Al using both the SAED analysis and the HRTEM image.

279

280 3.6 Faulted structure within β -Al₅FeSi

281 The defects in β -Al₅FeSi can be observed from the HRTEM in Fig.8d. The further investigation
282 on the β -Al₅FeSi was conducted and an example is shown in Fig.9. When observed under
283 TEM bright field mode, some defaults can be observed within the β -Al₅FeSi (Fig.9a). Fig.9b
284 illustrates the boundary between two β -Al₅FeSi regions. The boundary/interface between these
285 two β -Al₅FeSi regions was investigated with HRTEM. The HRTEM image (Fig.9c) shows a
286 clear interface which contains defects which are planar defects and are likely to be twins or
287 stacking faults. The inserted corresponding FFT patterns of β -Al₅FeSi from the top and bottom
288 grains were shown in Figs.9d-e. They demonstrate that these two grains have the exactly same
289 crystal orientation but there are extra reflections on the FFT collected from the region below
290 the interface as compared with the region above. The monoclinic crystal structure (Space group
291 symmetry C12/c1) of the β -Al₅FeSi phase mean that some reflections such as $(1\ 0\ 1)$ and $(1\ 0$
292 $0)$ are forbidden [4]. These forbidden reflections are visible in the FFT pattern recorded from
293 the area below the interface suggesting that the structure contain defects.

294

295 3.7 β -Al₅FeSi/ δ -Al₄FeSi₂ interface

296 In order to understand the phase transformation sequence observed in this alloy, a prepared
297 sampled was heat treated at 530°C for 30 minutes to observe whether the FIMCs will transform
298 further. The SEM image in Fig.1d shows the phase transition of Al-20Si-0.7Fe alloy after
299 heated treatment. It demonstrates that the volume of two phases (α -Al₈Fe₂Si + α -Al) structure
300 decreased significantly while a new phase, which was identified as δ -Al₄FeSi₂ with SEM-

301 EDXS and TEM was formed at the edge of the particles adjacent to smaller volume of β -
302 Al_5FeSi .

303 The interface between the β - Al_5FeSi and δ - Al_4FeSi_2 phases on primary $\text{Al}_{13}\text{Fe}_4$ particle in Al-
304 20Si-0.7Fe alloy after heat treated at 530°C for 0.5 hour was examined with HRTEM analysis.
305 Fig.10 shows that the β - Al_5FeSi has a faceted interface with the δ - Al_4FeSi_2 phase when viewed
306 along [1 1 0] zone direction of both β - Al_5FeSi and δ - Al_4FeSi_2 . A transition region of a few
307 nano-meter in thickness was observed at the interface between β - Al_5FeSi and δ - Al_4FeSi_2 . A
308 well-defined orientation relationship was identified from the HRTEM as: (0 0 2) [1 1 0] β -
309 Al_5FeSi // (0 0 2) [1 1 0] δ - Al_4FeSi_2 .

310

311 4. Discussion

312

313 4.1 Formation of $\text{Al}_{13}\text{Fe}_4$

314 The casting experiments carried under different conditions showed an interesting phenomenon.
315 When solidified at a very slow cooling rate (0.01K/s), some large size primary $\text{Al}_{13}\text{Fe}_4$ particles
316 with phase transformation at the surface were observed in the Al-20Si-0.7Fe alloy which has
317 composition supposed not be possible to form according to the calculated equilibrium phase
318 diagram, Fig 11 a and the solidification path calculation using the Scheil model Fig 11 b. The
319 phase diagram of Al-0.7Fe- x Si alloys ($x=6\sim 22\text{wt.}\%$) shows that the primary equilibrium phase
320 for Al-0.7Fe-(>14.48)Si alloys was calculated to be Si. The formation temperature range for
321 the equilibrium of primary Si is large which is up to 111K (Al-20Si-0.7Fe). However, when
322 the Si concentration decreases during solidification process to the range of 9.45~14.48wt.%,
323 the calculated equilibrium primary phase become β - Al_5FeSi . The solidification paths of the
324 studied Al-20Si-0.7Fe and the eutectic Al-12.6Si-0.7Fe alloys were calculated and shown in
325 Figs.11b-c.

