



HAL
open science

Solidification paths of Al-Cu-Sn alloys: comparison of thermodynamic analyses and solidification experiments using in situ X-radiography

Sarah de Albuquerque, Guillaume Reinhart, Danielle Cristina Camilo Magalhães, José Eduardo Spinelli, Hadjer Soltani, Wafa Boumechta, Felipe Bertelli, Henri Nguyen- Thi

► To cite this version:

Sarah de Albuquerque, Guillaume Reinhart, Danielle Cristina Camilo Magalhães, José Eduardo Spinelli, Hadjer Soltani, et al.. Solidification paths of Al-Cu-Sn alloys: comparison of thermodynamic analyses and solidification experiments using in situ X-radiography. *Materials Today Communications*, 2024, 40, pp.109545. 10.1016/j.mtcomm.2024.109545 . hal-04628528

HAL Id: hal-04628528

<https://hal.science/hal-04628528v1>

Submitted on 28 Jun 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Solidification paths of Al-Cu-Sn alloys: comparison of**
2 **thermodynamic analyses and solidification experiments using in**
3 **situ X-radiography**

4
5 Sarah de Albuquerque^{1,2}, Guillaume Reinhart^{1*}, Danielle Cristina Camilo Magalhães^{2,3}, José
6 Eduardo Spinelli^{2,3}, Hadjer Soltani⁴, Wafa Boumechta⁵, Felipe Bertelli⁶ and Henri Nguyen-
7 Thi¹

8
9 ¹ *Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, Marseille, France*

10 ² *Federal University of São Carlos, Graduate Program in Materials Science and Engineering,*
11 *13565-905 São Carlos, SP, Brazil*

12 ³ *Department of Materials Engineering, Federal University of São Carlos, 13565-905 São*
13 *Carlos, SP, Brazil*

14 ⁴ *Badji Mokhtar University, laboratory of foundry, BP 12, 23000, Annaba, Algeria*

15 ⁵ *Badji Mokhtar University, LMGM, BP 12, 23000 Annaba, Algeria*

16 ⁶ *Sea Science Department, Federal University of São Paulo – UNIFESP, 11030-400 Santos,*
17 *SP, Brazil*

18
19 * Corresponding author: guillaume.reinhart@im2np.fr

20
21 **Abstract**

22 The increasing importance of Al-Cu-Sn alloys as materials for producing self-lubricating
23 bearing materials in automotive industries requires the development of uniform microstructures
24 with improved performance, which could be achieved by a precise control of solidification
25 processes. Adding Sn to Al-Cu binary alloy could dramatically alters the solidification path,
26 generating liquid phase separation and monotectic reaction. In this paper, Al-10 wt.% Cu-X
27 wt.% Sn (with X = 0; 5; 10 and 20) alloys have their solidification paths investigated by three
28 different complementary approaches. Firstly, the solidification paths were calculated by using

29 the CALPHAD method through Thermo-Calc software revealing the sequence of
30 transformations that could occur during the solidification of these alloys, from the formation of
31 the initial α -Al dendrites to the final eutectic reaction. Secondly, experimental thermal analysis
32 was carried out by DSC (Differential Scanning Calorimetry), which reveals the successive
33 events that occur during the controlled melting and cooling of these alloys. Thirdly, directional
34 solidification was performed on all alloys, with in situ and real-time observations achieved
35 through the utilization of X-radiography. The comparison between the various approaches
36 showed a suitable correspondence between the history of the alloy solidifications computed by
37 Thermo-Calc and those obtained experimentally (DSC and directional solidification
38 experiments). Additional information about the dynamics of each reaction was obtained during
39 the directional solidification experiments in terms of microstructures, segregation, and the
40 genesis of the liquid phase separation that occurred for high Sn-content alloys.

41

42 **Keywords:** Al-Cu-Sn alloys; Thermo-Calc; solidification microstructures; liquid phase
43 separation; monotectic; DSC; in situ radiography

44

45

46 **1. Introduction**

47 Aluminium-based alloys with a miscibility gap in the liquid state such as Al-Pb, Al-Bi and Al-
48 Sn are excellent candidates for advanced bearings in aerospace or automotive industry. As a
49 general rule for these alloys soft metal elements such as lead, bismuth or tin could be formed
50 as droplets distributed in harder metal matrices to produce alloys for bearing applications with
51 very low friction coefficient and suitable wear resistance [1-8]. Although Sn has been shown to
52 be less efficient than Pb in sliding-bearing Al alloys [9], the growing environmental concern
53 for lead has rekindled interest in substituting appropriate soft alloying elements for such
54 element in Al alloys.

55 Due to the rise in engine bearing temperatures and strains brought on by current trends in engine
56 design, Al-Sn alloys are unable to withstand significant loads, even offering excellent
57 antifriction capabilities. Thus, copper could be added as an alternative to hardening the Al
58 matrix while keeping the soft Sn phase well distributed [10, 11]. Therefore, ternary Al-Cu-Sn
59 alloys are frequently used in the manufacturing of bearing parts because these alloys combine
60 high strength, wear resistance, and high machinability. Sn and Cu elements also contribute to
61 the increased dimensional stability of the components. Aside from the suitable strength, Al-Cu-
62 Sn alloys have high corrosion resistance, which is very significant for bearing applications
63 where components may be exposed to severe conditions both in temperature and pressure [10,
64 11]. In a recent paper, Bertelli and co-authors [12] investigated the correlation between
65 microstructures, tensile properties and wear resistance on directionally solidified Al-Cu-Sn
66 alloys. They concluded that the optimal microstructure configuration for wear resistance was
67 found to be regions with coarser α -Al dendritic phase and interdendritic regions constituted by
68 larger Sn pockets and Al_2Cu particles [13].

69 In the selection of metallic alloys for tribological applications, it is mandatory to consider not
70 only their chemical composition but also the microstructural features that occurs during the
71 solidification process. Actually, the formation of microstructures at the solid-liquid interface
72 (dendrites), the univariant reactions such as eutectic and monotectic, as well as the liquid phase
73 separation in two immiscible liquids dramatically influence the final mechanical properties. As
74 a consequence, further research into the phase transition features and solidification
75 microstructures of ternary monotectic alloys is warranted.

76 The ever-increasing use of numerical simulation and modelling of the solidification processes
77 is a very efficient way to understand or predict the microstructures formation. For instance, over
78 the last decades, several numerical methods have been developed and applied for simulating
79 the dendritic growth problem in its full geometrical complexity under different thermal and
80 solutal boundary conditions and assumptions [14, 15]. However, most of such approaches did
81 not consider the influence of gravity phenomena, such as convection in the melt and buoyancy
82 force acting on free solid particles, which are unavoidable on Earth [16-18]. These phenomena
83 can thus dramatically impact the solidification processes, so that the elaborated materials may
84 strongly differ from the expected ones based only on phase diagram analyses. In particular, it
85 is well known that fine and homogeneous dispersion of Sn or Al₂Cu particles is always difficult
86 to achieve under conventional conditions due to the large density difference between Al liquid
87 phase and Sn droplet or Al₂Cu particles. This disturbing gravity-induced effect is even more
88 serious for ternary monotectic alloys that have quaternary phase equilibria comprising two
89 immiscible liquids and two distinct solid phases. This can result in a complex variety of liquid
90 phase separation patterns and unexpected monotectic microstructures, opening up a previously
91 unexplored field in terms of both scientific significance and practical applications [19, 20]. One
92 possible way to mask these gravity effects, and thus to obtain materials with desired properties,
93 is to apply an external field during the solidification process. The effects of ultrasound on liquid

94 phase separation and monotectic structures of $\text{Al}_{62.6}\text{Sn}_{28.5}\text{Cu}_{8.9}$ alloy were recently investigated
95 by Zhai and co-workers [20]. The authors demonstrated that the power ultrasound is an effective
96 and promising way to improve the solidification microstructure and mechanical properties of
97 this alloy by preventing the spatial liquid phase separation and by reducing the
98 macrosegregation level as ultrasound power increases.

99 The best technique for revealing the dynamical evolution of dendritic microstructures formation
100 during the solidification of metal alloys is now well-established to be in situ and time-resolved
101 X-radiography [21-24]. However, studies of immiscible alloy solidification using this powerful
102 observation technique are hitherto very scarce. For example, Schaffer *et al.* investigated
103 spinodal decomposition in hyper-monotectic Al-Bi and Al-Bi-Zn alloys [25] and highlighted
104 the complex interactions between droplets. Lu *et al.* also studied liquid phase separation and
105 the impact of bubbles on the segregation in Al-Bi alloys [26, 27]. Recently, Zhang *et al.* [28]
106 successfully analysed the effect of solutal Marangoni force and lift force on the motion of
107 droplets also in a hyper-monotectic Al-Bi alloy.

108 The current study focuses on the solidification paths of ternary Al-10 wt.% Cu-X wt.% Sn (with
109 $X = 0$ wt.%, 5 wt.%, 10 wt.% and 20 wt.%) alloys. The experiments presented here used in situ
110 X-radiography to reveal the dynamics of the solidification process, with a special emphasis on
111 monotectic reactions and phase separations and comparing these findings with CALPHAD
112 calculations and DSC measurements.

113

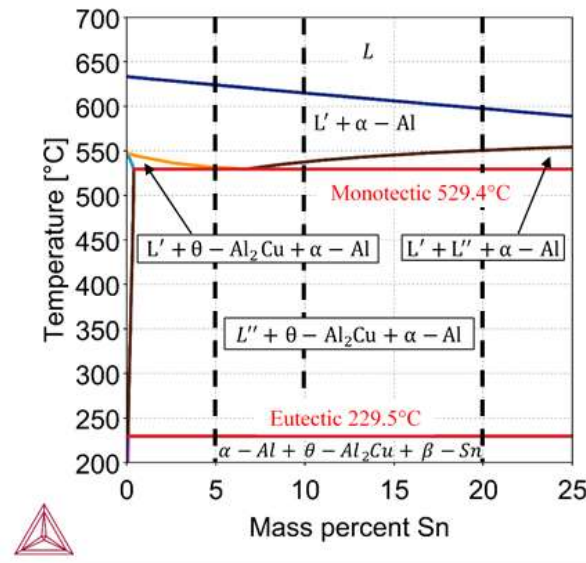
114 **2. Thermo-Calc calculations based on CALPHAD method**

115 The accurate knowledge of ternary alloy phase diagrams is a prerequisite for a better
116 understanding of alloy behaviour aiming at focused microstructure formation during
117 solidification. In that sense, thermodynamic calculations are an essential tool for materials

118 science and engineering and the CALPHAD (Computer Coupling of Phase Diagrams and
119 Thermochemistry) approach is now widely accepted as the most efficient strategy for
120 accelerating the development of materials. It can provide information about the phases and
121 properties of materials without or prior extensive experimental work. [Consequently](#), this
122 approach is particularly valuable. The major goal of this Section is to determine the
123 solidification paths for the different alloys of interest, with a clear description of the successive
124 events that might be then detected experimentally either by DSC (Differential Scanning
125 Calorimetry) or during the solidification experiments.

