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

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
α-Co FCC dendritic patterns

α-Ni FCC dendritic patterns

δ-Fe BCC dendritic patterns

Scale bar = 200 μm

$1254 \degree C$

$t = 495 \text{ s}$

$t = 1496 \text{ s}$

$t = 396 \text{ s}$

$t = 3960 \text{ s}$
1. Introduction

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

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

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

Most 4D solidification studies of metallic systems have been performed on Al-Cu based alloys [20]. These alloys provide excellent attenuation contrast between the solidifying face centred cubic (FCC) α-phase and the liquid. Although the morphological and kinetic aspects observed via the in situ tomography can be correlated with industrially viable Al alloys, there is no confirmation that the results can be extended to other FCC systems that solidify at very high temperatures. High temperature alloys such as nickel superalloys, cobalt superalloys, and iron alloys have yet to be
studied in the semi-solid state using 4D imaging, although high temperature solid state investigations have been performed[21]. Understanding pattern formation during the solidification of these high temperature advanced alloys is critical to predicting their strength, and preventing the formation of solidification defects such as freckles [17,22], and grain mis-orientation during directional (DX) and single crystal (SX) growth [23,24].

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

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

2. Materials and Methods

2.1. Alloy Design

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

During solidification, the solubility of the primary phase is interpreted in terms of the partition coefficient, $k$, where $k = C_s/C_L$, where $C_s$ and $C_L$ are the concentration of solute in the solid and liquid respectively, as shown in supplementary Fig. S1a. To meet criterion (a), the value of $k$ must be quite small, which also implies that criterion (b) is respected. For criterion (c), each element’s characteristic
X-ray absorption edges are exploited. Using a monochromatic beam just above this absorption edge enables clear identification between one phase and another. Second, when a polychromatic (white) X-ray spectrum interacts with materials, different phases absorb different amounts of X-rays. This is known as non-characteristic X-ray interaction. Consequently, depending on the alloy system, either a white beam or a monochromatic X-ray beam with an energy just above one of the characteristic edges may be used for achieving a good contrast between the solid and liquid phases.

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

In the present study, Ni-14 wt.%Hf, Fe-11 wt.%Hf and Co-18 wt.%Hf alloys were chosen for 4D imaging. The Co-Hf alloy used in this investigation was obtained by induction melting and 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 alloys were prepared in a vacuum arc melter using induction melted Ni-Hf and Fe-Hf master alloys, respectively. The cylindrical samples for the in situ solidification trials were extracted from the middle section of the as-cast sample.

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

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

The sample module (Fig. 1a), consists of an encapsulated cylindrical sample (1.4 mm ø x 8 mm) that is centrally seated and supported by an alumina sleeve and further supported by an alumina sample mount 60 mm in height. Encapsulation was required to minimize oxidation and to contain the specimen safely in liquid state. Each cylindrical sample was encapsulated in a 1.5 mm internal diameter quartz tube (Fig. 1b) filled with Ar gas. Within the encapsulation, the metallic sample was supported by using a glass rod which in turn was fused to one end of the quartz tube.
The heating module is shown in Fig. 2a, with the sample module inserted. The environmental cell setup on the I12 beamline at the Diamond Light Source is shown in Fig. 2b. In this device, porous MoSi$_2$ insulation fibre is enclosed in a water-cooled stainless steel shell to house a centrally placed u-shaped MoSi$_2$ high current heating element. MoSi$_2$ heating elements were chosen due to their high heat density and high temperature (> 1000 °C) stability in both oxidizing [34,35] and reducing environments [35]. Temperature was controlled by two R-type thermocouples placed at about 3 mm from the sample surface. The sample is separated from the heating element using a central dense alumina ceramic column. Further, to isolate the environmental cell chamber from the ambient atmosphere, fused quartz faceplates, 0.5 mm thick, were placed over square 10 mm X-ray windows.

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

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

3. Results and Discussion

3.1. Methodology Demonstration

The in situ, 4D evolution of patterns during the liquid to solid phase transformation in each of these alloys is shown in Fig. 3 and animated for the case of Co-Hf alloy in Supplementary Movie 1. The corresponding as-acquired 2D images from the middle of the Co specimen are shown in Supplementary Movie 2. These results demonstrate the methodology of combining a bespoke high temperature furnace with X-ray translucent windows, custom designed high X-ray attenuation
contrast alloys, encapsulation system and high-speed synchrotron X-ray tomographic imaging to
capture solidification pattern evolution in high temperature alloys.