326 During the casting process, when solidified at a very slow cooling rate as 0.01K/s, the primary
327 Si formed and grow consuming Si in the melt. Therefore, the alloy concentration in the
328 remaining melt moves to near the eutectic point. As the calculated phase diagram show,
329 Fig.11a, before the composition reached the eutectic point, the primary FIMCs may form. Our
330 previous report shows that the phase selection between FIMCs are competitive which due to
331 the difficulties in nucleation of these FIMCs [8]. Due to the smaller nucleation undercooling
332 required, the $\text{Al}_{13}\text{Fe}_4$ is nucleated and form initially, which is same as our other reported [10].
333 However, when the alloy solidified at a faster cooling rate such as 3.5K/s, the solidification
334 process goes quickly. Therefore, the expected primary FIMCs did not form and the primary
335 $\text{Al}_{13}\text{Fe}_4$ form in place of the expected FIMC in the Al-20Si-0.7Fe alloy.

336

337 4.2 Phase transformation sequence

338 In this study, the phase reaction between θ -Al₁₃Fe₄, α -Al₈Fe₂Si, β -Al₅FeSi and δ -Al₄FeSi₂ were
339 investigated with SEM, EBSD and TEM to understand the sequence of phase transformation
340 that may be observed in an Al-Si-Fe alloy. The relevant solidification curves using the Scheil
341 solidification model for the Al-20Si-0.7Fe alloy were calculated and shown in Fig.11b. The
342 phase diagram and the solidification path calculation (Scheil model) shows that β is the only
343 FIMC observed in this alloy. However, the experimental investigation does not support this
344 phase transformation path. The experimental results demonstrated that the θ -Al₁₃Fe₄
345 decomposed and transformed into α -Al₈Fe₂Si + α -Al two phase structure during the
346 solidification process at a very slow cooling rate (0.01K/s). The θ -Al₁₃Fe₄ observed in this
347 investigation could be considered to be a pseudo binary phase with some Si (~2 at.%) dissolved
348 in the compound. The phase transformation is likely to be controlled by the diffusion of Si and
349 Fe in liquid phase at the start of the reaction. The nature of the microstructure that forms during
350 the phase transformation reactions involved in this alloy suggest that the changes in the
351 composition of Al₁₃Fe₄ results in the formation of α -Al₈Fe₂Si and α -Al dual phase structure.
352 As the phase transformation reaction progressed further, the intermediate phase α -Al₈Fe₂Si
353 transformed into β -Al₅FeSi, and the nano-scaled α -Al grew in size. Both the parent θ -Al₁₃Fe₄
354 phase and the β -Al₅FeSi have monoclinic crystal structures with many inherent defects within
355 to accommodate the growth of these particles. Subsequent heat treatment after casting resulted
356 in the transformation of the β -Al₅FeSi finally to δ -Al₄FeSi₂ which has a similar crystal structure
357 to that of β -Al₅FeSi. The details of the phase transformation between β -Al₅FeSi and δ -Al₄FeSi₂
358 will be discussed in a subsequent contribution. The phase transformations observed in the
359 FIMC are complex and discussed as steps that occurred during processing below.

360 Step 1: θ -Al₁₃Fe₄ \rightarrow α -Al₈Fe₂Si + α -Al

361 During this step, it is expected that the diffusion of Si continues through the structure at the
362 elevated temperatures to allow the compositional change associated with transformation of θ -
363 Al₁₃Fe₄ phase into α -Al₈Fe₂Si + α -Al. The slow cooling rate kept the sample at high
364 temperatures for a significant long time. This allowed the alloying elements to diffuse from θ -
365 Al₁₃Fe₄ to surrounding α -Al, and the θ -Al₁₃Fe₄ transformed into the intermediate α -Al₈Fe₂Si
366 phase. Some α -Al formed within α -Al₈Fe₂Si to accommodate the compositional change
367 associated with the θ -Al₁₃Fe₄ transformation to α -Al₈Fe₂Si. Some of Fe and Si diffused into α -
368 Al resulting in the formation of lath like precipitates within the α -Al grains (Fig.5).

369 Step 2: α -Al₈Fe₂Si \rightarrow β -Al₅FeSi + α -Al

370 As the transformation progressed, the nano-scale α -Al cells grow which results in
371 destabilisation of α -Al₈Fe₂Si due to continuous reduction in Al and enrichment of Si. That
372 caused the α -Al₈Fe₂Si transform into β -Al₅FeSi. During this process, faceted interfaces
373 between α -Al₈Fe₂Si and β -Al₅FeSi is observed with an orientation relationship between the β -
374 Al₅FeSi and α -Al. During this step, diffusion of Al and Si are the most important factor that
375 contribute to the phase reaction.

