

Revealing Dendritic pattern formation in Ni, Fe and Co alloys using synchrotron tomography

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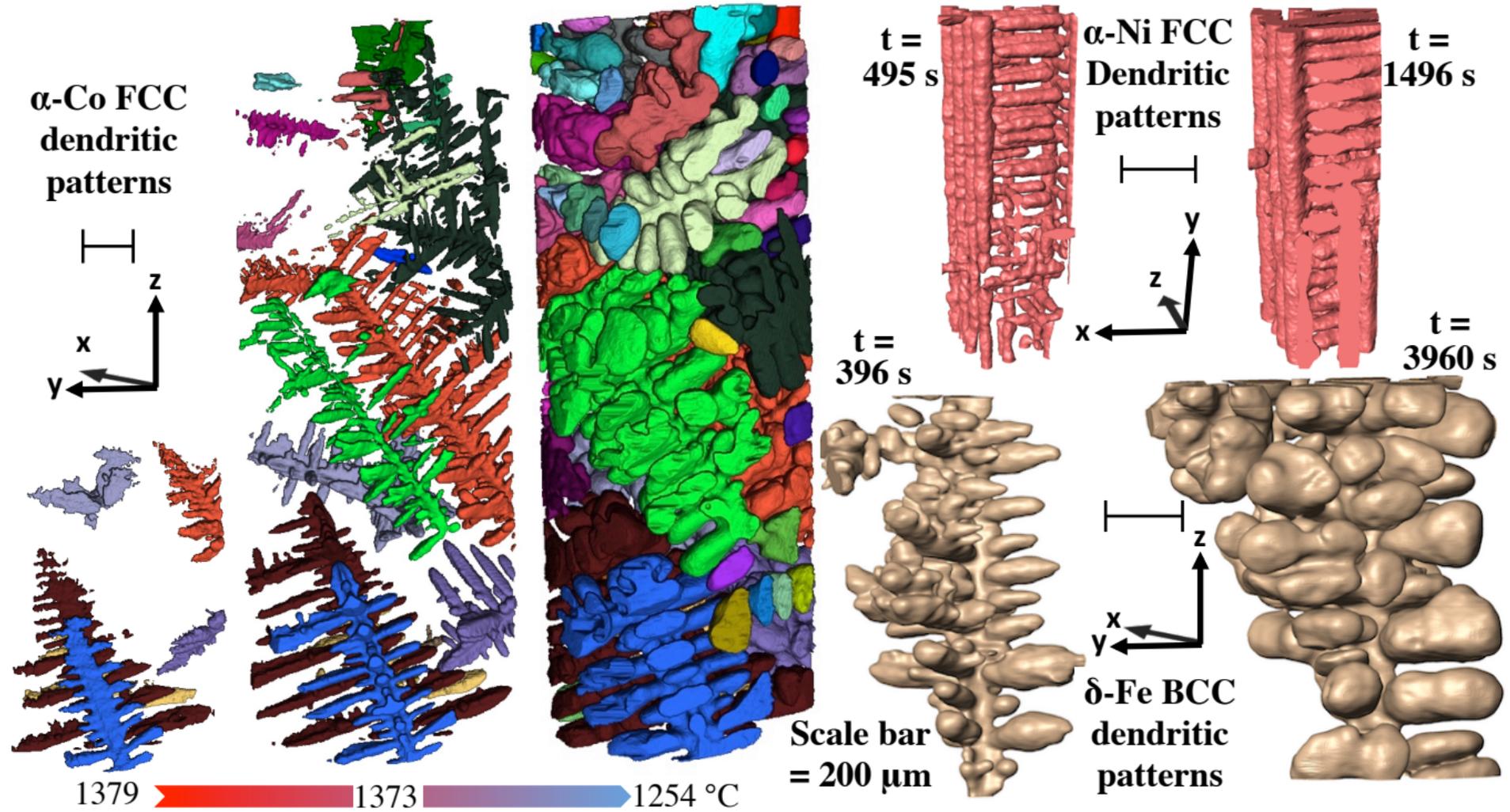
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Abstract The microstructural patterns formed during liquid to solid phase transformations control the properties of a wide range of materials. We developed a novel methodology that allows *in situ* quantification of the microstructures formed during solidification of high temperature advanced alloys. The patterns formed are captured in 4D (3D plus time) using a methodology which exploits three separate advances: a bespoke high temperature environment cell; the development of high X-ray contrast alloys; and a novel environmental encapsulation system. This methodology is demonstrated on Ni, Fe, and Co advanced alloy systems, revealing dendritic pattern formation. We present detailed quantification of microstructural pattern evolution in a novel high attenuation contrast Co-Hf alloy, including microstructural patterning and dendrite tip velocity. The images are quantified to provide 4D experimental data of growth and coarsening mechanisms in Co alloys, which are used for a range of applications from energy to aerospace.

Keywords: Superalloys; synchrotron tomography; interfacial patterns; 4D imaging; dendritic microstructures



30 1. Introduction

31 The patterns that form as materials transform from a liquid to solid directly affect the final properties
32 of material, be it a snowflake or aeroengine gas turbine (AGT) blade. Dendrites are one of the most
33 prevalent microstructural morphologies formed, for example in nickel superalloy AGTs [1] to lithium
34 depositing out in a battery [2]. The *in situ* observation of the patterns formed during the
35 transformation from liquid to solid phase, or solidification, was first performed using transparent
36 organic liquids (metallic analogues) [3–5] and optical microscopes. These results enabled the
37 validation of solidification models linking constitutional undercooling due to solute build-up with
38 interface motion, and the resulting crystal morphologies [4,6]. In areas such as the study of colloids,
39 organic analogue techniques continue to provide novel insights into the kinetic and morphological
40 aspects of crystal growth, and real-time, 2D full-field data of thermal and compositional distributions
41 [7]. However, in optically opaque systems, from magma to metallic alloys, other techniques are
42 required.

43 The first direct observations of dendritic pattern growth in metallic systems were captured in 2D using
44 *in situ* radiography in an Al-30wt% Cu alloy [8]. Subsequently, there have been many radiographic
45 studies of low temperature alloys using laboratory and synchrotron X-ray sources, including
46 elucidation of the growth of secondary phases [9] and defects such as porosity [10]. However, even
47 with radiography there is a paucity of studies on high melting point alloys, with only a few on Fe [11].