126 The solidification paths of hypo-eutectic binary Al-Cu and Al-Sn alloys are rather standard with
127 the formation of α -Al as primary phase and then a eutectic reaction from the residual liquid.
128 However, the comprehension of the solidification paths in the ternary alloys of the Al-Cu-Sn
129 system is more complex, in part due to the occurrence of multiple transformations during the
130 cooling process [10, 11]. In a first approach, an Al-Sn pseudo-binary phase diagram with a fixed
131 amount of Cu of 10 wt.% was calculated through the CALPHAD method. For this purpose, the
132 TCAL7: Al-Alloys v7.1 database was used with the Thermo-Calc software [29] in the present
133 investigation. The pseudo-binary phase diagram considers the variation in relation to the
134 temperature of two elements (Al and Sn) while keeping the quantity of a third one (Cu) fixed,
135 being easier to read than a ternary diagram. The pseudo-binary phase diagram of the Al-10
136 wt.% Cu-X wt.% Sn system is shown in Fig.1 for Sn content varying from 0 wt.% up to 25
137 wt.%, very similar to the one given in [19]. In this composition range, two reactions are
138 detected, one monotectic at approximately 529.4°C and an eutectic at approximately 229.5°C,
139 in addition to a liquid miscibility gap that occurs when Sn content is greater than 6.6 wt.% (L'
140 represents the liquid enriched in Sn during liquid phase separation). The pseudo-binary phase
141 diagram gives a general idea of what could occur during the solidification of the ternary alloy.
142 However, the information derived from the pseudo-binary phase diagrams is not complete and

143 sometime could be confusing because, although useful, it is only a cross-section of a three-
144 dimensional ternary alloy phase diagram.



145
146 **Fig.1:** Al-10 wt.%Cu- X wt.%Sn pseudo-binary diagram. The three investigated compositions
147 (5 wt.%, 10 wt.% and 20 wt.% Sn) are indicated by vertical dashed lines.

148
149 Consequently, the detailed calculation of the equilibrium solidification paths for the four alloys
150 were performed considering the variation of all elements. It is worth mentioning that
151 calculations using the Scheil solidification model would also provide complementary
152 information on the solidification paths but out-of-equilibrium. However, Scheil solidification
153 model would be less appropriate in the present case as it doesn't consider the liquid phase
154 separation. Table 1, Table 2 and Table 3 give the respective calculated sequence of equilibrium
155 phase transformations of the three ternary alloys. In addition, it is possible (if necessary) to
156 determine the mass fraction of all the phases as a function of temperature, that is, the proportion
157 in which they are formed or consumed along the solidification path. The Thermo-Calc software
158 also provides spreadsheets that show the chemical composition of each phase depending on
159 temperature variation, which is useful for identifying the reactions. Fig.2 depicts the

160 solidification paths for the four investigated alloys, with the successive steps during cooling
 161 (from the right side to the left side) in the form of the calculated phase fraction as a function of
 162 temperature.

163

164

Phase reactions	Temperature range (Thermo-Calc)	Temperature range (DSC ; Cooling)
L	Above 624°C	Above 610.5°C
$L' \rightarrow \alpha\text{-Al}$	From 624 to 531.5 °C	From 610.5 to 510.5 °C
$L' \rightarrow \alpha\text{-Al} + \theta\text{-Al}_2\text{Cu}$	From 531.5 to 524.8 °C	
$L' + \alpha\text{-Al} \rightarrow \theta\text{-Al}_2\text{Cu}$	From 524.8 to 229.5 °C	From 510.5 to 220.5 °C
$L' \rightarrow \alpha\text{-Al} + \theta\text{-Al}_2\text{Cu} + \beta\text{-Sn}$	At 229.5 °C (eutectic reaction)	At 220.5 °C (eutectic reaction)

165 **Table 1** – Temperature ranges of the different reactions calculated using Thermo-Calc and
 166 deduced from the temperature peaks in the DSC data during the cooling of the Al-10 wt.% Cu-
 167 5 wt.% Sn alloy.

168

169

170

Phase reactions	Temperature range (Thermo-Calc)	Temperature range (DSC ; Cooling)
L	Above 615°C	Above 600.5°C
$L' \rightarrow \alpha\text{-Al}$	From 615 to 537.5 °C	From 600.5 to 525.5 °C
$L' \rightarrow \alpha\text{-Al} + L''$	From 537.5 to 529.4°C	From 525.2 to 510.5°C
$L' \rightarrow \alpha\text{-Al} + L'' + \theta\text{-Al}_2\text{Cu}$	At 529.4 °C (monotectic reaction)	At 510.5 °C (monotectic reaction)
$L'' + \alpha\text{-Al} \rightarrow \theta\text{-Al}_2\text{Cu}$	From 529.4 to 229.5°C	From 510.5 to 220.5°C
$L'' \rightarrow \alpha\text{-Al} + \theta\text{-Al}_2\text{Cu} + \beta\text{-Sn}$	At 229.5 °C (eutectic reaction)	At 220.5 °C (eutectic reaction)

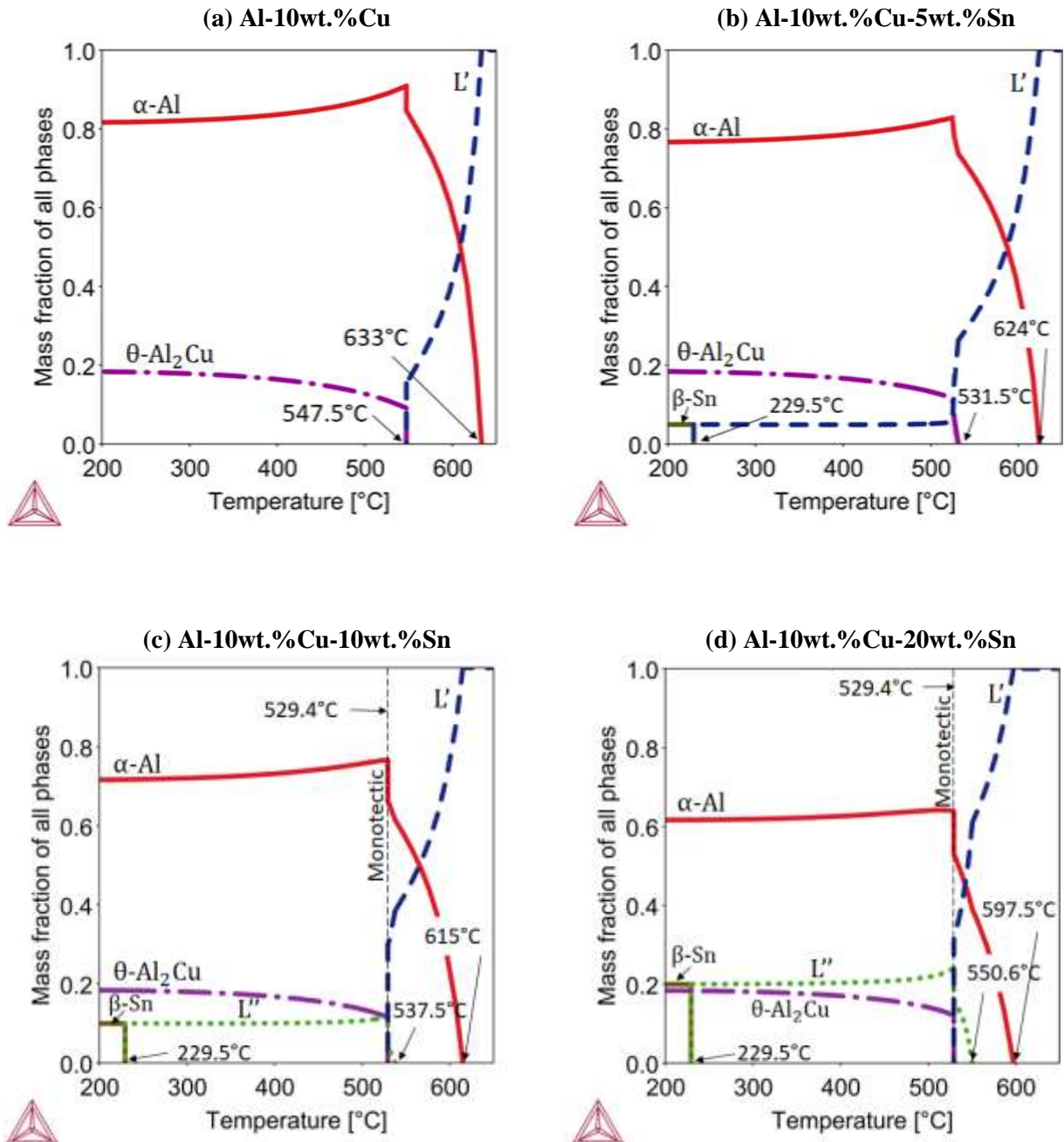
171 **Table 2** - Temperature ranges of the different reactions calculated using Thermo-Calc and
 172 deduced from the temperature peaks in the DSC data during the cooling of the Al-10 wt.% Cu-
 173 10 wt.% Sn alloy.

174

Phase reactions	Temperature range (Thermo-Calc)	Temperature range (DSC ; Cooling)
L	Above 597.5°C	Above 572.8°C
L' → α-Al	From 597.5 to 550.6 °C	From 572.8 to 530.3 °C
L' → α-Al + L''	From 550.6 to 529.4°C	From 530.3 to 517.8°C
L' → α-Al + L'' + θ-Al ₂ Cu	At 529.4 °C (monotectic reaction)	At 517.8 °C (monotectic reaction)
L'' + α-Al → θ-Al ₂ Cu	From 529.4 to 229.5°C	From 517.8 to 220.3°C
L'' → α-Al + θ-Al ₂ Cu + β-Sn	At 229.5 °C (eutectic reaction)	At 220.3 °C (eutectic reaction)

175 **Table 3** - Temperature ranges of the different reactions calculated using Thermo-Calc and
176 deduced from the temperature peaks in the DSC data during the cooling of the Al-10 wt.% Cu-
177 20 wt.% Sn alloy.

178



179

180

181 **Fig.2:** Equilibrium solidification paths for the four investigated alloys: a) Al-10 wt.% Cu, b)

182 Al-10 wt.% Cu-5 wt.% Sn, c) Al-10 wt.% Cu-10 wt.% Sn, d) Al-10 wt.% Cu-20 wt.% Sn.

183

184

185

186 From the Al-Sn pseudo-binary phase diagram (Fig.1 and Fig.2a), we can see that α -Al dendrites
187 are expected to form first at a temperature close to 633°C during the solidification of the binary
188 Al-10 wt.% Cu alloy. Due to the solute rejection during the solidification, the liquid
189 composition gradually increases until the formation of the eutectic phase (α -Al + θ -Al₂Cu) at
190 547.5°C. The Al-10 wt.% Cu alloy is a model binary alloy, that has been studied extensively in
191 the field of solidification. For instance, the influence of a permanent magnetic field on this two-
192 step solidification process was analysed in detail by Abou-Khalil *et al.* [30-32].

193 For a low addition of Sn (X = 5 wt.%), the ternary alloy Al-10 wt.% Cu-5 wt.% Sn has a similar
194 dynamic at the beginning of its solidification path. As shown in Fig.2b and Table 1,
195 solidification also begins with α -Al dendrites formation but at a slightly lower temperature of
196 624°C. Fig.2b also shows the simultaneous decrease of liquid phase L' proportion and increase
197 of aluminium solid phase during the solidification phase down to 531.5°C. Between the
198 temperatures 531.5°C and 524.8°C, the liquid phase L' gives birth to two solid phases (α -Al
199 and θ -Al₂Cu) and is enriched with Cu/Sn. Between 524.8°C and $T_{eutectic} = 229.5^\circ\text{C}$, the liquid
200 L' interacts with the solid α -Al to form solid θ -Al₂Cu, which explains the slow decrease from
201 right to left of α -Al (red line) and L' (blue line), simultaneously with an increase of θ -Al₂Cu
202 (purple dash-point line). Finally, the residual liquid L' solidifies through a eutectic reaction at
203 $T_{eutectic}$.