376 Step 3: $\beta\text{-Al}_5\text{FeSi} \rightarrow \delta\text{-Al}_4\text{FeSi}_2 + \alpha\text{-Al}$

377 The transformed $\beta\text{-Al}_5\text{FeSi}$ contain many defects as observed from the HRTEM (Fig.7d)
378 images. As the Fe and Si diffuse, the lattice parameter changed correspondingly. Interfaces
379 within a single crystal of $\beta\text{-Al}_5\text{FeSi}$ is observed (Fig.8b). With the further Si diffusion into the
380 $\beta\text{-Al}_5\text{FeSi}$ during heat treatment, the $\beta\text{-Al}_5\text{FeSi}$ transformed into $\delta\text{-Al}_4\text{FeSi}_2$.

381

382 4.3 Mechanism of phase transformation

383 The calculated phase diagram in Fig.11 shows that under equilibrium solidification conditions
384 the primary phase in this alloy to be Si. The experimental results show that the FIMCs particles
385 at the bottom of the crucible are not connected with the primary Si particles. Therefore, during
386 casting process, the Fe-containing intermetallic compounds may be nucleated on the other
387 potent substrates such as inclusions or crucible wall. Our recent paper [8] examined the
388 heterogeneous nucleation undercooling among several types of FIMCs and showed that the
389 $\text{Al}_{13}\text{Fe}_4$ requires smallest nucleation undercooling among 5 different types of FIMCs observed
390 in Al based casting alloys. Therefore, the $\text{Al}_{13}\text{Fe}_4$ phase nucleated initially as it is likely to be
391 the easier phase for heterogeneous nucleation. It was reported that the Si can be incorporated in
392 $\text{Al}_{13}\text{Fe}_4$ phase in Al-Fe-Si alloys forming a pseudo binary $(\text{Al},\text{Si})_{13}\text{Fe}_4$ phase [37]. The
393 extension of Si solubility in $\text{Al}_{13}\text{Fe}_4$ forms only as a metastable phase and with further cooling
394 and diffusion of Si and Fe through the structure results in $\text{Al}_{13}\text{Fe}_4$ becoming unstable and
395 transform into the other higher Si containing FIMCs such as $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$, $\beta\text{-Al}_5\text{FeSi}$ and $\delta\text{-Al}_4\text{FeSi}_2$.
396

397 As discussed above, the phase transformations between various FIMCs observed are diffusion-
398 controlled transformations. The phase transformation of FIMCs ($\text{Al}_{13}\text{Fe}_4$) with a low Si content
399 to finally other FIMCs with a higher Si content ($\delta\text{-Al}_4\text{FeSi}_2$) depends on the Fe and Si diffusion
400 at high temperature and long holding times. The TEM-EDX results from various FIMCs
401 observed in this study are listed in Table1. It shows that the Fe content decreased and the Si
402 content increased in each of the FIMC as the phase transformation sequence progressed,
403 confirming that in high Si containing Al alloys, the FIMCs such as $\delta\text{-Al}_4\text{FeSi}_2$ with higher Si
404 content is more stable than those with a lower Si content FIMCs such as $\text{Al}_{13}\text{Fe}_4$.

405 In this study, the β was calculated to be the equilibrium FIMC according to the Scheil model.
406 However, the experimental results showed that the selected primary FIMC is θ which contains
407 much lower Si content than all the other FIMCs reported in this manuscript. Then the non-
408 equilibrium θ particles transformed into intermediate $\alpha(\text{Al}_8\text{Fe}_2\text{Si})$ which contained a higher Si
409 content, which then transformed into β (higher Si content) during the solidification. However,
410 it can be seen from Fig.2a that the surface of θ only partially transformed during solidification.
411 Therefore, the phase transformation among FIMCs which starts from FIMCs with lower Si
412 content and then progress to FIMCs with higher Si content can be a continuous process driven