48 X-ray radiography is fast, but it requires thin samples that constrain the evolving microstructures, both
49 by restricting the orientation of patterns formed and by altering the growth kinetics. During the last
50 decade, there has been a dramatic rise in the use of X-ray tomography (often termed X-ray
51 microtomography (XMT or μ CT), X-ray computed tomography (XCT), or synchrotron computed
52 tomography (sCT)) to study the evolution of microstructures during solidification. Through recent
53 advances in synchrotron X-ray facilities and iterative reconstruction algorithms, it is now possible to
54 perform fast 4D (3D + time/stress/temperature) tomography on low temperature (<800 °C) metallic
55 alloys as they solidify [12,13]. Some researchers have also studied the influence of deformation on
56 semi-solid alloys [14–16]. These X-ray radiographic and tomographic investigations have helped to
57 inform and validate many new mathematical models developed for low temperature solidification
58 microstructures [17–19] and defects [10] in metals.

59 Most 4D solidification studies of metallic systems have been performed on Al-Cu based alloys [20].
60 These alloys provide excellent attenuation contrast between the solidifying face centred cubic (FCC)
61 α -phase and the liquid. Although the morphological and kinetic aspects observed via the *in situ*
62 tomography can be correlated with industrially viable Al alloys, there is no confirmation that the
63 results can be extended to other FCC systems that solidify at very high temperatures. High
64 temperature alloys such as nickel superalloys, cobalt superalloys, and iron alloys have yet to be

65 studied in the semi-solid state using 4D imaging, although high temperature solid state investigations
66 have been performed[21]. Understanding pattern formation during the solidification of these high
67 temperature advanced alloys is critical to predicting their strength, and preventing the formation of
68 solidification defects such as freckles [17,22], and grain mis-orientation during directional (DX) and
69 single crystal (SX) growth [23,24].

70 There is also an extensive field of modelling of pattern formation in high temperature advanced alloys
71 [1,25–29]. However, these computational simulations have only been validated against long-chain
72 organic analogues or low melting point metallic analogues [17]. Unfortunately, these analogue
73 systems have very different diffusion coefficients and interfacial energies as compared to high
74 temperature alloy systems. Thus, the possibility to visualize the formation of such defects/morphology
75 *in situ* in alloy systems based on Ni, Fe and Co could dramatically advance the design and production
76 of new superalloys.

77 In this study, a methodology incorporating three main advances is provided for tomographic
78 examination of the solidification patterns in high temperature alloys with melting points exceeding
79 1300 °C: (a) design criteria for high X-ray attenuation contrast alloys; (b) the development of an
80 environmental cell enabling the combination of high temperature solidification tests and synchrotron
81 X-ray tomography; and (c) a specimen environmental encapsulation system. These innovations are
82 applied to study the evolving solidification patterns in Ni, Fe and Co alloys in 4D (3D plus time).

83 **2. Materials and Methods**

84 **2.1. Alloy Design**

85 The majority of commercial Ni, Fe, and Co alloys form solidification phases with negligible X-ray
86 attenuation variation between them and the interdendritic liquid, making X-ray tomographic
87 characterization highly challenging. To perform 4D imaging of solidification in these materials, a
88 bespoke alloy must be used that meets four criteria: (a) the primary phase must contain little or no
89 solute, (b) at the first invariant reaction temperature there must be 40% - 60% liquid, (c) the X-ray
90 attenuation characteristics of the solute must be markedly different from the solidifying grains, and (d)
91 the primary phase that appears during solidification must be face centred cubic (body centred cubic in
92 the case of Fe). Criteria (a), (b) and (c) are necessary for achieving high X-ray contrast, while (d) is
93 essential for mimicking the solidification behaviour of alloys used in AGTs and industrial gas turbines
94 (IGTs).

95 During solidification, the solubility of the primary phase is interpreted in terms of the partition
96 coefficient, k , where $k=C_s/C_L$, where C_s and C_L are the concentration of solute in the solid and liquid
97 respectively, as shown in supplementary Fig. S1a. To meet criterion (a), the value of k must be quite
98 small, which also implies that criterion (b) is respected. For criterion (c), each element's characteristic

99 X-ray absorption edges are exploited. Using a monochromatic beam just above this absorption edge
100 enables clear identification between one phase and another. Second, when a polychromatic (*white*) X-
101 ray spectrum interacts with materials, different phases absorb different amounts of X-rays. This is
102 known as non-characteristic X-ray interaction. Consequently, depending on the alloy system, either a
103 *white* beam or a monochromatic X-ray beam with an energy just above one of the characteristic edges
104 may be used for achieving a good contrast between the solid and liquid phases.

105 To develop the high X-ray contrast Ni, Fe and Co alloys, various metallic elements were examined.
106 For Co, of the elements having smaller atomic numbers, only Mg forms a eutectic with very small k .
107 However, Co and Mg have nearly identical non-characteristic X-ray absorption behaviour and both
108 lack absorption edges at X-ray energies found at high-energy synchrotron beamlines, such as the I12
109 at the Diamond Light Source where the experiments were conducted. Of the elements having larger
110 atomic number than Co, only Hf fits the stated criteria. For the Co-Hf system [30,31], photon energies
111 in the range of 65 to 80 keV were found to yield a substantial attenuation difference between the
112 solidifying α -Co dendrites and Hf rich interdendritic liquid. This difference arises mainly as a result of
113 the k -absorption edge of Hf at 65.351 keV [32]. Similar arguments can be made for Ni and Fe.

114 In the present study, Ni-14 wt.%Hf, Fe-11 wt.%Hf and Co-18 wt.%Hf alloys were chosen for 4D
115 imaging. The Co-Hf alloy used in this investigation was obtained by induction melting and
116 conventional casting in an oxide ($\text{Al}_2\text{O}_3/\text{ZrO}_2$) crucible followed by air-cooling. The Ni-Hf and Fe-Hf
117 alloys were prepared in a vacuum arc melter using induction melted Ni-Hf and Fe-Hf master alloys,
118 respectively. The cylindrical samples for the *in situ* solidification trials were extracted from the
119 middle section of the as-cast sample.

120 **2.2. High temperature environmental cell and experimental setup for *in situ* XCT**

121 The high temperature environmental cell developed in this study consists of two modules, a sample
122 module and a heating module, and achieves a number of design requirements. These include the
123 ability for *in situ* XCT of solidifying alloys with melting point exceeding 1300 °C, slow cooling rates
124 on the order of 10^{-2} °C s^{-1} , thermal precision of ± 0.5 °C over a sample length of at least 10 mm, and
125 easy integration with bespoke mechanical rigs such as the P2R [15,33] for *in situ* thermo-mechanical
126 investigations in the semi-solid or solid states.

127 The sample module (Fig. 1a), consists of an encapsulated cylindrical sample (1.4 mm ϕ x 8 mm) that
128 is centrally seated and supported by an alumina sleeve and further supported by an alumina sample
129 mount 60 mm in height. Encapsulation was required to minimize oxidation and to contain the
130 specimen safely in liquid state. Each cylindrical sample was encapsulated in a 1.5 mm internal
131 diameter quartz tube (Fig. 1b) filled with Ar gas. Within the encapsulation, the metallic sample was
132 supported by using a glass rod which in turn was fused to one end of the quartz tube.