204 For the two alloys with higher Sn compositions (X = 10 wt.% and X = 20 wt.%), solidification
205 paths are similar to one another but more complex than for alloys with low Sn-content because
206 of the miscibility gap in the phase diagram. As seen in Fig.2c and Fig.2d d as well as Table 2
207 and Table 3, additional transformations are expected during the solidification paths. Similarly,
208 as occurred for the two low Sn-content alloys, solidification begins with α -Al dendrites
209 formation but at different temperatures, at 615°C for the Al-10 wt.% Cu-10 wt.% Sn (Table 2)

210 and 597.5°C for the Al-10 wt.% Cu-20 wt.% Sn (Table 3). Fig.2c and 2d shows the
211 simultaneous decrease of liquid phase proportion and increase of aluminium solid phase during
212 the initial solidification phase.

213 In contrast to the two previous alloys, both solidification paths for Al-10 wt.% Cu-10 wt.% Sn
214 and Al-10 wt.% Cu-20 wt.% Sn cross the liquid miscibility gap (Fig. 1) during the solidification.
215 Inside this miscibility gap, α -Al dendrites continue to grow but a liquid phase separation occurs
216 concomitantly. A dense Sn-rich liquid L'' begins to separate from L' in the form of droplets,
217 resulting in the formation of two distinct immiscible liquids. The number and size of droplets
218 directly depend on the initial liquid composition [33].

219 The liquid phase separation is clearly visible for Al-10 wt.% Cu-20 wt.% Sn in Fig.2d. For this
220 alloy, the liquid phase separation begins at 550.6°C, with a change in the slope of the initial
221 homogeneous liquid L' line (in blue), concomitantly with a formation of Sn-rich liquid droplet
222 L'' (in green) and a change in the slope of the α -Al line (in red). Based on Fig.2 the respective
223 proportion and composition of the different phases could be calculated as a function of the
224 temperature. The same liquid phase separation occurs for Al-10 wt.% Cu-10 wt.% Sn (Fig.2c)
225 but for a very narrow range of temperature (from 537.5°C to 529.4°C), which makes it difficult
226 to visualize in Fig.2c.

227 At $T_{monotectic} = 529.4^\circ\text{C}$, the invariant ternary monotectic reaction occurs, with the formation of
228 two solid phases (α -Al and θ -Al₂Cu), concomitantly with the Cu/Sn-enrichment of the residual
229 liquid phase L' due to Cu/Sn rejection during the liquid to solid phase transformation. Between
230 $T_{monotectic}$ and $T_{eutectic} = 229.5^\circ\text{C}$, the residual liquid interacts with the solid α -Al to form the
231 solid θ -Al₂Cu. This slow reaction explains the slow decrease from right to left of α -Al (red line)
232 and L' (blue line), simultaneously with an increase of θ -Al₂Cu (purple dash-point line). The

233 residual liquid finally gives birth to the eutectic phase consisting of β -Sn, α -Al and θ -Al₂Cu at
234 $T_{eutectic} = 229.5^{\circ}\text{C}$.

235

236 **3. Differential Scanning Calorimetry (DSC) measurements**

237 The differential scanning calorimetry (DSC) technique has been used to investigate the
238 solidification paths of the different Al-Cu-Sn alloys. Calorimetric measurements are
239 particularly convenient for monitoring the kinetics of phase transformations such as melting or
240 solidification [34]. Changes in heat content in a solidifying material are directly proportional to
241 the amount of solidification which has taken place and are closely related to the thermodynamic
242 forces driving the solidification process [35]. The objective of this section is to describe the
243 three DSC experiments that were carried out on three samples with the compositions: Al-10
244 wt.% Cu-X wt.% Sn (with X = 5, 10 and 20).

245

246 **3.1. Experimental details**

247 DSC measurements were carried out with a NETZCH SAT 449 F3, Jupiter differential scanning
248 calorimeter (Selb, Germany) at School of Mines and Metallurgy Annaba (Algeria). The
249 calorimeter was calibrated with the melting points and enthalpies of fusion (or sensibility) of
250 high-purity elements In, Sn, Bi, Zn, Al, Ag, Au and Ni metals. In this work, three samples with
251 the compositions: Al-10 wt.% Cu-X wt.% Sn (with X = 5, 10 and 20) were studied, cutting
252 from ingots that were prepared at the University of Campinas (Brazil) [12]. Their chemical
253 compositions in copper and tin were confirmed at ± 0.2 wt.% by ICP-MS (Inductively Coupled
254 Plasma – Mass Spectrometer) at Aix-Marseille University (AGILENT 7800). Each sample of
255 small slice in form, with approximately $20 \text{ mg} \pm 3 \text{ mg}$ in weight, was placed in a sealed alumina
256 crucible, while a second empty crucible was used as a reference. Both crucibles were inserted

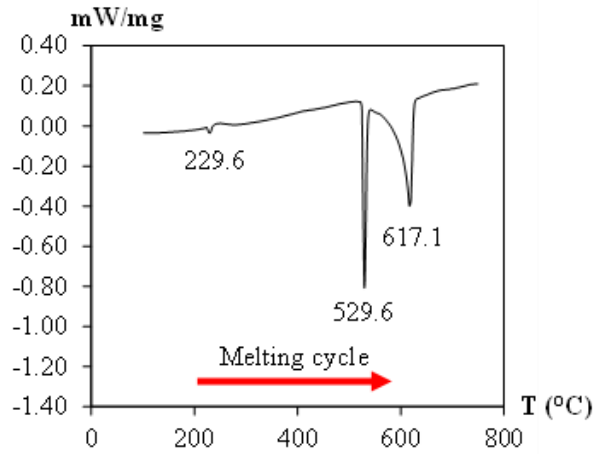
257 into a DSC cell under a protective nitrogen atmosphere with a flow rate of 20 mL/min. The
258 heating/cooling cycles are similar for the three experiments, at a rate of 5 K/min, in a
259 temperature range extending from room temperature to 750°C, which is a much higher value
260 than the melting point of the studied alloys to ensure the homogeneity of the samples. At 750°C,
261 a holding period of 15 min was applied to homogenize the composition and liquid temperature.

262

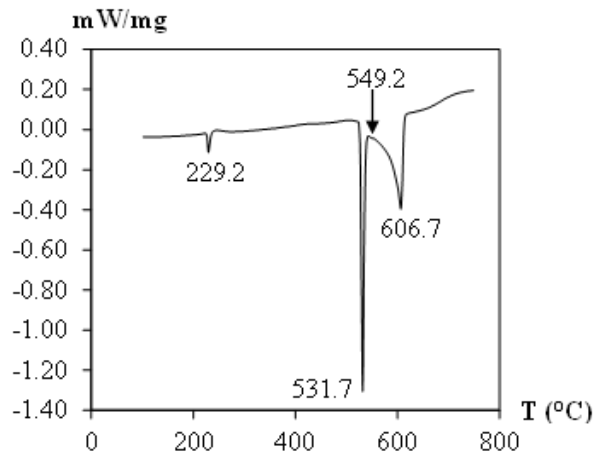
263 **3.2. DSC curves**

264 The DSC curves obtained from the heating (melting) and the cooling (solidification) processes
265 are presented in Fig.3 and Fig.4 respectively, for the three compositions. It is worth noticing
266 that the heating/cooling cycles were introduced beforehand to draw a baseline or reference line
267 with respect to nitrogen. By subtracting the baseline from the line drawn during the
268 experiments, the transformation points presented with DSC curves will be revealed. The critical
269 values corresponding to phase transformation temperatures on cooling are summarized in Table
270 1, Table 2 and Table 3.

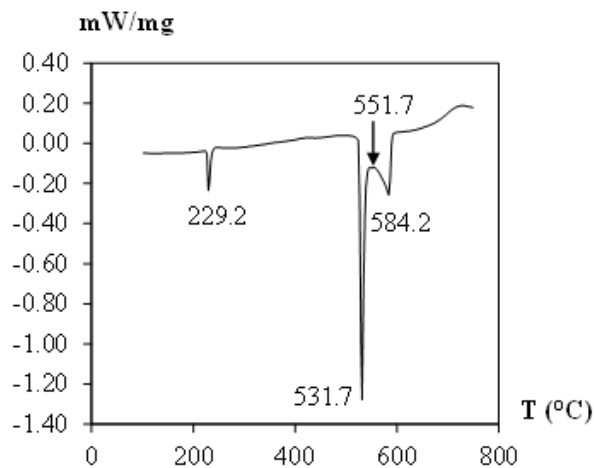
271



(a) Al-10 wt.% Cu-5 wt.% Sn



(b) Al-10 wt.% Cu-10 wt.% Sn



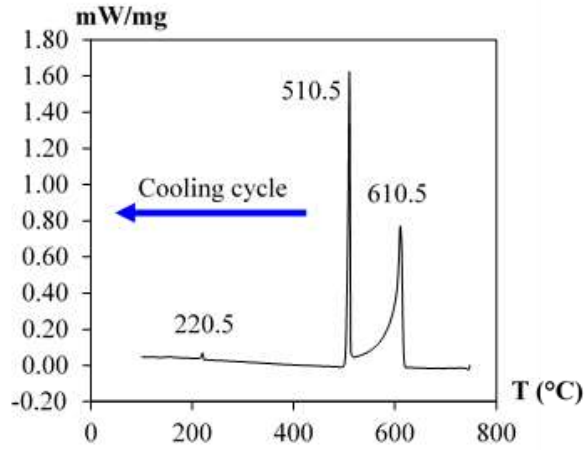
(c) Al-10 wt.% Cu-20 wt.% Sn

272

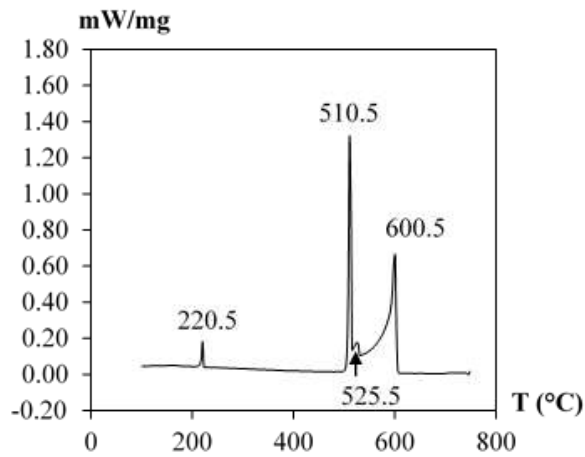
273 **Fig.3:** Melting DSC curves of the three different alloys recorded during sample heating, showing the

274 endothermic peak of each transformation: (a) Al-10 wt.% Cu-5 wt.% Sn; (b) Al-10 wt.% Cu-10 wt.%

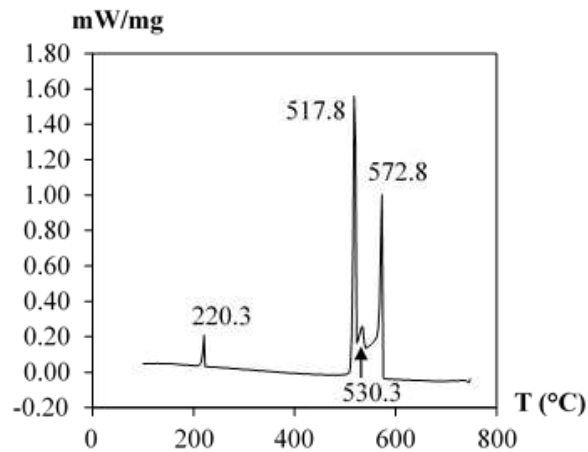
275 Sn and (c) Al-10 wt.% Cu-20 wt.% Sn.



(a) Al-10 wt.% Cu-5 wt.% Sn



(a) Al-10 wt.% Cu-10 wt.% Sn



(a) Al-10 wt.% Cu-20 wt.% Sn

276

277 **Fig.4:** Cooling DSC curves of the three different alloys showing the exothermic peak of each

278 transformation: (a) Al-10wt.%Cu-5wt.%Sn; (b) Al-10wt.%Cu-10wt.%Sn and (c) Al-10wt.%Cu-

279 20wt.%Sn.