413 by diffusion of Si until the rate of diffusion is not sufficient to feed the phase transformation.
414 The phase transformation following the heat treatment from β to δ indicates that the stability
415 of β is lower than that of δ . In addition, some defected structures (Fig.9) observed in the
416 transformed β also indicate that the β phase may not be the stable phase. However, it does not
417 mean that the δ is the most stable phase, further phase transformation still might be possible
418 with further heat treatment. However, according to the calculated equilibrium phase diagram
419 β -Al₅FeSi should be the only FIMC forming in this system. It is noted that the majority of
420 equilibrium phase diagrams for Al-Fe-Si system are verified through experimental
421 investigations where specimens were continuously cooled rather than held isothermally to
422 promote phase transformations [41-42]. In this case β -Al₅FeSi and δ -Al₄FeSi₂ phase
423 transformation was only observed following isothermal heating following very slow cooling at
424 0.01K/s. Therefore, we propose that the current version of the Al-Fe-Si phase diagram based
425 on cooling and heating experiments and microstructure characterisation with bulk techniques
426 such as X-ray diffraction (XRD) may not have captured a localised phase transformation from
427 β -Al₅FeSi and δ -Al₄FeSi₂.

428 To understand the crystal structure transformation during cooling and heat treatment, the lattice
429 parameters of these relevant FIMCs were measured to compare with the literature data [4-6]
430 and shown in Table 2. The phase transformation from Al₁₃Fe₄ to α -Al₈Fe₂Si is discussed in
431 detail below to illustrate the crystal structure change associated with the phase transformation.

432 Grin. et.al [6] reported the monoclinic structure of Al₁₃Fe₄ by considering a cell with $a=$
433 15.492Å, $b= 8.078$ Å, $c= 12.471$ Å, $\beta=107.69^\circ$. In Grin's model, in the monoclinic Al₁₃Fe₄
434 crystal, there are 15 Al positions, 5 Fe positions. The Al₂ position in the structure is partially
435 occupied (0.92) and the occupancy of Si in each Al positions is 0.08. All Fe positions in the
436 crystal structure are fully occupied (1). Our recent paper [38] show that Fe can partially occupy
437 Al₅, Al₇ and Al₉ positions in the structure. In a perfect Al₁₃Fe₄ crystal, the number of positions
438 Si occupied sites are limited. With increased Si in the Al₁₃Fe₄ crystal Al will be replaced with
439 Si to accommodate the Si resulting in a lattice parameter change. In this study, with the
440 formation of Al cells from Al₁₃Fe₄, the Si content in the Al₁₃Fe₄ phase is enriched causing nano-
441 scaled faults within the structure and lattice parameters variation. Corby et.al (1977) [39]
442 reported a hexagonal structure of α -Al₈Fe₂Si with a cell with $a=b=12.404$ Å, $c=26.234$ Å,
443 $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$. There are 18 Al positions and 5 Fe positions. All Al positions are
444 partially occupied, and Si can replace Al in each of the Al positions. The TEM-EDX results in
445 Table 1 shows that the Si content increased from 2.7±0.2 at.% to 11.6±0.1 at.% when phase
446 transit from Al₁₃Fe₄ to α -Al₈Fe₂Si. This result indicated that the increased Si content occupied
447 the rest Al positions and causing the crystal transform to α -Al₈Fe₂Si.

448
449 The monoclinic β -Al₅FeSi was reported [4] with $a= 6.1676$ Å, $b= 6.1661$ Å, $c= 20.8093$ Å,
450 $\beta=91^\circ$. In the monoclinic β -Al₅FeSi crystal, there are 6 Al positions, 1 Fe positions. And each
451 Al position is partial occupied (0.82). The occupancy of Si in each Al positions is 0.18.

452 Compared with α -Al₈Fe₂Si, the capacity accommodate Si is higher in the β -Al₅FeSi. Therefore,
453 in the high Si content Al alloys, the non-equilibrium FIMCs will transit into the higher FIMCs
454 with Si content. Thus, following heat treatment, the β -Al₅FeSi finally transformed into the δ -
455 Al₄FeSi₂ which has highest capacity to accommodate Si among the Fe-containing intermetallic
456 compounds reported [29]. The details of the phase transformation from β -Al₅FeSi to δ -Al₄FeSi₂
457 will be discussed in detail in a subsequent contribution.