133 The heating module is shown in Fig. 2a, with the sample module inserted. The environmental cell
134 setup on the I12 beamline at the Diamond Light Source is shown in Fig. 2b. In this device, porous
135 insulation fibre is enclosed in a water-cooled stainless steel shell to house a centrally placed u-shaped
136 MoSi₂ high current heating element. MoSi₂ heating elements were chosen due to their high heat
137 density and high temperature (> 1000 °C) stability in both oxidizing [34,35] and reducing
138 environments [35]. Temperature was controlled by two R-type thermocouples placed at about 3 mm
139 from the sample surface. The sample is separated from the heating element using a central dense
140 alumina ceramic column. Further, to isolate the environmental cell chamber from the ambient
141 atmosphere, fused quartz faceplates, 0.5 mm thick, were placed over square 10 mm X-ray windows.

142 During the *in situ* high temperature solidification experiment, a 0.0165 nm (75 keV) monochromatic
143 X-ray beam with PCO edge camera at a pixel size of 1.3 μm was used for tomographic imaging with
144 900 projections and 0.1 s exposure. The experiment was conducted as follows. First, the sample was
145 heated to 1400 °C, held isothermally for 10 minutes, and then cooled at a rate of 0.05 °Cs⁻¹.
146 Concurrently, a series of X-ray tomographic images were acquired. The imaging conditions described
147 above allowed for acquisition of 27 tomograms within the semi-solid regime. The reconstructions
148 were performed by standard filtered back projection [36].

149 To improve the sample alignment, and to ensure safe operation resulting from the high temperatures,
150 thermal modelling of the environmental cell was performed using SolidWorks[37] software.
151 Boundary conditions were set on the insulating fibre block (50 °C) and heating element surface (1800
152 °C). The model included radiative heat transfer, but the contact thermal resistance between the mating
153 surfaces was ignored. The modelled temperature profile in the central block of the environmental cell
154 is shown in Supplementary Fig. S2a. In addition to isolating the sample from the heating elements, the
155 central alumina core was observed to promote radiative heating, homogenizing the temperature across
156 the central sample volume. The temperature profile across the entire quartz tube is shown in
157 Supplementary Fig. S2b. Based on the model results, the location of the X-ray field of view was
158 chosen such that there was minimum thermal gradient within the imaged volume. The model
159 predicted < 3 °C variation across sample height in the FOV.

160 **3. Results and Discussion**

161 **3.1. Methodology Demonstration**

162 The *in situ*, 4D evolution of patterns during the liquid to solid phase transformation in each of these
163 alloys is shown in Fig. 3 and animated for the case of Co-Hf alloy in Supplementary Movie 1. The
164 corresponding as-acquired 2D images from the middle of the Co specimen are shown in
165 Supplementary Movie 2. These results demonstrate the methodology of combining a bespoke high
166 temperature furnace with X-ray translucent windows, custom designed high X-ray attenuation

167 contrast alloys, encapsulation system and high-speed synchrotron X-ray tomographic imaging to
168 capture solidification pattern evolution in high temperature alloys.

169 The formation of dendritic patterns in solidifying Ni and Fe alloys shown in Fig. 3a-d captures the
170 formation of primary, secondary and tertiary dendritic arms in these alloys. The alloys were solidified
171 at a relatively slow cooling rate of $0.05\text{ }^{\circ}\text{C}\text{s}^{-1}$. In Ni, this cooling rate is sufficient to induce single
172 crystal growth as can be seen in Fig 3a and b. In this experiment, solidification begins with the
173 nucleation of a grain on the sample surface, forming dendrites which branch into secondaries in the
174 horizontal plane, which in turn form tertiary arms, which grow quickly upwards in the available
175 sample space ahead forming a forest of single crystal primary dendrites. These dendrites grow
176 vertically upwards, almost perpendicular to the sample axis (z). The resulting structure is an
177 interlocking dendritic mesh extending across the entire sample. The growth of secondary arms is
178 limited by solute interaction with the neighbouring patterns; several instances of direct tip-tip
179 interaction can also be observed.

180 The growth of a BCC δ -Fe primary dendrite under identical solidification conditions at the beginning
181 and late stages of solidification are shown in Fig.3c and d. These images show how the evolving
182 patterns are dominated by pattern thickening, coalescence and coarsening in the late stages of
183 solidification, as quantified previously in magnesium[38] and other light alloys[13]. Further, they
184 allow the coarsening kinetics to be quantified for the first time in an Fe alloy.

185 **3.2. Morphological Aspects of Dendrite Growth of Co alloys**

186 Having demonstrated that the methodology is applicable to Ni and Fe, we will use the Co alloy as an
187 example to demonstrate how detailed mechanistic and quantitative patterning data can be extracted to
188 inform and validate models.

189 **3.2.1. Qualitative observations of Co solidification and dendritic pattern formation**

190 Figure 3e-h shows the evolution of Co dendrites during solidification at a cooling rate of $0.05\text{ }^{\circ}\text{C}\text{s}^{-1}$.
191 Four images are provided, spanning 125°C and an evolution in fraction solid from 1.6% to 40.9%.
192 The observed four-fold symmetry is characteristic of an FCC structure. The dendrites nucleate on the
193 sample surface and grow inwards with no discernible preferred orientation relative to the sample axis.
194 A 20-30 μm Hafnium oxide layer was present on the sample surface, as characterised by post-
195 solidification SEM-EDX examination. This oxide layer was visible in the tomograms due to
196 attenuation difference even when the sample was molten; therefore, we hypothesise that this oxide
197 assists nucleation of the α -Co phase.

198 The first grain to nucleate and grow is labelled as G1 in Fig. 3e. Note that two dendrites are marked as
199 G1 (coloured blue and brown) since the 4D images reveal that they are both part of the same single
200 crystal. We hypothesise this since both have identically aligned primary directions. The secondary

201 arms also have the identical 4-fold symmetry directions, further confirming they are part of the same
202 crystal. These two primary dendrites will have started from a nucleus on the bottom surface, which
203 initially forms a single primary arm, most likely the brown one since it is larger, that then forms
204 secondaries, and subsequently, tertiary dendrite arms. One of these tertiary arms, just sufficiently far
205 from the original primary, will grow quick with the same crystal orientation as the first primary
206 (brown). This tertiary becomes another primary dendrite (G1, blue), establishing the repeating 4-fold
207 patterning of an FCC crystal structure.