280 3.3. Solidification paths recorded by DSC

281 During the melting cycles for the three alloys (Fig.3), the curves show three clear endothermic
282 peaks with different widths and amplitudes. For increasing temperature (from the left side to
283 the right side of each DSC melting curves), the successive key temperatures are:

284 (i) $T_{eutectic}$: The first transformation corresponds to the melting of ternary eutectic β -Sn + θ -
285 Al_2Cu + α -Al constituent. The melting temperature of the eutectic phase seems roughly
286 identical for the three alloys, with a maximum peak slightly lower than 230°C.

287 (ii) $T_{monotectic}$: Secondly, a very narrow and intense peak is recorded, which corresponds to the
288 monotectic reaction, with the melting of both θ - Al_2Cu and α -Al phases. These monotectic
289 temperatures are almost the same for the three alloys, approximately 530°C.

290 (iii) By magnifying the DSC melting curves just after the sharp monotectic peak, a very shallow
291 peak could be detected for the two high Sn-content alloys, at about 549.2°C for Al-10 wt.% Cu-
292 10 wt.% Sn alloy and 551.7°C for Al-10 wt.% Cu-20 wt.% Sn alloy. This shallow peak is most
293 likely the signature of the liquid phase homogenization.

294 (iv) $T_{\alpha-Al}$ is the temperature of the latest deep peak, which is related to the melting temperature
295 of the α -Al dendrites. This temperature is the most sensitive to the Sn content. The larger the
296 Sn content, the lower this temperature is.

297 During the cooling cycles, the number of exothermic peaks is different for the alloy with a low
298 Sn content (Fig.4a and Table 1, Al-10 wt.% Cu-5 wt.% Sn) compared to the two alloys with
299 larger Sn content (Fig.4b and Table 2, Al-10 wt.% Cu-10 wt.% Sn and Fig. 4c and Table 3, Al-
300 10 wt.% Cu-20 wt.% Sn). For the two high Sn-content samples, the transformations are (from
301 the right to the left side of the DSC curves):

302 (i) A first transformation at $T_{\alpha\text{-Al}}$, which corresponds to the solidification of primary $\alpha\text{-Al}$
303 dendrites. $T_{\alpha\text{-Al}}$ decreases from 610.5°C to 572.8°C when the Sn composition increases from 5
304 to 20 wt.%.

305 (ii) A small peak is visible at 525.5°C for Al-10 wt.% Cu-10 wt.% Sn alloy and at 530.3°C for
306 Al-10 wt.% Cu-20 wt.% Sn alloy, which corresponds to the liquid phase separation, when the
307 homogeneous liquid comes into the miscibility gap (Fig.1).

308 (iii) The monotectic reaction at $T_{\text{monotectic}}$ gives birth to a very narrow and intense peak, with the
309 formation of both $\theta\text{-Al}_2\text{Cu}$ and $\alpha\text{-Al}$ phases.

310 (iv) The last transformation occurs at T_{eutectic} and ends the solidification path with the formation
311 of the eutectic phases $\beta\text{-Sn} + \theta\text{-Al}_2\text{Cu} + \alpha\text{-Al}$.

312 In conclusion of the DSC section, the main and unique difference between DSC cooling curves
313 between the high Sn-content alloys (Al-10 wt.% Cu-10 wt.% Sn, and Al-10 wt.% Cu-20 wt.%
314 Sn) and the low Sn-content alloy (Al-10 wt.% Cu-5 wt.% Sn) is a small peak that appears at a
315 temperature between $T_{\alpha\text{-Al}}$ and $T_{\text{monotectic}}$, which most likely corresponds to the liquid phase
316 separation, when the homogeneous liquid comes into the miscibility gap.

317

318 **4. *In situ* and real time observation of Al-Cu-Sn solidification experiments**

319 It is now well established that *in situ* and time-resolved X-radiography is a method of choice
320 for unveiling the dynamical evolution of dendritic microstructures and grain structure formation
321 during the solidification of metal alloys, on Earth and onboard of microgravity platforms [36].
322 Recently, new opportunities have arisen with the improvement of compact micro-focus sources
323 and X-ray sensitive detectors that enable *in situ* and time-resolved radiography to be used in
324 laboratory devices, with sufficient spatial and time resolutions to distinguish the microstructure

325 features [37, 38], enabling different orientations of the sample with respect to gravity [39] and
326 compatible with microgravity platforms [40, 41]. Such a laboratory device was successfully
327 used by Xavier *et al.* to analyse the morphology of the solidification interface at different
328 cooling rates for an Al-Bi-Cu monotectic alloy [42].

329

330 **4.1. Solidification experiments with *in situ* observation**

331 In this work, directional solidification of Al-10 wt.% Cu-X wt.% Sn samples (with X = 0, 5, 10
332 20) were reported, using the SFINX (Solidification Furnace with IN situ X-radiography)
333 laboratory device [37, 38]. The experimental procedure is identical to the one presented in
334 details in [43]. The crucible-sample set was inserted inside the furnace, in direct contact with
335 the two heaters to apply a temperature gradient along the sample. The two heating elements
336 were controlled by two K-type thermocouples positioned 13.5 mm apart from each other. The
337 respective temperatures of the heaters (T_{hot} and T_{cold}) were monitored independently to impose
338 a longitudinal temperature gradient $G_{app} = (T_{hot} - T_{cold})/13.5$. For the experiments presented in
339 this paper, solidification experiments were performed by applying a longitudinal temperature
340 gradient G_{app} of 5.55 °C/mm. The samples were solidified by applying the same cooling rate R
341 of 0.15 °C/s on both heaters (power-down method) and keeping constant the applied
342 temperature gradient along the whole solidification experiment. Previous experiments have
343 shown that these parameters lead to the formation of microstructures with features that are well
344 distinguishable with the current imaging device. The furnace was set in horizontal position,
345 with the main sample surface perpendicular to the gravity vector \mathbf{g} . This configuration is chosen
346 to damp gravity-related phenomena such as buoyancy [39]. The sample were prepared from the
347 same raw ingots used for the DSC measurements, which will allow a direct comparison between
348 the two approaches. All samples were grounded and polished to achieve dimensions of
349 approximately 5 mm in width, 50 mm in length, and 0.20 mm in thickness.

350 The X-radiography system figures a micro-focus X-ray source with a molybdenum target (3
351 μm focal spot) providing enough photon flux and has two peaks of energy at 17.4 keV and 19.6
352 keV ensuring a good image contrast to study Al-based alloys [40]. In the presented
353 experiments, a geometric magnification of approximately 5 was used for a Field-of-View (FoV)
354 of about $5 \times 5 \text{ mm}^2$ leading to an effective pixel size of approximately $4 \mu\text{m}$. The acquisition
355 rate was 2 frames per second. For the studied alloys, the three elements have significantly
356 different absorption contrast so that the liquid and solid phases that are expected to form during
357 the solidification sequence will be clearly distinguishable. The solidification sequence will be
358 described based on the observation of the recorded images.

359

360 **4.2 Image processing**

361 Although there are significant variations in absorption contrast among the elements, certain
362 artefacts inherent to the device make the raw images difficult to read. The artefacts result from
363 various factors, including fluctuations in the temporal and spatial intensities of the X-ray beam
364 or the detector background. Consequently, two different image processing were necessary,
365 which provide complementary information about the solidification process. These image
366 processing were done using the ImageJ software [44].

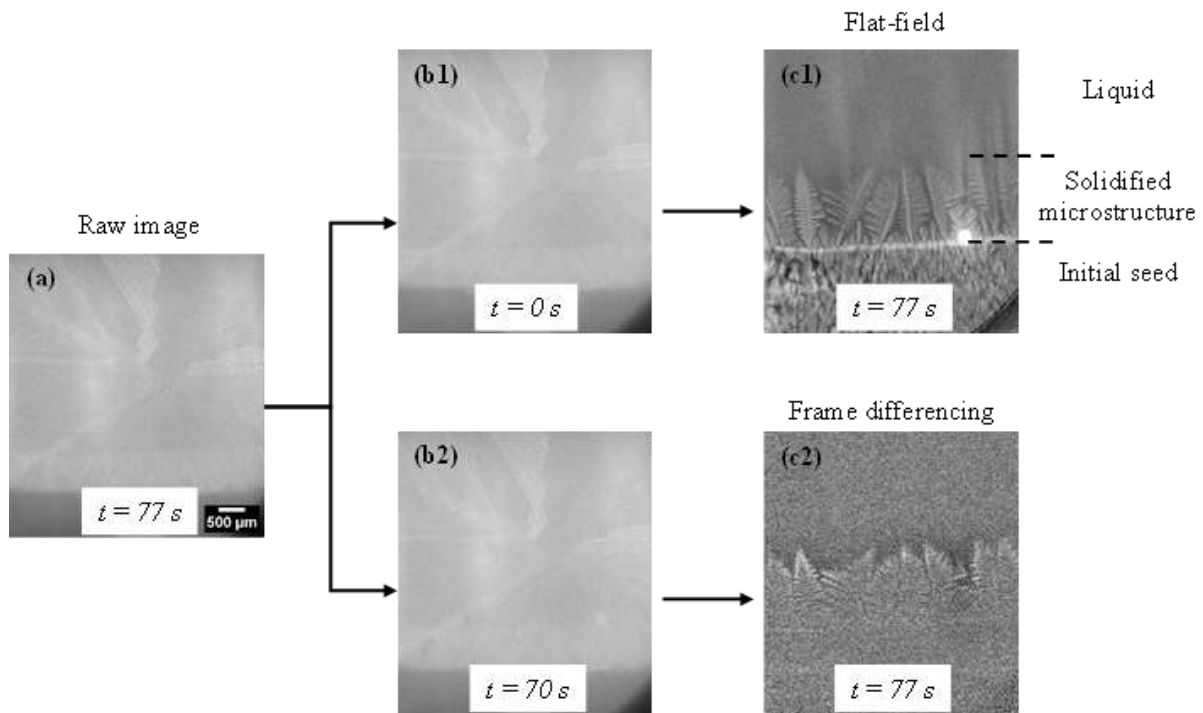
367 A first and commonly employed image processing technique is the *flat-field correction*, which
368 consist in dividing the raw images (Fig.5a) by a reference image recorded just before the
369 beginning of the solidification (Fig.5b1), when the part of the sample in the Field-of-View is
370 almost entirely liquid [41]. The resulting image (Fig.5c1) displays a notable enhancement in
371 readability, with an increased grey level contrast observed between the dendrites (rich in
372 aluminium) and the liquid (enriched in copper and tin because of solute rejection during the

373 phase transformation). Variations in grey level in the liquid phase are related to solute
374 composition.

375 A second and less known image processing, called *frame differencing*, was also applied. This
376 technique is widely used in computer vision to highlight differences between two frames and
377 has been successfully extended to solidification studies [45, 46]. For this purpose, the raw image
378 of interest (Fig.5a) is divided by a raw image recorded a few seconds prior (Fig.5b2). The time
379 interval between the two images was chosen to ensure distinct grey level contrast in the
380 resulting images and depends on the time evolution of the solidification microstructure. In the
381 present experiments, a value in the range of 5 to 7 seconds was chosen. This image processing
382 was especially useful for either following the dendrite growth as depicted in Fig.5c2, where the
383 brightest pixels reveal the solid formed during the time interval, or for detecting phase
384 transformations for which the change in contrast is very small and was hardly distinguishable
385 by using only the flat-field correction, such as the eutectic reaction.

386 In the framework of this paper, both image processing techniques were utilised to analyse the
387 successive solidification steps during the sample cooling of the three ternary alloys.