458

459 5. Conclusions

460 Multi-step phase transformations between Fe-containing intermetallic compounds in high Si
461 Al alloys were observed following solidification sequence. The phase transformation sequence
462 can be described as:

- 463 ① $L \rightarrow \theta\text{-Al}_{13}\text{Fe}_4$;
464 ② $\theta\text{-Al}_{13}\text{Fe}_4 \rightarrow \alpha\text{-Al}_8\text{Fe}_2\text{Si} + \alpha\text{-Al}$;
465 ③ $\alpha\text{-Al}_8\text{Fe}_2\text{Si} \rightarrow \beta\text{-Al}_5\text{FeSi} + \alpha\text{-Al}$;
466 ④ $\beta\text{-Al}_5\text{FeSi} \rightarrow \delta\text{-Al}_4\text{FeSi}_2 + \alpha\text{-Al}$.

467 The phase transformation is controlled by the diffusion of constituent elements especially Si in
468 the FIMCs. Some nano-size α -Al reservoirs were observed to form within the FIMCs to
469 accommodate the changes in composition of FIMCs allowing smaller diffusion paths. The α -
470 Al₈Fe₂Si forms as the intermediate FIMC during the phase transformation from Al₁₃Fe₄ with a
471 low Si content to higher Si containing β -Al₅FeSi. Small amount Fe and Si remains in the α -Al
472 cells which caused the precipitation of Fe and Si rich phase and these precipitates were thought
473 to be β -Al₅FeSi. Clearly defined orientation relationships were observed at the interfaces
474 between $\theta\text{-Al}_{13}\text{Fe}_4//\alpha\text{-Al}_8\text{Fe}_2\text{Si}$, $\alpha\text{-Al}_8\text{Fe}_2\text{Si}//\beta\text{-Al}_5\text{FeSi}$, $\alpha\text{-Al}_8\text{Fe}_2\text{Si}//\alpha\text{-Al}$ and $\beta\text{-Al}_5\text{FeSi}//\alpha\text{-Al}$.

475

476

477 Acknowledgement

478 The EPSRC is gratefully acknowledged for providing financial support under Grant
479 EP/N007638/1.

480

481 References

- 482 [1] L. Zhang, J. Gao, L. Nana, W. Damoah, D. G. Robertson, Removal of Iron from aluminium:
483 A Review, Min. Proc. Ext. Met. Rev. 33 (2012) 99–157.
484 [2] X. Fang, G. Shao, Y.Q. Liu and Z. Fan, Effects of intensive forced melt convection on the
485 mechanical properties of Fe containing Al–Si based alloys, Mater. Sci. Eng. A 445–446
486 (2007) 65-72.
487 [3] M. Cooper, The crystal structure of the ternary alloy α (AlFeSi), Acta Crystall., 23 (1967)
488 1106-1107.