208 Similarly, the orange and the light green dendrites (Fig. 3f) form part of a single grain (G2). A third
209 large grain, depicted in dark green (G3) has sufficient space to form a remarkable pattern of primary,
210 secondary and tertiary arms forming in a 4-fold spidery star shape. Until now, the complexity of these
211 shapes has only been visualised via computational simulations (e.g. [1,25–29]). Using 4D in situ
212 synchrotron observations we can determine the key phenomena to inform model development, and
213 validate the microstructural simulations for real engineering alloy systems, such as Ni- and Co-
214 superalloys and alloy steels.

215 The morphological data which can be easily extracted from these unique observations is demonstrated
216 by examining zoomed regions of the Co alloy 4D images given in Fig. 4. The initial stages of growth
217 just after nucleation are captured in Fig. 4a, where two spindly primary dendrites (G1) grow very
218 rapidly into the liquid. Here, we can measure the average tip velocity per tomogram by dividing the
219 length they grow by the time per image. This provides the first value for tip velocity during the
220 solidification of a Co alloy, $11 \pm 2 \mu\text{m/s}$. (Note, this is the value just after nucleation in the temperature
221 range of 1379-1373 °C, where the growth was unobstructed, approximating unconstrained
222 conditions.)

223 New insights into the growth of secondary arms during solidification pattern formation can further be
224 analysed from the images. For example, for grain G1 in Fig. 3e,f and 4a,b, the majority of secondary
225 arm growth can be observed to be in the plane normal to the direction (depicted by a red arrow in Fig.
226 4a) in which the primaries are connected (below the field of view, FOV). This preferential growth of
227 the secondary arms is not expected crystallographically, and makes the dendritic patterns more plate-
228 like rather than a perfect 4-fold symmetric tree. This can be explained from the 3D images of G1- the
229 spacing between the first primary (brown) and second forming (blue) will be a minimum, hence the
230 secondaries that grow in this plane will have solute fields that quickly impinge, slowing their growth.
231 In the plane normal to this, the secondary tips experience free growth until their solute fields impinge
232 on the specimen walls, growing out quickly.

233 Many models for aerospace and industrial gas turbine (AGT/IGT) blades are focused on grain mis-
234 orientation and spurious grain growth[18,39]. In the Co alloy 4D images we observed, a number of
235 distinct competitive growth mechanisms were observed, which provide the first, 3D direct evidence of

236 the microstructural factors that promote the formation of these defects. Firstly, examining grain G1,
237 the secondary arms of the blue primary are completely restricted in three directions, two of these by
238 the walls and in one direction by the neighbouring brown primary, as shown in Fig. 4b-d. This
239 scenario does not arise in case of grains G2 and G3 due to the larger relative distance between the
240 fully developed parallel arms. Secondly, again referring to grain G1 and Fig. 4b, the primary blue
241 dendrite is clearly overgrown by a secondary growing from the brown primary dendrite. As
242 solidification progresses (Fig. 4c and d), local re-melting takes place on the lower side of the brown
243 dendrites blocking secondary arm, whilst on the top half tertiary arms form and start growing
244 upwards. This type of local remelting has been shown to lead to fragmentation in Al alloys [40–43].
245 Thirdly, in Fig. 4e-h growth competition is shown between two randomly oriented grains that nucleate
246 at almost same time and then grow in close proximity to each other. As can be seen, the growth of the
247 secondary arms in the middle of grain G2 is arrested by grain G4. These roles are reversed near the tip
248 of G4 where the secondary arms are suppressed by the growth of secondary and tertiary arms of G2,
249 although this may not seem obvious from the current viewing angle.

250 In many low temperature alloy solidification experiments, grain competition is seen to result in stray
251 grains, and re-melting is seen to culminate in pinch-off where a dendrite arm completely detaches
252 from its parent [40–43]. This kind of interaction is also reported in other metallic alloy systems where
253 experiments were performed radiographically [44], however the exact morphology, for example the
254 development of this cup-like morphology becomes apparent through a 3D tomographic examination.
255 These types of observations are critical for developing accurate models of dendrite fragmentation in
256 order to improve processing of Co and other high temperature advanced alloys, ultimately reducing
257 component costs.

258 3.3. Quantitative Observations

259 3.3.1. Fraction solid evolution

260 These tomographic imaging observations showed that the α -Co dendrite tip velocities are remarkably
261 fast, given the slow cooling rate of $0.05\text{ }^{\circ}\text{C s}^{-1}$. At this cooling rate, the difference in temperature
262 between tomograms is $\sim 5\text{ }^{\circ}\text{C}$ per tomogram. At the end of first and second scans, the observed solid
263 fraction was 1.6 and 8.5% respectively. The latter amounts to 25% of the overall expected solid
264 fraction just above eutectic temperature during equilibrium cooling. The rate of primary phase
265 formation (fraction solid, f_s Fig. 5a) reduces as solidification progresses and the eutectic temperature
266 is approached. The f_s as estimated from the lever and Scheil equation are also plotted in Fig. 5a, using
267 a partition coefficient, k , of 0.07 (the method adopted for estimation of k is provided in supplementary
268 note 1). The experimental solid fraction variation was close to the Scheil estimate, indicating that the
269 Hf partitions readily to the liquid upon the growth of dendrites/solid during solidification. Therefore,
270 even at this slow cooling rate the experiment is far from equilibrium.

271 3.3.2. Surface area evolution

272 The evolution of surface area per unit volume of the solid (S_v) in the Co-Hf alloy is shown in Fig. 5b,
 273 both for the whole volume (containing many grains) and the single largest grain (G2). Generally, S_v is
 274 high during the initial stages of solidification [13,38,45] due to the high surface area to volume ratio
 275 given by the high curvature nascent patterns/grains. As the solidification progresses, a steep decrease
 276 in S_v is observed as a result of growth (increase in length) of each pattern, Fig. 4b and f. Eventually
 277 the growth ceases, the patterns start to thicken and the local curvature reduces, Fig. 4c and g, until the
 278 end of solidification, Fig. 4d and h. During thickening, the patterns also coarsen via the reduction in
 279 tip curvature and coalescence of secondary arms, which reduces the surface area. After the initial
 280 growth, S_v continues to reduce through combination of thickening and coarsening at a gradually
 281 declining rate.

282 It is clear from the competitive growth scenarios described earlier that the impingement of patterns
 283 happens at various scales and at different stages during the course of solidification. This affects the
 284 overall growth and coarsening. One way to quantify this is to observe the evolution of entire solid
 285 surface area normalized by the volume of liquid and solid, S_v^* as a function of fraction solid, f_s , as
 286 given by Rath [46] and Cahn equation [47];

$$S_v^* = A \times f_s^m \times (1 - f_s)^n \quad (1)$$

287 where, A is a proportionality constant and $m = n = 2/3$ for Cahn and $0 < (m, n) < 1$ for Rath. The
 288 Rath equation is applicable for growth of features with varied aspect ratios while Cahn equation is
 289 more suitable for near equiaxed (spherical) features.