388



389

390 **Fig.5:** Illustration of the two image processing procedures used to improve the legibility of the
 391 images. (a) Raw image, (b1) reference image recorded before applying the cooling rate, (c1)
 392 result of the flat-field correction revealing more clearly the growth microstructure, (b2) raw
 393 image recorded 7 seconds before the first raw image and (c2) result of the frame differencing
 394 procedure showing the amount of solidified α -Al during the time interval.

395

396 4.3. Solidification paths observed during experiments with in situ observation

397 For a sake of comparison, directional solidifications of Al-10 wt.% Cu-X wt.% Sn alloys were
 398 conducted using the same cooling rate ($R = -0.15$ °C/s) and applied thermal gradient ($G_{app} =$
 399 5.55 °C/mm). The outcomes are shown in Fig.6 for the Al-10 wt.% Cu-5 wt.% Sn alloy, in
 400 Fig.7 for Al-10 wt.% Cu-20 wt.% Sn alloy and in Fig.8 for Al-10 wt.% Cu-10 wt.% Sn alloy.
 401 Supplementary materials are provided containing videos of the solidification for all the
 402 investigated alloys. In the following figures, the displayed temperatures T_{avg} corresponds to the
 403 average value of the thermocouple temperatures used to regulate the heater elements at the time

404 of image capture. It will be assumed thereafter that this average temperature T_{avg} is
405 representative of the temperature at the centre of the field of view.

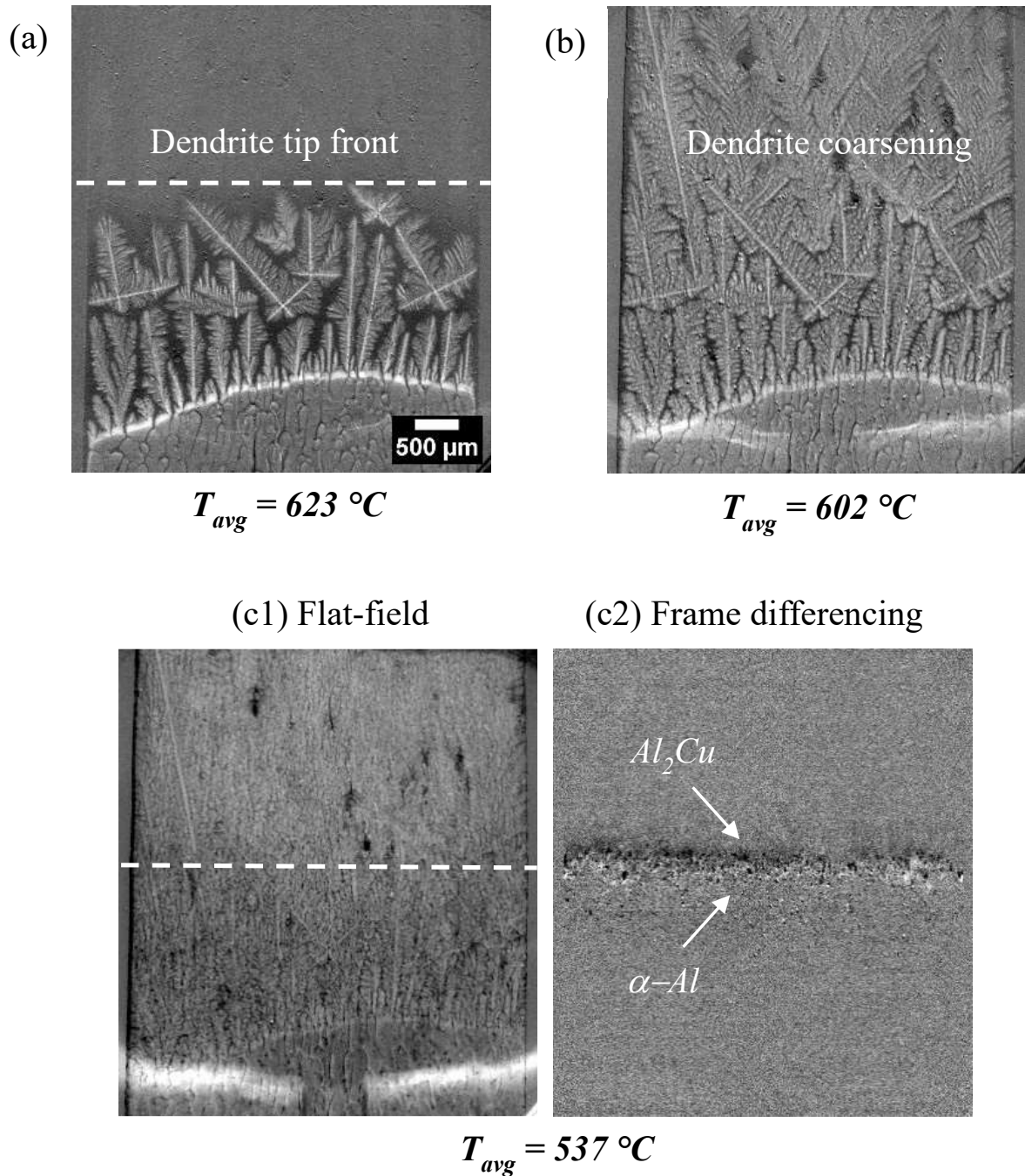
406

407 *a. Low tin content alloy (Al-10 wt.% Cu-5 wt.% Sn)*

408 For the low tin content alloy, the growth of elongated α -Al grains initiates a few seconds after
409 cooling begins, as depicted in Fig. 6a. The radiograph clearly shows dendrites in white,
410 separated by a liquid which appears in dark grey because of copper and tin rejection during
411 solidification. Those α -Al grains have random orientations and developed preferentially in the
412 temperature gradient direction [37, 38]. The solidification front corresponding to the position
413 of the dendrite tips (indicated by the dashed line) is quite flat, indicating that there is no
414 significant transverse temperature gradient. As solidification proceeds, the entire field of view
415 is filled with dendrites that have grown and coarsened, as depicted in Fig. 6b when the average
416 sample temperature reaches 602°C.

417

418



419

420 **Fig. 6:** Sequence of radiographs of Al–10 wt.% Cu–5 wt.% Sn solidification ($R = -0.15 \text{ K/s}$ and
 421 $G_{app} = 5.55 \text{ K/mm}$). Radiographs show (a) the development of columnar dendritic structures,
 422 the dashed lines indicate the position of the tip of the dendrite, (b) growth and coarsening in the
 423 dendrites throughout the field of view, and (c) the reaction $L' \rightarrow \alpha-Al + \theta-Al_2Cu$. Left-hand
 424 side: flat-field image. Right-hand side: image with frame differencing correction highlighting
 425 the formation of Al_2Cu and $\alpha-Al$.

426

427 Fig.6c shows observations made at a much lower temperature of 537°C by applying flat-field
428 correction (Fig.6c1) and frame differencing (Fig.6c2) to the same radiograph. In Fig.6c1, the
429 dendritic network has experienced a long coarsening period, and the secondary and ternary arms
430 are now difficult to distinguish. In addition, the half-top part of the sample is brighter than the
431 half-bottom part of the sample. This change in grey level is abrupt as indicated by the dashed
432 line, which means that a phase transformation occurs at a given temperature. Fig. 6c2 (frame
433 differencing image) reveals the formation of a dark layer above a white layer at this given
434 temperature. The white layer can be attributed to the formation of the α -Al phase, which is less
435 absorbing, and the dark layer can be attributed to the formation of the Al_2Cu phase, as it is more
436 absorbing than the initial liquid phase. Accordingly, Al_2Cu formation is probably the cause of
437 the darkening seen in the lower part of Fig. 6c1. The formation of these phases at this
438 temperature would be in line with the theoretical solidification path (Fig.2 and Table 1).

439

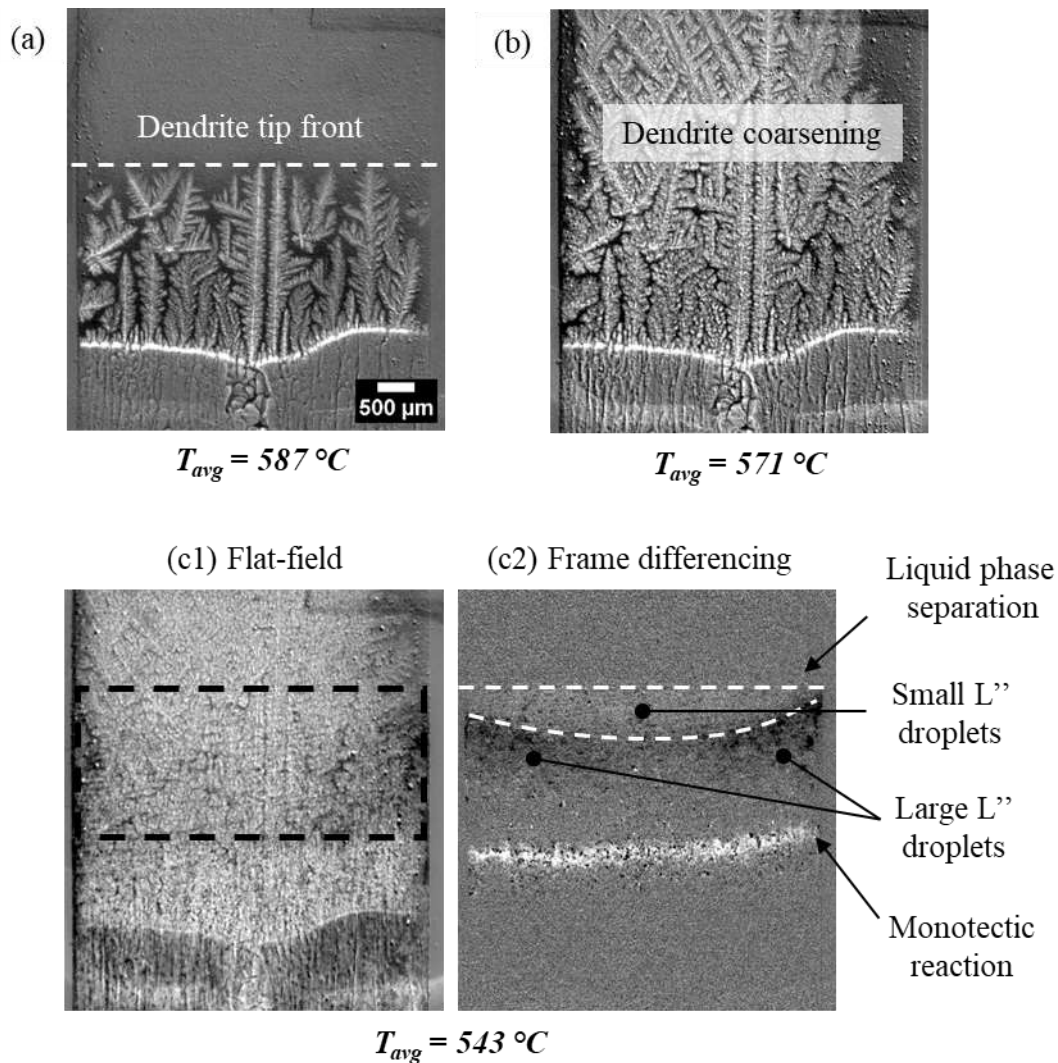
440 *b. Medium and high tin content alloys (Al-10 wt.% Cu-10 wt.% Sn and Al-10 wt.% Cu-20 wt.%*
441 *Sn)*

442 For the two alloys with higher Sn compositions ($X = 10 \text{ wt.}\%$ and $X = 20 \text{ wt.}\%$), the expected
443 reactions following the formation of the primary α -Al phase are (i) the liquid phase separation
444 and (ii) a monotectic reaction. Similar observations have been made for the two alloy
445 compositions and therefore the following section will focus first on the solidification of Al-10
446 wt.% Cu-20 wt.% Sn for which the phenomena were observed more clearly.