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

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

3.2. Morphological Aspects of Dendrite Growth of Co alloys

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

3.2.1. Qualitative observations of Co solidification and dendritic pattern formation

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

The first grain to nucleate and grow is labelled as G1 in Fig. 3e. Note that two dendrites are marked as
G1 (coloured blue and brown) since the 4D images reveal that they are both part of the same single
crystal. We hypothesise this since both have identically aligned primary directions. The secondary
arms also have the identical 4-fold symmetry directions, further confirming they are part of the same crystal. These two primary dendrites will have started from a nucleus on the bottom surface, which initially forms a single primary arm, most likely the brown one since it is larger, that then forms secondaries, and subsequently, tertiary dendrite arms. One of these tertiary arms, just sufficiently far from the original primary, will grow quick with the same crystal orientation as the first primary (brown). This tertiary becomes another primary dendrite (G1, blue), establishing the repeating 4-fold patterning of an FCC crystal structure.

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

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

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

Many models for aerospace and industrial gas turbine (AGT/IGT) blades are focused on grain mis-orientation and spurious grain growth[18,39]. In the Co alloy 4D images we observed, a number of distinct competitive growth mechanisms were observed, which provide the first, 3D direct evidence of
the microstructural factors that promote the formation of these defects. Firstly, examining grain G1, the secondary arms of the blue primary are completely restricted in three directions, two of these by the walls and in one direction by the neighbouring brown primary, as shown in Fig. 4b-d. This scenario does not arise in case of grains G2 and G3 due to the larger relative distance between the fully developed parallel arms. Secondly, again referring to grain G1 and Fig. 4b, the primary blue dendrite is clearly overgrown by a secondary growing from the brown primary dendrite. As solidification progresses (Fig. 4c and d), local re-melting takes place on the lower side of the brown dendrites blocking secondary arm, whilst on the top half tertiary arms form and start growing upwards. This type of local remelting has been shown to lead to fragmentation in Al alloys [40–43]. Thirdly, in Fig. 4e-h growth competition is shown between two randomly oriented grains that nucleate at almost same time and then grow in close proximity to each other. As can be seen, the growth of the secondary arms in the middle of grain G2 is arrested by grain G4. These roles are reversed near the tip of G4 where the secondary arms are suppressed by the growth of secondary and tertiary arms of G2, although this may not seem obvious from the current viewing angle.

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

3.3. Quantitative Observations

3.3.1. Fraction solid evolution

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

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

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

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

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

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

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

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

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References


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**Fig. 1.** (a) Schematic of the sample module with alumina sample mount and quartz encapsulated sample and (b) image of the as-encapsulated sample, held in place at one end of the encapsulation by a quartz rod.

**Fig. 2.** (a) Schematic of one half of environmental cell with heating and sample module and (b) schematic of the environmental cell setup at the I12 beamline of Diamond Light Source. Scale bar = 32.5 mm.

**Fig. 3.** The 3D evolution of dendritic patterns in Ni-14 wt. % Hf, Fe-11 wt. % Hf and Co-18 wt. % Hf alloys during solidification at a cooling rate of 0.05 °Cs⁻¹ are shown. The interlocking FCC α-Ni dendritic patterns at 495 and 1496 s after the start of solidification are shown in (a) and (b) respectively. The development of a single δ-Fe pattern during solidification via thickening, coarsening and coalescence mechanisms captured at 396 and 3960 s are shown in (c) and (d) respectively. The development of α-Co patterns during solidification of the Co alloy is shown in (e)-(h). The corresponding temperatures and volume fractions are provided below each subfigure, where, (e) is captured at ~3 °C below the equilibrium liquidus temperature of the alloy and (h) at ~24 °C above the reported equilibrium eutectic temperature. The raw data of the reconstructed volume corresponding to (h) is shown in (i). Scale bar = 200 µm.

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**Fig. 5.** The evolution of (a) volume fraction of α-Co phase during solidification of Co-18wt. % Hf alloy at a cooling rate of 0.05 °Cs⁻¹. Lever rule and Scheil estimates are also provided and (b) evolution of volume normalised surface area, $S_v$, of α-Co dendritic patterns with temperature, on a single grain and sample scale.

**Fig. 6.** The evolution of total volume normalized surface area of the solid during solicitation in the current Co-18wt. % Hf alloy is shown. The behaviour is interpreted in terms of Rath and Cahn equations. The observed/Rath plot of the α-Al dendritic structure during solidification in Al-10Cu as reported by Limodin et al.¹³ (black graph) is also provided along side for comparison.
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Supplementary

Supplementary Movie M1 | Evolution of $\alpha$-Co dendritic patterns: Sequence of 3D X-ray tomographic images showing the evolution of $\alpha$-Co dendritic patterns in high contrast Co-18 wt. % Hf alloy during solidification at a cooling rate of 0.05 °Cs$^{-1}$. 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 $\alpha$-Co dendritic patterns in high contrast Co-18 wt. % Hf alloy during solidification at a cooling rate of 0.05 °Cs$^{-1}$. 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 Nishizawa$^{40}$. 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 Nishizawa 30.
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)).