- 489 [4] V. Hansen, B.C. Hauback, M. Sundberg, C. Romming, J. Gjønnes, β -Al_{4.5}FeSi, A
490 Combined Synchrotron Powder Diffraction, Electron Diffraction, High-Resolution
491 Electron Microscopy and Single-Crystal X-ray Diffraction Study of a Faulted Structure,
492 Acta Crystall., Section B: Structural Science 54 (1998) 351-357.
- 493 [5] C. Gueneau, C. Servant, F. d'Yvoire, N. Rodier, Acta Crystall., Section C: Crystal Structure
494 Communications, 51(1995) 177-179.
- 495 [6] J. Grin, U. Burkhardt, M. Ellner, K. Peters. Refinement of the Fe₄Al₁₃ structure and its
496 relationship to the quasihomological homeotypical structures, Z. Kristallograp. (1979-
497 2010) 209 (1994) 479.
- 498 [7] V. Stefaniay, A. Griger, and T. Turmezey, Intermetallic phases in the aluminium-side
499 corner of the AlFeSi-alloy system, J. Mater. Sci., 22 (1987) 539-546.
- 500 [8] Z.P. Que, Y.P. Zhou, Y. Wang and Z. Fan, Composition templating for heterogeneous
501 nucleation of intermetallic compounds, Solidification Processing, 2017: 158-161.
- 502 [9] Z.P. Que, Y. Wang, Z. Fan, Formation of the Fe-containing intermetallic compounds during
503 solidification of Al-5Mg-2Si-0.7 Mn-1.1 Fe alloy, Metall. Mater. Trans. A, 49 (2018)
504 2173-2181.
- 505 [10] Z.P. Que, C.L. Mendis. Heterogeneous nucleation and phase transformation of Fe-rich
506 intermetallic compounds in Al-Mg-Si alloys, J. Alloys Comp., 836(2020):155515.
- 507 [11] C.M. Dinnis, J.A. Taylor, A.K. Dahle, As-cast morphology of iron-intermetallics in Al-Si
508 foundry alloys, Scr. Mater., 53 (2005), 955-958.
- 509 [12] S. Terzi, J.A. Taylor, Y.H. Chao, L. Salvo, M. Suery, E. Boller, A.K. Dahle, In situ study
510 of nucleation and growth of the irregular α -Al/ β -Al₅FeSi eutectic by 3-D synchrotron X-
511 ray microtomography, Acta Mater., 58(16) (2010) 5370-5380.
- 512 [13] K.K. Fung, X.D. Zou, C.Y. Yang, Transmission electron microscopy study of Al₁₃Fe₄
513 tenfold twins in rapidly cooled Al-Fe alloys, Philosophical Magazine Letters, 55(1) (1987)
514 27-32.
- 515 [14] Z.P. Que, Y.P. Zhou, Y. Wang, and Z. Fan, Effect of MgO on Phase Selection in Al-Mg-
516 Si-Fe-Mn Alloys, Trans. Indian. Inst. Met., 68, 1167 (2015).
- 517 [15] X. Zhu, S. Ji, The formation of Al₆(Fe,Mn) phase in die-cast Al-Mg alloys, IOP
518 Conference Series: Materials Science and Engineering, 529 (1), 2019, 012011, DOI:
519 10.1088/1757-899X/529/1/012011.
- 520 [16] T. Gao, Y. Wu, C. Li, X. Liu, Morphologies and growth mechanisms of α -Al(FeMn)Si in
521 Al-Si-Fe-Mn alloy, Mater. Lett., 110 (2013) 191-194.
- 522 [17] Hyun You Kim, Tea Young Park, San Won Han, Hyuck Mo Lee, Effects of Mn on the
523 crystal structure of α -Al(Mn,Fe)Si particles in A356 alloys, J. Cryst. Growth, 15 (2006)
524 207-211.
- 525 [18] S.G. Shabestari and M. Ghanbari, Effect of plastic deformation and semisolid forming on
526 iron-manganese rich intermetallics in Al-8Si-3Cu-4Fe-2Mn alloy, J. Alloys Compd.,
527 508 (2010) 315-319.