447 As for the low tin content alloy, the first stages of solidification consist of the formation of
448 elongated grains with random orientations and developing in the temperature gradient direction
449 (Fig. 7a and Fig. 7b), followed by a coarsening period. Fig.7c shows observations made at a

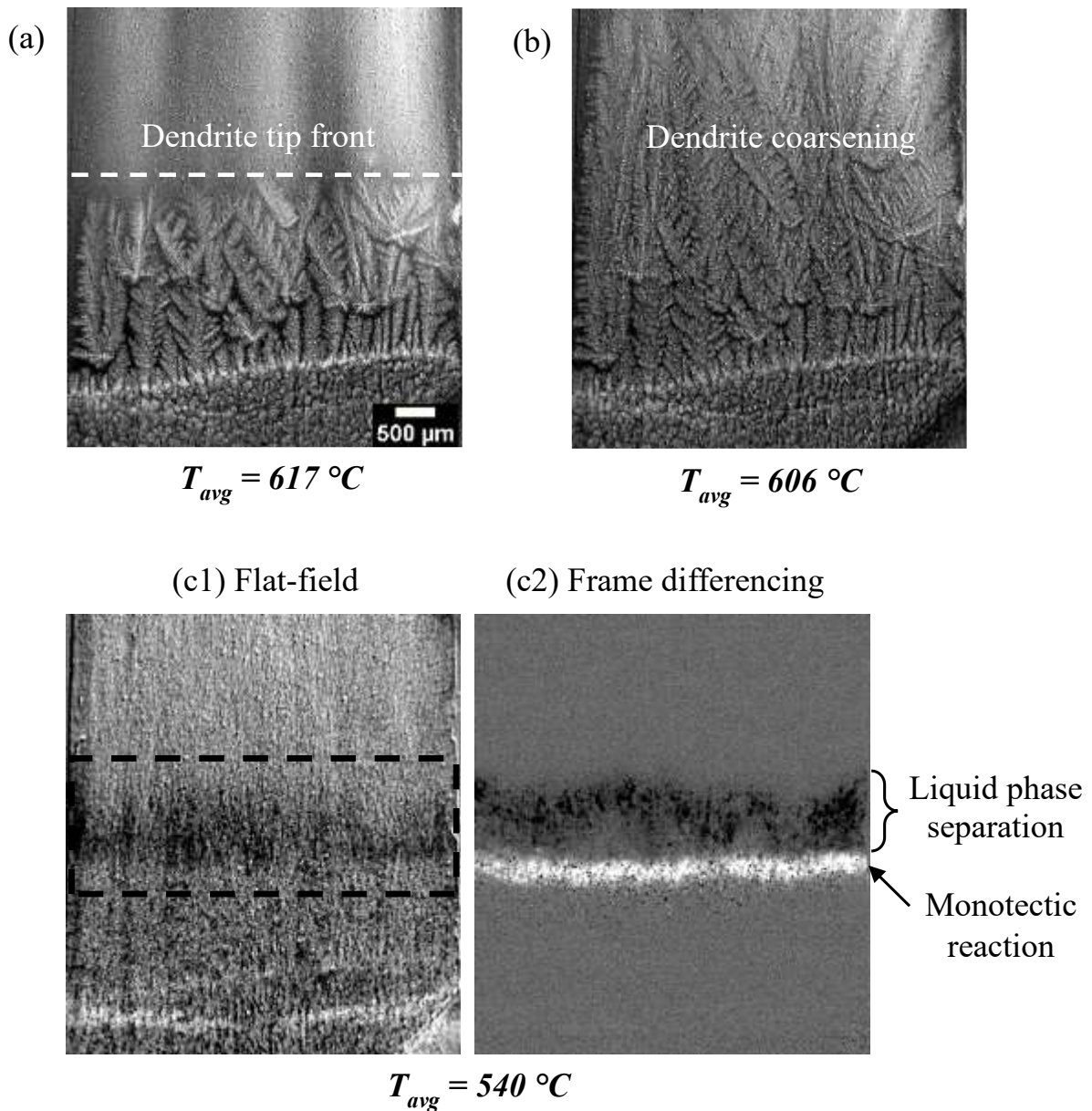
450 lower temperature of 543°C by applying flat-field correction (Fig.7c1) and frame differencing
451 (Fig.7c2) to the same radiograph. This time, three regions with different contrasts indicated by
452 dashed lines can be distinguished in Fig. 7c1: the top part and bottom parts of the image are
453 brighter than the middle part. Fig. 7c2 (frame differencing image) reveals, from top to bottom,
454 a light grey layer containing small black dots above a dark layer, and a white region also
455 containing small black dots. The light grey layer can be attributed to the depletion in Sn of the
456 L' liquid due to the formation of the Sn-rich L'' liquid, appearing as small black droplets. The
457 black layer corresponds to the sudden formation of a large amount of the Sn-rich liquid L''
458 during the liquid phase separation and is the cause of the darkening seen in the middle part of
459 Fig.7 c1. Finally, the white region agrees with the formation of a high amount of α -Al as
460 expected during the monotectic reaction and is the cause of the brightening seen in the bottom
461 part of Fig.7 c1. It is worth mentioning that in the latter case the black dots in the white layer
462 can be either Al₂Cu or L'' phases that are both absorbing and thus couldn't be distinguished
463 with the current spatial resolution. This sequence of phase formation would only partly be in
464 line with the theoretical solidification path (Fig.2 and Table 1), as the phase separation leading
465 to the formation of the Sn-rich liquid L'' didn't occur with a linear increase of the mass fraction
466 of L'' but in two steps: firstly, the progressive formation of small droplets and secondly the
467 sudden occurrence of a large amount of L'' as indicated in Fig.7 c2.

468 For a sake of completeness, the image sequence for the Al-10 wt.% Cu- 10 wt.% Sn alloy is
469 displayed in Fig.8. The same steps are visible: formation of elongated grain (Fig.8a), coarsening
470 (Fig.8b), phase separation and monotectic reaction (Fig.8c). It is worth noting that the light grey
471 layer wasn't detected in Fig.8c, most probably because the phase separation and the monotectic
472 reaction occurred at closer temperatures and the change in composition of L' was lower.



473

474 **Fig. 7:** Sequence of radiographs of Al-10 wt.% Cu- 20 wt.% Sn solidification ($R = -0.15\text{ K/s}$
 475 and $G_{app} = 5.55\text{ K/mm}$). Radiographs show (a) the development of columnar dendritic
 476 structures, the dashed lines indicate the position of the tip of the dendrite, (b) growth and
 477 coarsening in the dendrites throughout the field of vision, and (c) the liquid phase separation
 478 and monotectic reaction. On the left-hand side: flat-field image with the separation of the liquid
 479 phase highlighted in the frame. On the right-hand side: image with frame differencing
 480 correction, highlighting the liquid phase separation ($L'+L''$) and the monotectic reaction.



481
 482 **Fig. 8:** Sequence of radiographs of Al-10 wt.% Cu- 10 wt.% Sn solidification ($R = -0.15\text{ K/s}$
 483 and $G_{app} = 5.55\text{ K/mm}$). Radiographs show (a) the development of columnar dendritic
 484 structures, the dashed lines indicate the position of the tip of the dendrite, (b) growth and
 485 coarsening in the dendrites throughout the field of vision, and (c) the liquid phase separation
 486 and monotectic reaction. On the left-hand side: flat-field image with the separation of the liquid
 487 phase highlighted in the frame. On the right-hand side: image with frame differencing
 488 correction, highlighting the liquid phase separation (L") and the monotectic reaction.

489

490 **5. Discussion**

491 In summary, the solidification paths of Al-10 wt.% Cu-X wt.% Sn (with X = 0; 5; 10 and 20)
492 alloys were successfully investigated by using three different and complementary approaches,
493 namely Thermo-Calc calculations, DSC thermal analysis and solidification experiments with
494 *in situ* X-radiography monitoring. All these approaches clearly establish that the addition of tin
495 element in alloys dramatically alters the solidification behaviour and associated microstructure,
496 that could generate liquid phase separation and monotectic reaction. Since these alloys are
497 multi-element alloy systems, theoretical understanding of the successive steps during the
498 solidification phase is rather difficult, due to the metallurgical complexity. Qualitatively, the
499 three analysis methods show an excellent agreement for the successive steps that are observed
500 during the solidification but large discrepancies are found for the temperatures of reactions.

501 For the three ternary alloys considered in this study, Al-10 wt.% Cu-X wt.% Sn (with X = 5;
502 10 and 20), the first solid consists of elongated α -Al grains, more or less oriented along the
503 imposed temperature gradient as expected. The only difference between the three alloys is the
504 temperature $T_{\alpha-Al}$ at which dendrites are expected to form. According to the phase diagram, the
505 higher the Sn composition is, the lower $T_{\alpha-Al}$. Thermo-calc calculations give decreasing values
506 from 624°C to 597.5°C, while DSC measurements during cooling show peaks starting at values
507 that decrease from 610°C to 572.8°C when the Sn composition increases from 5 to 20 wt.%.
508 From solidification experiments with *in situ* observation, $T_{\alpha-Al}$ values can be estimated from
509 623°C to 587°C. The discrepancies between all those values are within the range of uncertainty
510 of each method. Indeed, Thermo-Calc values are calculated at equilibrium based on phase
511 diagram, whereas (i) the DSC curves are measured during sample melting/cooling, slightly out
512 of equilibrium, which requires careful control of melting/cooling rates and volume fractions of
513 the disperse phase to obtain accurate results, and (ii) estimates from solidification experiments

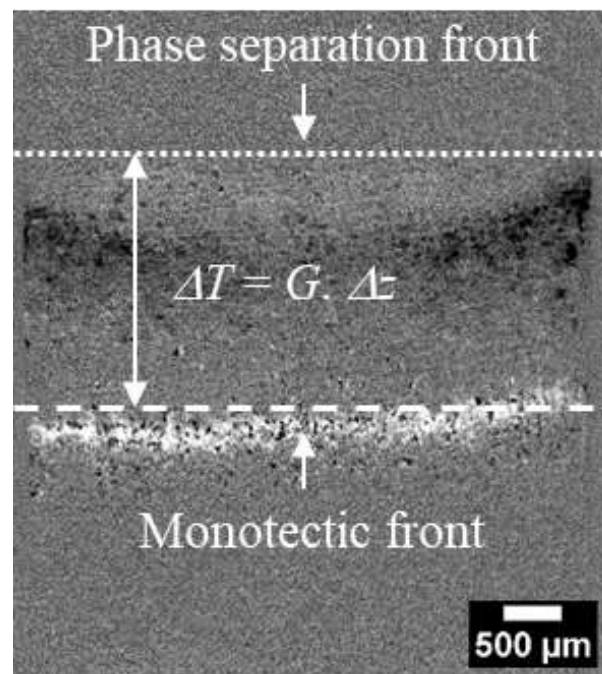
514 are limited by the approximate knowledge of temperature distribution along the sample in the
515 Field-of-View.

516 For the low tin content alloy, Thermo-Calc calculations predict a second phase transformation,
517 in a very narrow range of temperature, between 531.5°C and 524.8°C (see Table 1). This phase
518 transformation appears as a sharp peak in DSC cooling curve at a much lower temperature of
519 510.5°C (Fig.4 and Table 1) and has also been revealed during solidification experiment at a
520 mean temperature of 537°C. For this phase transformation, solidification experiment and
521 Thermo-Calc calculations are in good agreement, whereas temperature value from DSC
522 analysis seems too low. A third and final phase transformation is the eutectic reaction, which
523 occurs at about 230°C according to Thermo-Calc calculations, 220.5°C from both DSC cooling
524 curve and solidification experiment. Like for the temperature $T_{\alpha-Al}$ at which dendrites are
525 expected to form, those discrepancies are most likely due to uncertainty inherent to each
526 method.