290 The evolution of S_v^* as a function of f_s for the Co-Hf alloy is shown in Fig. 6, along with the Cahn and
 291 the Rath curves for the current observation. The Rath curve of S_v^* for the α -Al dendritic growth in Al-
 292 10 wt.% Cu, reproduced from [13] is also provided for comparison. The S_v^* in the current alloy
 293 increases continuously but at a gradually reducing rate during the course of solidification. This
 294 indicates that the rate of thickening of dendrites is still faster than the rate of coalescence of secondary
 295 arms. Prior studies comparing experimental coarsening rates to the Cahn and Rath equations were in
 296 alloys with a very low fraction eutectic (f_e), such as the study by Limondin et al. [13] in Al 10wt% Cu
 297 where their results show a f_e of <0.12 , while for the Co-Hf alloy, Fig. 6, shows the f_e is approximately
 298 0.6, or 60% as compared to their 12%. In the Co-Hf alloy (under continuous cooling conditions),
 299 although secondary arm coalescence/coarsening is occurring it does not exceed the influence of
 300 fraction solid increase upon S_v^* as the fraction primary phase is so low. As shown by Guo et al., if an
 301 alloy is held isothermally (MgZn in their case), then the coarsening dominates as expected[38].

302 4. Conclusions

303 A novel methodology was developed enabling 4D (3D plus time) tomographic examination of pattern
304 formation during the solidification of high temperature advanced alloys with melting temperatures
305 exceeding 1300°C. The methodology combines three key advances: a bespoke high temperature
306 environment cell; the development of high X-ray attenuation contrast alloys; and a specimen
307 environmental encapsulation system. This method was successfully demonstrated on Ni, Fe and Co
308 alloy systems.

309 For a Co-Hf alloy system, the time-resolved tomographic datasets were examined in detail,
310 elucidating novel insights into the nucleation and growth mechanisms in Co alloys, which are a
311 critical aerospace alloy system. The results were quantitatively analysed, with quantities measured as
312 a function of time/temperature including: dendrite tip velocity, fraction solid, specific surface area and
313 coarsening. Key competitive growth and coarsening mechanisms were also elucidated. The insights
314 and quantitative data obtained will help to both inform and validate new computational models of
315 pattern formation during the liquid to solid phase transformation in high temperature advanced alloys
316 and many other systems.

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324 size, but representative sample data is included in the Figures and supplementary data.

325

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457 **Fig. 2.** (a) Schematic of one half of environmental cell with heating and sample module and (b)
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460 **Fig. 3.** The 3D evolution of dendritic patterns in Ni-14 wt. % Hf, Fe-11 wt. % Hf and Co-18 wt. % Hf
461 alloys during solidification at a cooling rate of $0.05\text{ }^{\circ}\text{C s}^{-1}$ are shown. The interlocking FCC α -Ni
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470 **Fig. 4.** Competitive growth, a case of interaction between dendritic arms of the same grain (G1) is
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476 front end of G4 is restricted by G2. Scale bar = $200\text{ }\mu\text{m}$.

477 **Fig. 5.** The evolution of (a) volume fraction of α -Co phase during solidification of Co-18wt. % Hf
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479 evolution of volume normalised surface area, S_v , of α -Co dendritic patterns with temperature, on a
480 single grain and sample scale.

481 **Fig. 6.** The evolution of total volume normalized surface area of the solid during solidification in the
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483 equations. The observed/Rath plot of the α -Al dendritic structure during solidification in Al-10Cu as
484 reported by Limodin et al.¹³ (black graph) is also provided along side for comparison.

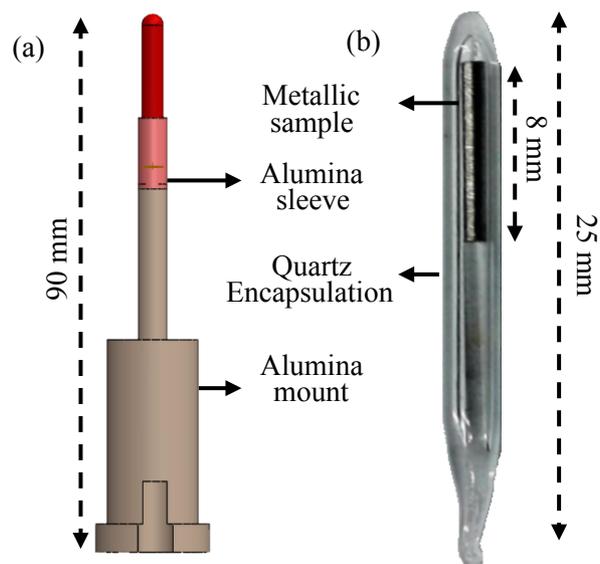


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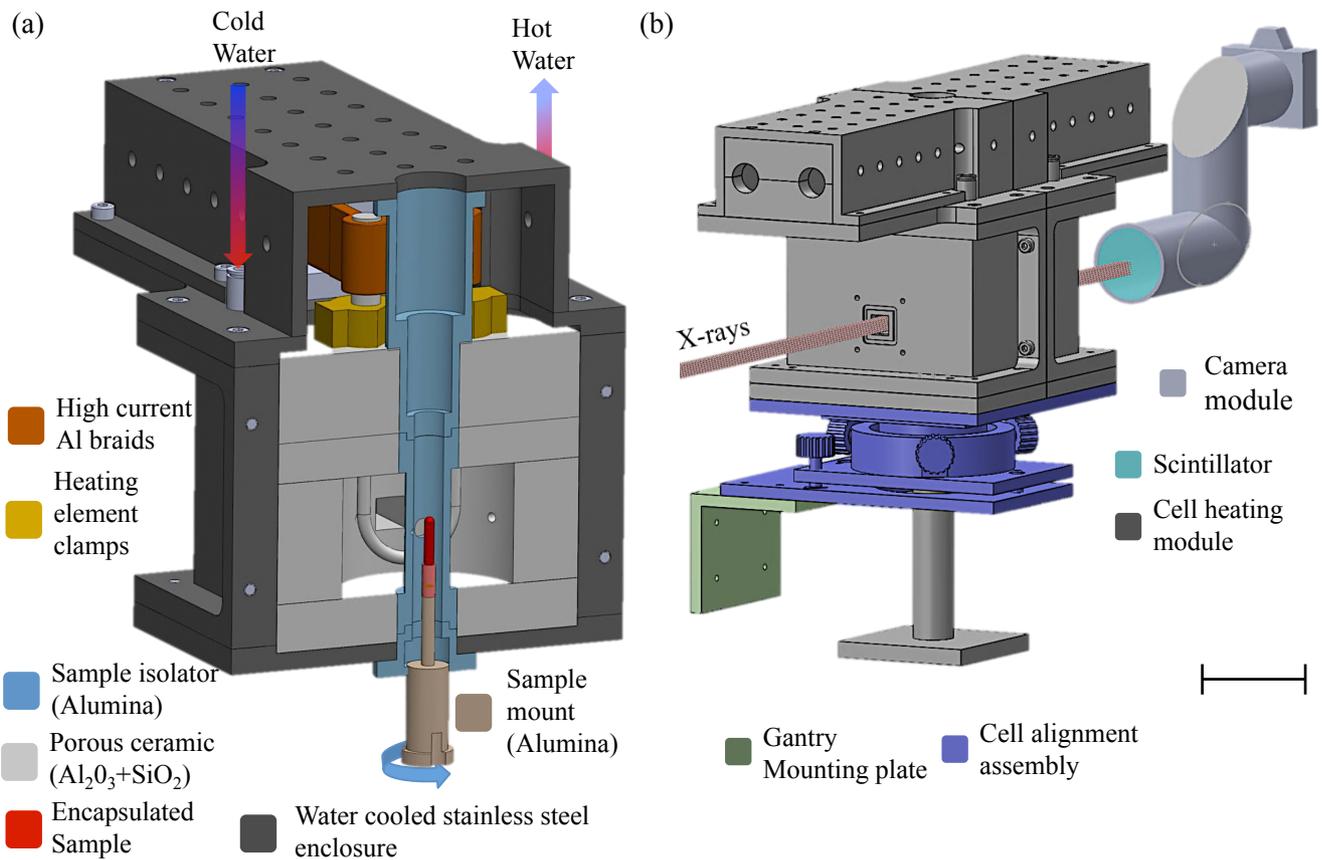


