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

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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 enables *in situ* quantification of the microstructures formed during solidification of high temperature advanced alloys via synchrotron tomography. 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.

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, be it in nickel superalloy AGTs [1] or 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-30 wt% 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

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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 (called Alice) 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 65–80 keV were found to yield a substantial attenuation difference between the solidifying α-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 (Al_2O_3/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 Alice 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 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