527 For the two alloys with higher Sn compositions ($X = 10$ wt.% and $X = 20$ wt.%), the expected
528 reactions following the formation of the primary $\alpha-Al$ phase are (i) the liquid phase separation
529 followed by (ii) a monotectic reaction and a final transformation by (iii) the eutectic reaction.
530 Those observations have been indeed made for the two alloy compositions whatever the
531 approach is. The liquid phase separation is predicted at 537.5°C and 550.6°C for Al-10 wt.%
532 Cu-10 wt.% Sn and Al-10 wt.% Cu-20 wt.% Sn respectively by Thermo-Calc software (Table
533 2 and Table 3). Values obtained by DSC measurements during cooling are significantly lower,
534 at 510.5°C and 517.8°C for the two alloys (Fig. 4, Table 2 and Table 3), but only slightly lower
535 at 533°C and 540°C by DSC measurements during melting (Figure 3). Directional solidification
536 experiments give roughly the same value of 540°C for both alloys. For the directional
537 solidification experiments, these very approximate values are most likely due to the uncertainty
538 about the temperature distribution in the Field-of-View, as well as the limited spatial resolution

539 which prevents the determination of an accurate value for the first Sn droplet nucleation. Nor
540 should we rule out the possibility of convection or buoyancy effects on Sn droplets at this stage
541 [25, 47]. The subsequent reaction is the monotectic reaction, that is scheduled by Thermo-Calc
542 calculations at a plateau of 529.4°C for both alloy compositions. The peaks obtained by DSC
543 measurements during cooling start at 510.8°C and 517.8°C for Al-10 wt.% Cu-10 wt.% Sn and
544 Al-10 wt.% Cu-20 wt.% Sn respectively, but 525.5 and 522.8°C by DSC measurements during
545 melting, which better agrees with the Thermo-Calc calculated value of 529.4°C.

546 As previously mentioned, the approximate value of the temperature for the directional
547 solidification experiments makes it hard to compare with Thermo-Calc calculations and DSC
548 measurements. However, it is possible to estimate the temperature difference ΔT between the
549 beginning of the phase separation and the monotectic reaction based on their respective position
550 in the field of view in the radiographs (Fig.9).



551
552 **Fig. 9:** Determination of the temperature difference between the beginning of the phase
553 separation (dotted line) and the monotectic reaction (dashed line). (Al-20 wt.% Cu- 10 wt.%
554 Sn, $R = 0.15$ K/s and $G_{app} = 5.55$ K/mm).

555

556 It has been previously shown in [37] that the actual temperature gradient in the sample G_{sample}
557 can be estimated by measuring the propagation velocity of the solidification front V_{front} and then
558 using the relation $G_{\text{sample}} = R/V_{\text{interface}}$ with R the applied cooling rate. Here, the propagation of
559 the monotectic front was used for both alloys to determine G_{sample} . The temperature difference
560 between the phase separation and the monotectic reaction is then $\Delta T = G_{\text{sample}} \cdot \Delta z$, with Δz the
561 distance between the beginning of the phase separation and the monotectic front. A temperature
562 difference of 4°C is obtained for the Al-10 wt.% Cu-10 wt.% Sn alloy, and a temperature
563 difference of 11°C is obtained for the Al-10 wt.% Cu-20 wt.% Sn alloys. From Thermo-Calc
564 calculation a temperature difference of 8.1°C is predicted for the Al-10 wt.% Cu-10 wt.% Sn
565 alloy and a temperature difference of 21.2°C is predicted for the Al-10 wt.% Cu-20 wt.% Sn
566 alloys. The impact of Sn content on the temperature difference qualitatively agrees between the
567 measured and the predicted values.

568 Those discrepancies can be attributed to various factors, such as the fact that Thermo-Calc
569 calculations don't consider the impact of nucleation and growth undercoolings. It is indeed
570 well-known in directional solidification that the temperature of dendrite tips is lower than the
571 equilibrium temperature due to solute rejection leading to the occurrence of constitutional
572 undercooling [48]. The same remark applies to the monotectic and eutectic solidification fronts.
573 Droplet formation also occurs at a different temperature than the phase separation equilibrium
574 temperature as they most probably appear on the sample wall by heterogeneous nucleation.
575 Another factor is that the composition of the sample could have changed in the field of view
576 due to segregation occurring during the stabilisation and solidification steps. The temperature
577 difference wasn't estimated from the DSC measurements as it wasn't possible to accurately
578 determine the beginning of the phase separation and monotectic reaction due to the
579 superimposition of their respective peaks in the curves.

580 Ultimately, the final eutectic phase transformation, which is predicted at about 230°C in
581 Thermo-Calc calculations, is observed at 223°C from both DSC cooling curve and solidification
582 experiment, which is in good agreement.

583

584 **6. Conclusions**

585 Determination of reliable solidification paths for ternary alloys is difficult. In the literature,
586 several different approaches are used that give sometime diverging results and subject to large
587 uncertainties. In this paper, the solidification paths of Al-10 wt.% Cu-X wt.% Sn (with X = 0;
588 5; 10 and 20) alloys were successfully investigated by using three different and complementary
589 approaches, namely Thermo-Calc calculations, thermal analysis and solidification experiments
590 with in situ X-radiography monitoring. This paper provides a comparison between those
591 methods, both qualitatively (nature of the successive phase transformations) and quantitatively
592 (temperature at which each phase transformation occurs).

593 The main qualitative conclusion is that all these methods describe correctly the successive phase
594 transformations, from the initial α -Al dendrite growth to the final eutectic transformation of the
595 residual liquid. Depending on the alloy composition, the liquid phase separation and the
596 monotectic reactions are successfully predicted by Thermo-Calc calculations and
597 experimentally detected during DSC measurements or solidification experiments with in situ
598 observation. It should be emphasized that in situ observation revealed some unexplained
599 features that occur during the liquid phase separation. It would be easy to justify these
600 phenomena by convection and/or buoyancy effects associated to gravity but further studies are
601 required to clearly determine their origins.

602 Evaluation of the temperature at which each phase transformation occurs has been also carried
603 out by the different methods. A wide dispersion has been found, up to 10°C for some phase

604 transformations. Thermo-Calc calculations and thermodynamic measurements have intrinsic
605 limitations. For solidification experiment, the main weakness is the accurate knowledge of the
606 temperature distribution in the Field-of-View. Further improvements of the current apparatus
607 are required to achieve the necessary temperature resolution. It is also worth mentioning that
608 investigations focused on the effect of Sn addition and of the various solidification parameters
609 on the growth of α -Al dendrites and Sn droplet size and spatial distribution could be performed
610 based on the X-radiography images. Unfortunately, analyses of the X-ray images to determine
611 phase fractions, as performed in other studies [49-51] was not possible. This is due to the use
612 of a polychromatic laboratory source in this study, which prevents a straightforward phase
613 fraction extraction. Additionally, significant coarsening of the phases during cooling may
614 hinder direct comparison of the 3D reconstructions and radiographs, as successfully carried out
615 by Chao *et al.* [49]. Such investigations will be the topic of future complementary studies.

616

617 **Acknowledgments**

618 This research work is supported by the French National Space Agency (CNES) n°200761/00.
619 Mrs Sarah De Albuquerque benefits a PhD grant from the French Embassy in Brazil. Pr. Amauri
620 Garcia and Pr. Noé Cheung are also acknowledged for their help to the first analyses and ingot
621 preparation. This study was financed in part by the Coordenação de Aperfeiçoamento de
622 Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001.

623

624 **Appendix A. Supplementary data**

625 Supplementary data related to this article can be found at (link to supplementary material)

626

627

628 **References**

- 629 [1] X.F. Wu, G.A. Zhang, F.-F. Wu, Effect of Sn addition and heat treatment on microstructure and wear
630 resistance of hypereutectic Al-Si-Cu-Mg alloy, *Cailiao Rechuli Xuebao/Transactions of Materials*
631 *and Heat Treatment*, 33 (2012) 85-90.
- 632 [2] G. Ran, J.-E. Zhou, S. Xi, P. Li, Microstructure and morphology of Al-Pb bearing alloy synthesized
633 by mechanical alloying and hot extrusion, *Journal of Alloys and Compounds*, 419 (2006) 66-70.
- 634 [3] X. Wu, G.A. Zhang, Influence of Sn Content on the Microstructure and Dry Sliding Wear Behaviour
635 of Hypereutectic Al-20Si Alloy, *Advanced Materials Research*, 299-300 (2011) 265-268.
- 636 [4] Z.C. Lu, M.Q. Zeng, Y. Gao, M. Zhu, Significant improvement of wear properties by creating
637 micro/nano dual-scale structure in Al-Sn alloys, *Wear*, 296 (2012) 469-478.
- 638 [5] F. El-Salam, A. El-Khalek, R. Nada, L. Wahab, H. Zahran, Effect of Sn content on the structural and
639 mechanical properties of Al-Si alloy, *Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process.*,
640 527 (2010) 1223-1229.
- 641 [6] X. Liu, M.Q. Zeng, Y. Ma, M. Zhu, Promoting the high load-carrying capability of Al-20 wt%Sn
642 bearing alloys through creating nanocomposite structure by mechanical alloying, *Wear*, s 294-295
643 (2012) 387-394.
- 644 [7] Q. Yang, Z.P. Sun, Z.M. Wang, Effects of Sn, Si, and Cu addition on the microstructure and
645 properties of hypermonotectic Al₉₂Bi₈ alloy, *Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct.*
646 *Process.*, 756 (2019) 71-81.
- 647 [8] N.I. Noskova, N.F. Vil'danova, Y.I. Filippov, R.V. Churbaev, I.A. Pereturina, L.G. Korshunov, A.V.
648 Korznikov, Preparation, deformation, and failure of functional Al-Sn and Al-Sn-Pb nanocrystalline
649 alloys, *Phys. Metals Metallogr.*, 102 (2006) 646-651.
- 650 [9] R. Mittal, A. Tomar, D. Singh, Wear Behavior of Disk Shape Spray Formed Al-Si-Pb Alloys, *Journal*
651 *of Materials Engineering and Performance*, 23 (2014) 975-981.
- 652 [10] H.R. Kotadia, A. Das, E. Doernberg, R. Schmid-Fetzer, A comparative study of ternary Al-Sn-Cu
653 immiscible alloys prepared by conventional casting and casting under high-intensity ultrasonic
654 irradiation, *Mater. Chem. Phys.*, 131 (2011) 241-249.
- 655 [11] H.R. Kotadia, E. Doernberg, J.B. Patel, Z. Fan, R. Schmid-Fetzer, Solidification of Al-Sn-Cu Based
656 Immiscible Alloys under Intense Shearing, *Metall. Mater. Trans. A-Phys. Metall. Mater. Sci.*, 40A
657 (2009) 2202-2211.
- 658 [12] F. Bertelli, C. Brito, I.L. Ferreira, G. Reinhart, H. Nguyen-Thi, N. Mangelinck-Noel, N. Cheung,
659 A. Garcia, Cooling thermal parameters, microstructure, segregation and hardness in directionally
660 solidified Al-Sn-(Si;Cu) alloys, *Materials & Design*, 72 (2015) 31-42.
- 661 [13] F. Bertelli, E.S. Freitas, N. Cheung, M.A. Arenas, A.C.d. Campo, J.d. Damborenea, A. García,
662 Microstructure, tensile properties and wear resistance correlations on directionally solidified Al-
663 Sn-(Cu; Si) alloys, in, Elsevier, 2017,