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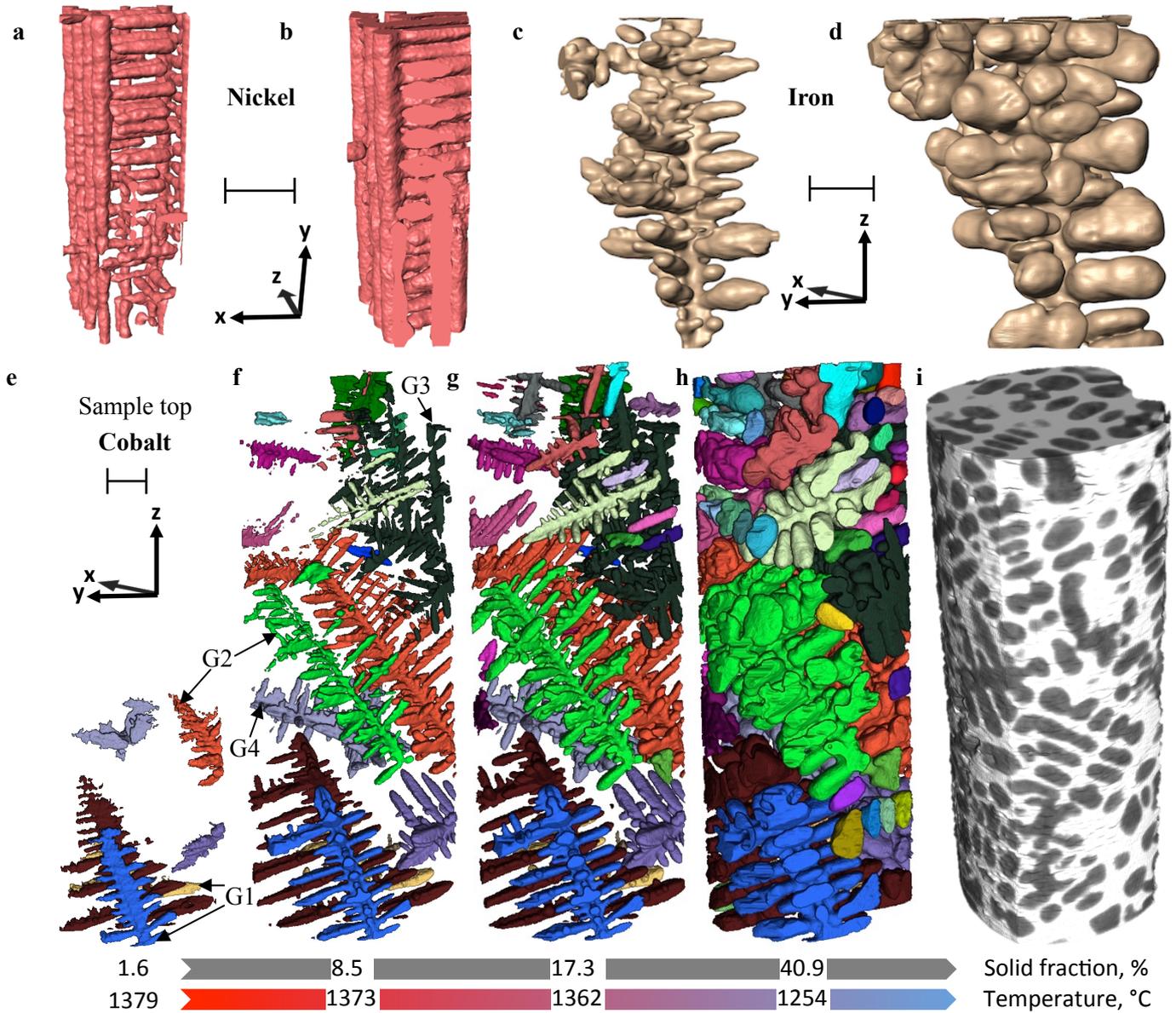