- 528 [19] Z.P. Que, Y. Wang, Z. Fan, Heterogeneous nucleation of eutectic structure in Al-Mg-Si
529 alloys, *Metall. Mater. Trans. A*, (2020), published online.
- 530 [20] V. Stefaniay, A. Griger, and T. Turmezey, Intermetallic phases in the aluminium-side
531 corner of the AlFeSi-alloy system, *J. Mater. Sci.*, 22 (1987) 539-546.
- 532 [21] S. Belmares-Perales, M. Castro-Roman, M. Herrera-Trejo, L. E. Ramirez-Vidaurre, Effect
533 of cooling rate and Fe/Mn weight ratio on volume fraction of α -AlFeSi and β -AlFeSi
534 phases in Al-7.3Si-3.5Cu alloy, *Metal. Mater. Inter.*, 41(3) (2008) 307-314.
- 535 [22] P. Popčević, A. Smontara, J. Ivkov, M. Wencka, M. Komelj, P. Jeglič, S. Vrtnik, M.
536 Bobnar, Z. Jagličić, B. Bauer, P. Gille, H. Borrmann, U. Burkhardt, Yu. Grin, and J.
537 Dolinšek, Anisotropic physical properties of the Al₁₃Fe₄ complex intermetallic and its
538 ternary derivative Al₁₃(Fe,Ni)₄, *Phys. Rev. B*, 81 (2010), 184203.
- 539 [23] Y. Yang, S.Y. Zhong, Z. Chen, M. Wang, N. Ma, H. Wang, Effect of Cr content and heat-
540 treatment on the high temperature strength of eutectic Al-Si alloys, *J. Alloys Compd.*, 647
541 (2015) 63-69.
- 542 [24] C. Freiburg, B. Grushko. An Al₁₃Fe₄ phase in the AlCuFe alloy system. *J. Alloys*
543 *Compd.*, 210(1-2) (1994) 149-152.
- 544 [25] K. Saito, K. Sugiyama, K. Hiraga, Al₁₃M₄-type structures and atomic models of their
545 twins, *Mater. Sci. Eng. A*, 294-296 (2000) 279-282.
- 546 [26] A. Gorny, J. Manickaraj, Z. Cai, S. Shankar, Evolution of Fe based intermetallic phases
547 in Al-Si hypoeutectic casting alloys: influence of the Si and Fe concentrations, and
548 solidification rate, *J. Alloys Compd.*, 577 (2013) 103-124.
- 549 [27] N.C.W. Kuijpers, F.J. Vermolen, C. Vuik, P.T.G. Koeins, K.E. Nilsen, S.V.D. Zwaag,
550 The dependence of the β -AlFeSi to α -Al(FeMn)Si transformation kinetics in Al-Mg-Si
551 alloys on the alloying elements, *Mater. Sci. Eng. A*, 394 (2005) 9-19.
- 552 [28] H. Becker, T. Bergh, P.E. Vullum, A. Leineweber, Y. Li. β - and δ -Al-Fe-Si intermetallic
553 phase, their intergrowth and polytype formation, *J. Alloys Compd.*, 780 (2019) 917-929.
- 554 [29] Y.S. Choi, J.S. Lee, W.T. Kim, H.Y. Ra. Solidification behavior of Al-Si-Fe alloys and
555 phase transformation of metastable intermetallic compound by heat treatment, *J. Mater.*
556 *Sci.*, 34 (1999) 2163.
- 557 [30] Z. Asghar, G. Requena, F. Kubel, The role of Ni and Fe aluminides on the elevated
558 temperature strength of an AlSi₁₂ alloy, *Mater. Sci. Eng. A*, 527 (2010), 5691-5698.
- 559 [31] A. Couture, Iron in aluminum casting alloys-a literature survey, *Inter. Cast. Met. J.*, 6
560 (1981), 9-17.
- 561 [32] S. Shabestari, The effect of iron and manganese on the formation of intermetallic
562 compounds in aluminum-silicon alloys, *Mater. Sci. Eng. A*, 383 (2004) 289-298.
- 563 [33] Q. Li, Y. Zhu, S. Zhao, Y. Lan, D. Liu, G. Jian, Q. Zhang, H. Zhou, Influences of Fe, Mn
564 and Y additions on microstructure and mechanical properties of hypoeutectic Al-7%Si
565 alloy, *Intermetallics*, 120 (2020) 106768.
- 566 [34] Standard Test Procedure for Aluminium Alloy Grain Refiners: TP-1, Aluminium
567 Association, Washington DC, 1987.

- 568 [35] Silicon, Wikipedia, <https://en.wikipedia.org/wiki/Silicon>.
- 569 [36] Aluminium, Wikipedia, <https://en.wikipedia.org/wiki/Aluminium>.
- 570 [37] V. Stefániay, A. Griger and T. Turmezey, Intermetallic phases in the aluminium-side
571 corner of the AlFeSi-alloy system, *J. Mater. Sci.*, 22 (1987) 539-546.
- 572 [38] C.M. Fang, A. Dinsdale, Z. P. Que, Z. Fan, Intrinsic defects in and electronic properties
573 of θ -Al₁₃Fe₄: an ab initio DFT study, *J. Phys. Materials*, 2 (2019) 015004.
- 574 [39] R.N. Cory, P.J. Black, The structure of α -(AlFeSi) by Anomalous-Dispersion Methods,
575 *Acta Cryst. B*, 33 (1977) 3468-3475.
- 576 [40] A.S. Cooper, Precise lattice constants of germanium, aluminum, gallium arsenide,
577 uranium, sulphur, quartz and sapphire, *Acta Crystall.*, 15 (1962) 578-582.
- 578 [41] Y. Du, J.C. Schuster, etc, A thermodynamic description of the Al-Fe-Si system over the
579 whole composition and temperature ranges via a hybrid approach of CALPHAD and key
580 experiments. *Intermetallics*, 16 (2008) 554-570.
- 581 [42] N. Krendelsberger, F. Weitzer, J.C. Schuster, On the reaction Scheme and Liquidus
582 surface in the ternary system Al-Fe-Si. *Metall. Mater. Trans. A*, 38A (2007) 1681-1691.
- 583