- 664 [14] A. Karma, D. Tournet, Atomistic to continuum modeling of solidification microstructures, *Current*
665 *Opinion in Solid State and Materials Science*, 20 (2016) 25-36.
- 666 [15] W. Kurz, M. Rappaz, R. Trivedi, Progress in modelling solidification microstructures in metals and
667 alloys. Part II: dendrites from 2001 to 2018, *Int. Mater. Rev.*, (2020) 1-47.
- 668 [16] H. Nguyen-Thi, G. Reinhart, B. Billia, On the interest of microgravity experimentation for studying
669 convective effects during the directional solidification of metal alloys, *Comptes Rendus*
670 *Mécanique*, 345 (2017) 66-77.
- 671 [17] N. Bergeon, G. Reinhart, F.L. Mota, N. Mangelinck-Noël, H. Nguyen-Thi, Analysis of gravity
672 effects during binary alloy directional solidification by comparison of microgravity and Earth
673 experiments with in situ observation, *The European Physical Journal E*, 44 (2021) 98.
- 674 [18] D.J. Browne, F. Garcia-Moreno, H. Nguyen-Thi, G. Zimmermann, F. Kargl, R.H. Mathiesen, A.
675 Griesche, O. Minster, Overview of In Situ X-Ray Studies of Light Alloy Solidification in
676 Microgravity, in: K.N. Solanki, D. Orlov, A. Singh, N.R. Neelameggham (Eds.) *Magnesium*
677 *Technology 2017*, Springer International Publishing Ag, Cham, 2017, pp. 581-590.
- 678 [19] D. Mirković, J. Gröbner, R. Schmid-Fetzer, Solidification paths of multicomponent monotectic
679 aluminum alloys, *Acta Mater.*, 56 (2008) 5214-5222.
- 680 [20] W. Zhai, H.M. Liu, B. Wei, Liquid phase separation and monotectic structure evolution of ternary
681 Al_{62.6}Sn_{28.5}Cu_{8.9} immiscible alloy within ultrasonic field, *Materials Letters*, 141 (2015) 221-
682 224.
- 683 [21] H. Nguyen-Thi, L. Salvo, R.H. Mathiesen, L. Arnberg, B. Billia, M. Suery, G. Reinhart, On the
684 interest of synchrotron X-ray imaging for the study of solidification in metallic alloys, *Comptes*
685 *Rendus Physique*, 13 (2012) 237-245.
- 686 [22] R.H. Mathiesen, L. Arnberg, H. Nguyen-Thi, B. Billia, In Situ X-Ray Video Microscopy as a Tool
687 in Solidification Science, *Jom*, 64 (2012) 76-82.
- 688 [23] Y. Wang, S. Jia, M. Wei, L. Peng, Y. Wu, X. Liu, Research progress on solidification structure of
689 alloys by synchrotron X-ray radiography: A review, *Journal of Magnesium and Alloys*, 8 (2020)
690 396-413.
- 691 [24] Y. Zhao, W. He, D. Song, W. Zhang, F. Shen, B. Ma, Y. Jia, Z. Sun, Y. Fu, R. Fernández, In-situ
692 synchrotron X-ray radiography study of primary Fe-rich phases growth in Al-Fe(Cu) alloys,
693 *Materials Characterization*, 195 (2023) 112539.
- 694 [25] P.L. Schaffer, R.H. Mathiesen, L. Arnberg, M.D. Sabatino, A. Snigirev, In situ investigation of
695 spinodal decomposition in hypermonotectic Al-Bi and Al-Bi-Zn alloys, *New Journal of Physics*,
696 10 (2008) 053001.
- 697 [26] W. Lu, S. Zhang, W. Zhang, G. Kaptay, J. Yu, Y. Fu, J. Li, Direct observation of the segregation
698 driven by bubble evolution and liquid phase separation in Al-10 wt.% Bi immiscible alloy, *Scr.*
699 *Mater.*, 102 (2015).

- 700 [27] W. Lu, S. Zhang, J. Li, Segregation driven by collision and coagulation of minor droplets in Al–Bi
701 immiscible alloys under aerodynamic levitation condition, *Materials Letters*, 107 (2013) 340-343.
- 702 [28] Y. Zhang, Y. Wu, Y. Tang, J. Ma, B. Mao, Y. Xue, H. Xing, J. Zhang, B. Sun, In situ study on the
703 oscillation of mobile droplets and force analysis during the directional solidification of Al-Bi alloy,
704 *Journal of Materials Science & Technology*, 177 (2024) 1-9.
- 705 [29] <https://thermocalc.com>, Thermo-Calc Software: Computational Materials Engineering
- 706 [30] L. Abou-Khalil, J. Wang, G. Salloum-Abou-Jaoude, M. Garrido, X. Li, Z. Ren, G. Reinhart, H.
707 Nguyen-Thi, Y. Fautrelle, Investigation of Thermo-Electro-Magnetic force on equiaxed grain
708 motion during upward directional solidification, *Int. J. Therm. Sci.*, 145 (2019) 106047.
- 709 [31] Y. Fautrelle, J. Wang, G. Salloum-Abou-Jaoude, L. Abou-Khalil, G. Reinhart, X. Li, Z. Ren, H.
710 Nguyen-Thi, Thermo-Electric-Magnetic Hydrodynamics in Solidification: In Situ Observations
711 and Theory, *JOM Journal of the Minerals, Metals and Materials Society*, 70 (2018) 764 - 771.
- 712 [32] G. Salloum-Abou-Jaoude, J. Wang, L. Abou-Khalil, G. Reinhart, Z. Ren, N. Mangelinck-Noel, X.
713 Li, Y. Fautrelle, H. Nguyen-Thi, Motion of equiaxed grains during directional solidification under
714 static magnetic field, *Journal of Crystal Growth*, 417 (2015) 25-30.
- 715 [33] U. Hecht, L. Gránásy, T. Pusztai, B. Böttger, M. Apel, V. Witusiewicz, L. Ratke, J. De Wilde, L.
716 Froyen, D. Camel, B. Drevet, G. Faivre, S.G. Fries, B. Legendre, S. Rex, Multiphase solidification
717 in multicomponent alloys, *Materials Science and Engineering: R: Reports*, 46 (2004) 1-49.
- 718 [34] W. Boettinger, U. Kattner, K.-W. Moon, J. Perepezko, NIST Recommended Practice Guide: DTA
719 and Heat-Flux DSC Measurements of Alloy Melting and Freezing, in, Elsevier, Kidlington, -1,
720 2006,
- 721 [35] S. Curiotto, L. Battezzati, E. Johnson, N. Pryds, Thermodynamics and mechanism of demixing in
722 undercooled Cu-Co-Ni alloys, *Acta Mater.*, 55 (2007) 6642-6650.
- 723 [36] S. Akamatsu, H. Nguyen-Thi, In situ observation of solidification patterns in diffusive conditions,
724 *Acta Mater.*, 108 (2016) 325-346.
- 725 [37] H. Soltani, G. Reinhart, M.C. Benoudia, F. Ngomessse, M. Zahzouh, H. Nguyen-Thi, Equiaxed
726 grain structure formation during directional solidification of a refined Al-20wt.%Cu alloy: In situ
727 analysis of temperature gradient effects, *Journal of Crystal Growth*, 587 (2022) 126645.
- 728 [38] H. Soltani, G. Reinhart, M.C. Benoudia, F. Ngomessse, M. Zahzouh, H. Nguyen-Thi, Impact of
729 growth velocity on grain structure formation during directional solidification of a refined Al-20
730 wt.%Cu alloy, *Journal of Crystal Growth*, 548 (2020) 125819.
- 731 [39] H. Soltani, G. Reinhart, M.C. Benoudia, M. Zahzouh, H. Nguyen-Thi, Impact of gravity-related
732 phenomena on the grain structure formation: comparative study between horizontal and vertical
733 solidification of a refined Al-20wt.%Cu alloy, *IOP Conference Series: Materials Science and
734 Engineering*, 529 (2019) 012019.

- 735 [40] F. Ngomesse, G. Reinhart, H. Soltani, G. Zimmermann, D.J. Browne, W. Sillekens, H. Nguyen-
736 Thi, In situ investigation of the Columnar-to-Equiaxed Transition during directional solidification
737 of Al–20 wt.%Cu alloys on Earth and in microgravity, *Acta Mater.*, 221 (2021) 117401.
- 738 [41] H. Nguyen-Thi, G. Reinhart, G.S. Abou Jaoude, R.H. Mathiesen, G. Zimmermann, Y. Houltz, D.
739 Voss, A. Verga, D.J. Browne, A.G. Murphy, XRMON-GF: A novel facility for solidification of
740 metallic alloys with in situ and time-resolved X-ray radiographic characterization in microgravity
741 conditions, *Journal of Crystal Growth*, 374 (2013) 23-30.
- 742 [42] M.G.C. Xavier, R.A.V. Reyes, L.F. Gomes, J.E. Spinelli, N. Mangelinck-Noël, H. Nguyen-Thi, G.
743 Reinhart, Combined growth of α -Al and Bi in a Al-Bi-Cu monotectic alloy analyzed by in situ X-
744 ray radiography, *Journal of Crystal Growth*, 536 (2020) 125592.
- 745 [43] G. Reinhart, F. Ngomesse, F. Bertelli, P. Benigni, A. Campos, H. Nguyen-Thi, Investigation of Al-
746 20Sn-10Cu alloy directional solidification by laboratory X-radiography, *IOP Conference Series:
747 Materials Science and Engineering*, 1274 (2023) 012054.
- 748 [44] C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH Image to ImageJ: 25 years of image analysis,
749 *Nature Methods*, 9 (2012) 671-675.
- 750 [45] H. Nguyen-Thi, G. Reinhart, A. Buffet, T. Schenk, N. Mangelinck, H. Jung, N. Bergeon, B. Billia,
751 H. Härtwig, J. Baruchel, In situ and Real-time analysis of TGZM phenomena by synchrotron X-
752 ray radiography, *J. of Crystal Growth*, 310 (2008) 2906-2914.
- 753 [46] G. Reinhart, D. Grange, L. Abou-Khalil, N. Mangelinck-Noël, N.T. Niane, V. Maguin, G.
754 Guillemot, C.A. Gandin, H. Nguyen-Thi, Impact of solute flow during directional solidification of
755 a Ni-based alloy: In-situ and real-time X-radiography, *Acta Mater.*, 194 (2020) 68-79.
- 756 [47] P.L. Schaffer, R.H. Mathiesen, L. Arnberg, L-2 droplet interaction with alpha-Al during
757 solidification of hypermonotectic Al-8 wt.% Bi alloys, *Acta Mater.*, 57 (2009) 2887-2895.
- 758 [48] W. Kurz, D.J. Fisher, M. Rappaz, *Fundamentals of Solidification*, Trans Tech Publications Ltd, ,
759 2023.
- 760 [49] P. Chao, G.R. Lindemann, A.H. Hunter, A.J. Shahani, Pseudo-4D view of the growth and form of
761 locked eutectic colonies, *Acta Mater.*, 240 (2022) 118335.
- 762 [50] W.U. Mirihanage, K.V. Falch, I. Snigireva, A. Snigirev, Y.J. Li, L. Arnberg, R.H. Mathiesen,
763 Retrieval of three-dimensional spatial information from fast in situ two-dimensional synchrotron
764 radiography of solidification microstructure evolution, *Acta Mater.*, 81 (2014) 241-247.
- 765 [51] N. Wang, Y. Tang, Y. Wu, Y. Zhang, Y. Dai, J. Zhang, R. Zhang, Y. Xu, B. Sun, Dynamic evolution
766 of microstructure morphology in thin-sample solidification: Deep learning assisted synchrotron X-
767 ray radiography, *Materials Characterization*, 181 (2021) 111451.

768