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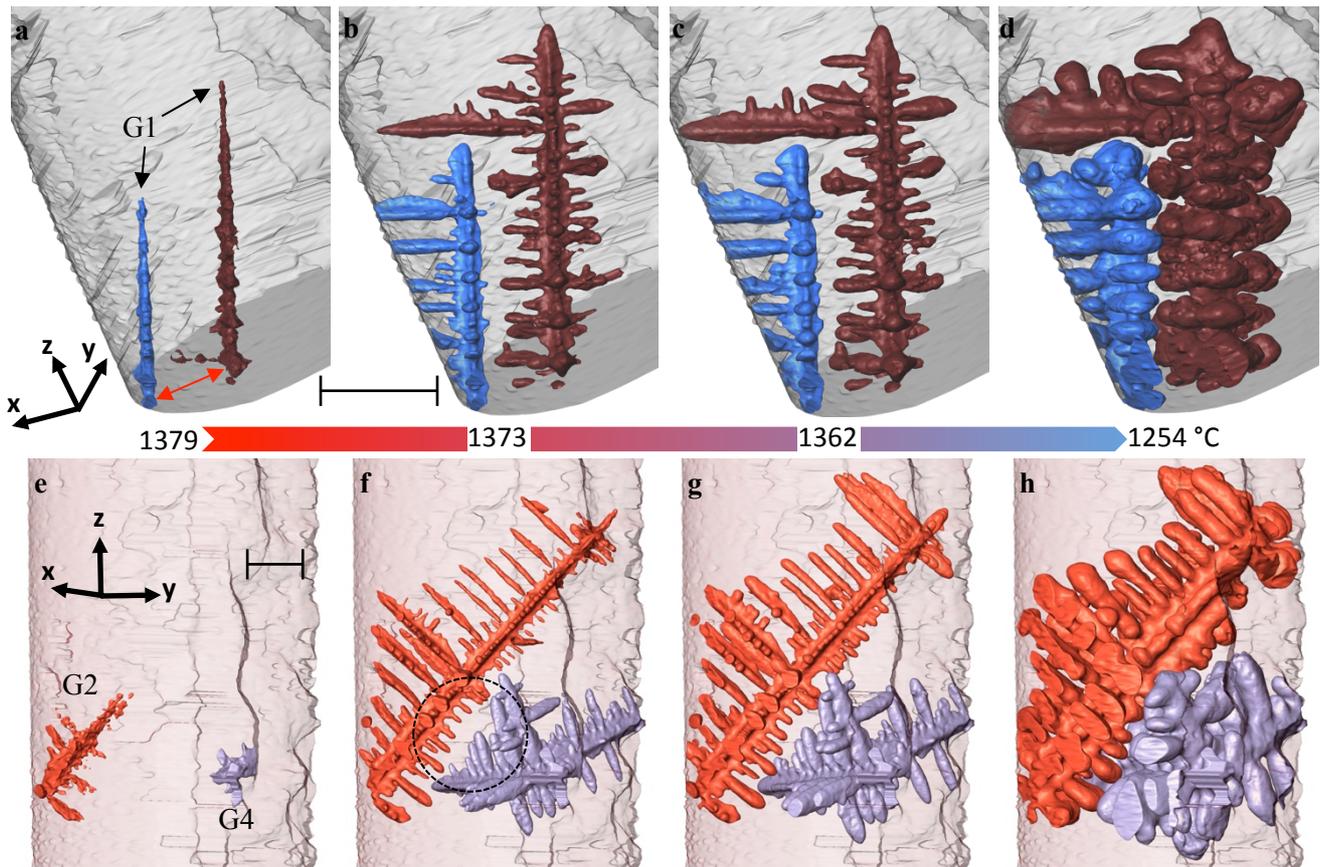


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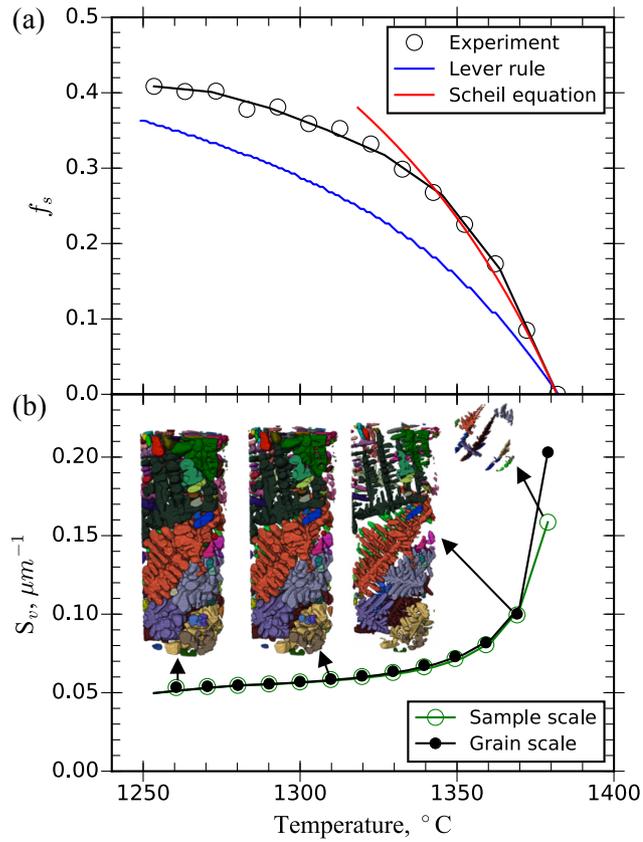


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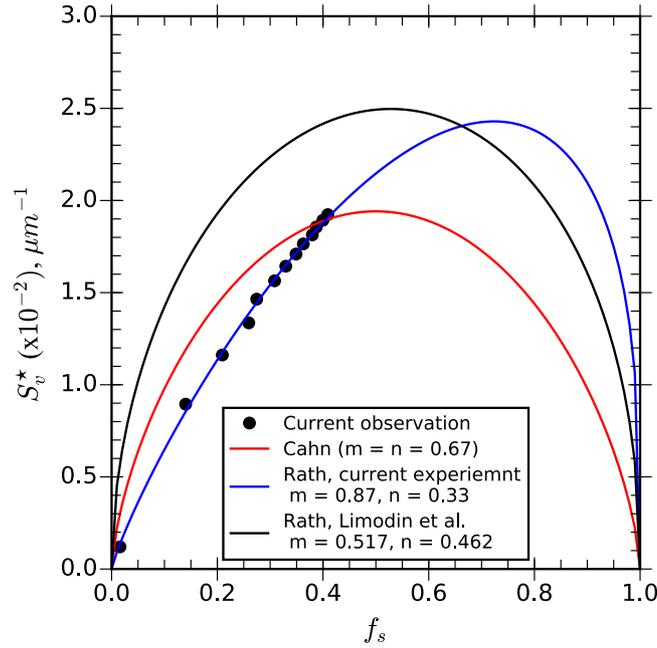


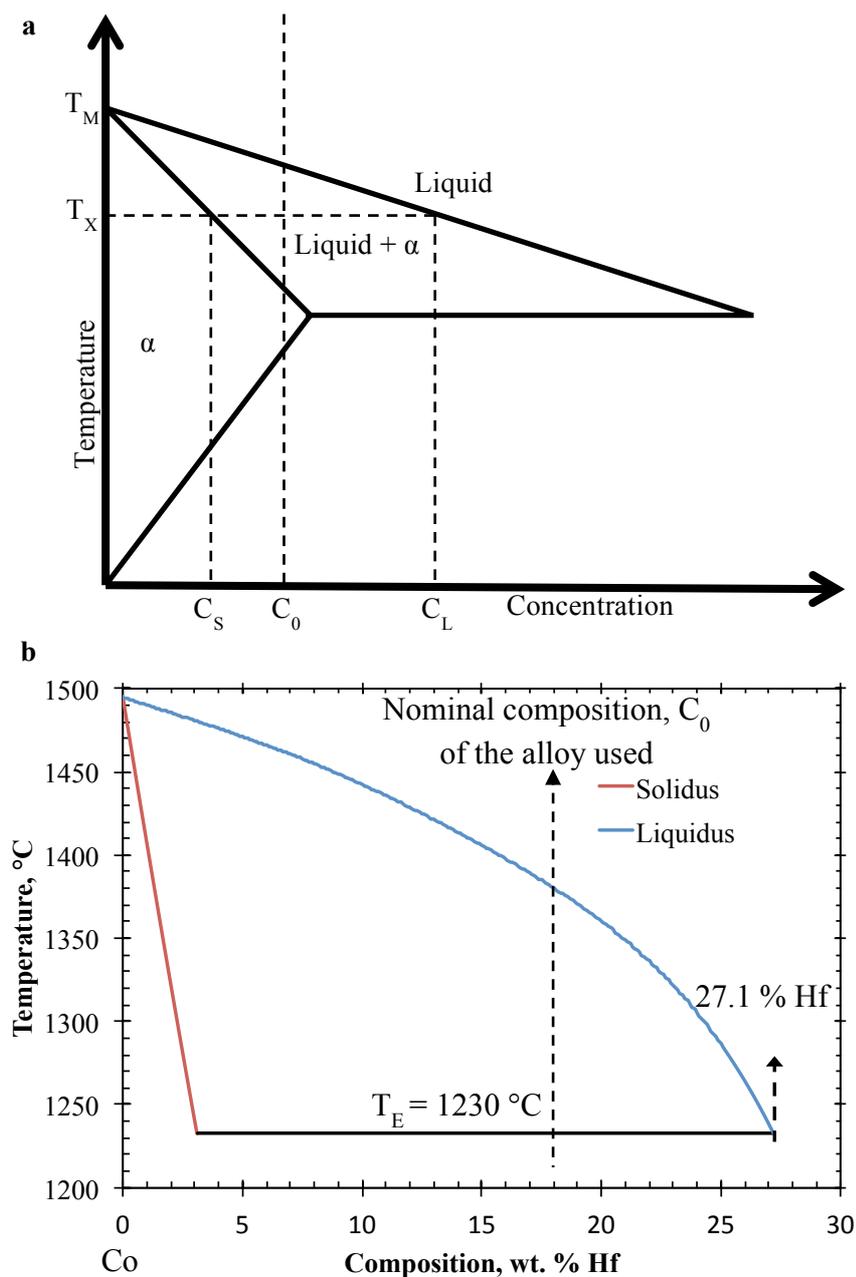
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Supplementary

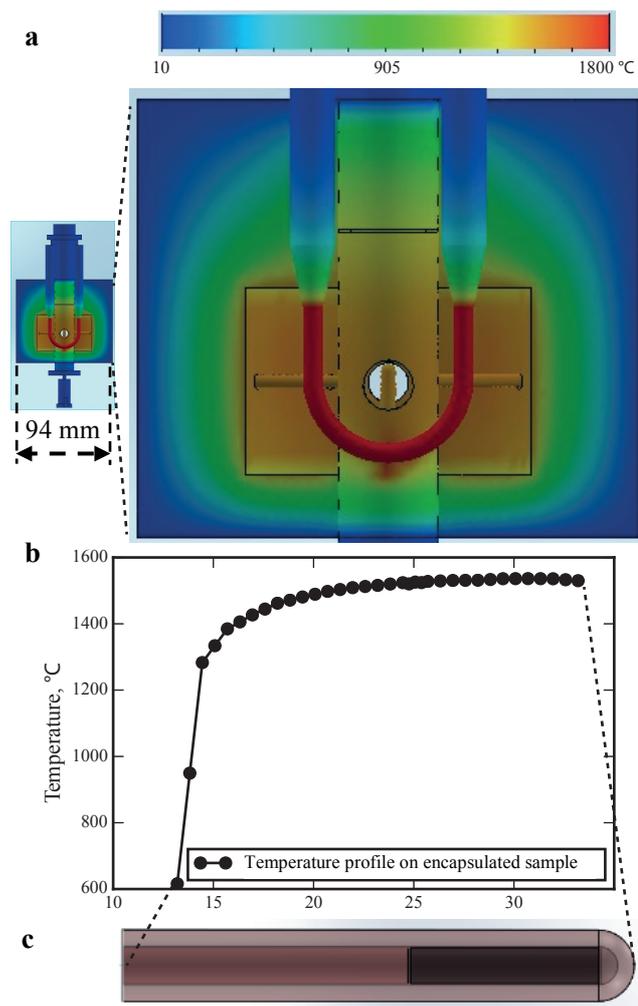
Supplementary Movie M1 | Evolution of α -Co dendritic patterns: Sequence of 3D X-ray tomographic images showing the evolution of α -Co dendritic patterns in high contrast Co-18 wt. % Hf alloy during solidification at a cooling rate of $0.05 \text{ }^\circ\text{C s}^{-1}$. The outer oxide ring is removed by image processing for the sake of visualization.

Supplementary Movie M2 | 2D images of as-acquired tomograms: As acquired 2D time series showing the evolving morphology of α -Co dendritic patterns in high contrast Co-18 wt. % Hf alloy during solidification at a cooling rate of $0.05 \text{ }^\circ\text{C s}^{-1}$. The white arrows indicate the location where an instance of competitive growth is occurring between two intersecting dendrites.

Supplementary Note 1 | Estimation of partitioning coefficient: During solidification of an alloy, the separation of solute between solid and liquid phases is interpreted in terms of partitioning coefficient or the Scheil proportionality constant, k . A schematic of the hypoeutectic binary alloy system is shown in Fig. S1a, k is estimated by the ratio of the concentration of the solid (C_S) to the concentration of liquid C_L . Under equilibrium cooling conditions, the Co-Hf alloy system has a liquidus line with increasing slope as the eutectic composition is approached, as shown in Fig. S1b, after Ishida, K. and Nishizawa⁴⁰. The Scheil proportionality constant k measured from the equilibrium phase diagram was found to be 0.11, however a k of 0.07 is used in the calculation so as to make the Scheil graph concurrent with the 0% solid fraction on the composition axis (Fig. 3a).



Supplementary Fig. S1. (a) Schematic of the hypoeutectic region of a binary phase diagram, where C_L and C_S represent the concentration of liquid and solid respectively, C_0 is the nominal composition of alloy of interest, T_M the melting point of the pure species and T_X is a temperature of interest. (b) hypoeutectic region of the the Co-Hf phase diagram, after Ishida and Nishizawa³⁰.



Supplementary Fig. S2. Thermal modeling of (a) temperature distribution inside the furnace shown here in the front view, (b) temperature profile on the sample encapsulation (schematically shown in (c)).