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# Synchrotron quantification of graphite nodule evolution during the solidification of cast iron

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ABSTRACT

In cast iron, graphite develops in conjunction with the metallic matrix during solidification. The morphology and distribution of the embedded graphite is pivotal for mechanical properties from yield strength to fatigue. A novel high temperature environmental cell was developed and combined with *in situ* synchrotron tomography to investigate and quantify microstructural evolution, including graphite nodule nucleation and growth rates in ductile cast iron. The mechanisms of degenerate graphite nodule formation were also revealed. The formation of a coherent primary gamma phase dendritic network before the graphite nucleation is demonstrated. The graphite nodule nucleation rate, mobility and growth rates are compared to classical models, highlighting the limitations in these models. The results provide unique insights to tune the temperature pathways during cast iron solidification to achieve desired uniform rounded graphite morphologies and size distributions.



## 1. Introduction

Cast iron, with its wide range of graphite forms, excellent castability, and range of properties has been the most widely used metal in cast form for centuries. The continued use of cast iron is due to increasing demand from the renewable energy and maritime sectors, as well as heavy equipment manufacturing [1]. The graphite phases in cast iron(s) develops in conjunction with the metallic matrix during solidification – understanding and controlling their structure, number density and morphology is key to cast iron's properties.

Although many high strength alloys from steels to Ni superalloys are currently strengthened by carbon additions via the formation of nano to micron-sized carbides, very few alloys other than cast irons, based on the Fe-C system with >2 wt% carbon, use the formation of graphite to provide ease of melt processing coupled with high strength and fatigue properties. The size, distribution, crystallography and shape of the graphite particles can be controlled by changing the solidification pathways and by addition of modifying elements such as Mg [2], Ti [3], Ce etc. The resulting composites are referred to by different names depending on their mechanical properties, morphology of the graphite particles, properties or appearance (for example grey, nodular/ductile).

One form is nodular cast iron, named for the spherical shape of the graphite phase. Cast irons have exceptional stiffness, better than that of Al, Mg and Ti alloys [4–6]. The excellent castability of cast iron, in combination with the high damping capacity of the graphite phase make cast irons a material of choice for complex shaped components exposed to vibration and fatigue loading.

The damping capacity reduces as the graphite features become more rounded; therefore, cast irons with flaky graphite have much greater damping capacity than those with spherical graphite; however, the ductility of spherical graphite cast irons is higher. Complex structures with dynamic load bearing capacity, such as wind turbines [1], automotive engines, maritime drive systems and hydroelectric power systems, benefit from the balance of these properties provided by nodular cast iron. Unfortunately, finding the processing route for reliably obtaining uniform spherical nodules has been difficult for solidification at low cooling rates and the mechanisms behind the shape development have previously not been observed.

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Globally, the combined share of cast irons by tonnage is the highest of all metal castings used [7]. Thus cast irons, which are easily recyclable, play a key technological role whilst having a low impact on the environment during the full life cycle of the components.

The graphite nodules and their distribution in nodular cast irons almost entirely dictate the mechanical response of the composite microstructures. In the absence of modifying agents, the graphite grows in a flaky fashion, reducing ductility [8]. Methods for transforming the flaky morphology into spherical nodules during solidification were first identified in the mid-20th century [9] and ever since, empirically established methods to improve the morphology have been developed [10–12]. During eutectic solidification, the graphite nodules are encapsulated in an austenite ($\gamma$-Fe) shell, which develops from pre-existing austenite dendrites or nucleates on the surface of the graphite. This shell isolates the nodule from liquid; the resulting flow of carbon is limited by diffusion through the shell wall and thus maintains the spherical morphology of the encapsulated nodule. However, several researchers have observed that a significant proportion of nodules in industrial castings are not spherical, they are observed to develop distinct peripheral extensions [2,13,14], and other degenerate morphologies [15]. These variant graphite morphologies appear during nominally identical thermal conditions, highlighting our lack of fundamental understanding of the nucleation and growth kinetics of carbon phases emerging from molten metallic melts during freezing.

In this investigation, we combine *in situ* synchrotron tomography, a novel high temperature environmental cell, and a bespoke encapsulation technique to reveal the previously hidden nucleation and growth mechanisms. Real-time nucleation of graphite, growth, their respective rates, size distribution and interaction between the nodule and the shell are systematically captured and evaluated. The results provide essential information that may be used to tune temperature pathways during solidification of metal-carbon composites in order to achieve uniform rounded morphologies and desired size distribution.

These observations would not have been possible without the availability of advanced *in situ* X-ray imaging facilities. *In situ* X-ray radiography (2D plus time) [16] and tomography (4D, 3D plus time) [17–20] have been used before to capture nucleation, growth and evolution of metallic microstructural features ranging from a few microns to several hundreds of microns. The technique was recently used to capture the formation of graphite in a Mg modified hyper-eutectic iron-carbon alloy [21]. Radiography may be performed at higher speed, capturing fast evolving features, but due to constraining 2D geometries it may not be representative of the bulk behaviour. Third generation synchrotron sources allowed fast 4D (3D + time/stress/temperature) tomography, they were used to investigate low temperature metallic alloys as they solidify [18,19], up to 700 °C, informing and validating models developed for predicting dendritic microstructures [22–25] and defects in metals [26].

Using the combination of a novel bespoke high temperature environmental cell enabling temperatures up to 1500 °C [17] and a methodology to contain cast iron in an X-ray transparent module at temperatures exceeding 1000 °C, we have performed the first 4D imaging of graphite formation in a high temperature alloy, cast iron.

## 2. Methods

The composition of the cast iron alloy used in this investigation is provided in Table 1, Mg was added to promote the formation of regular spherical nodules. The synchrotron X-ray tomography experiment was performed at the I12 beamline [27] of the Diamond Light Source, UK. A schematic of the beamline set-up and the sample module used in this investigation is shown in Fig. 1a and b respectively. The experiment was performed on a Ø 2 × 8 mm tall cylindrical specimens, encapsulated in a ~2.1 mm internal diameter quartz tube tapered at the top to pinch the specimen. A glass rod was used to hold the sample at one end of the ~25 mm tall encapsulated tube to prevent it from moving during the course of solidification. This arrangement provided an X-ray imaging set up with very little contact between the specimen and the quartz crucible, (see Supplementary Fig. S1 and movie M1), thus minimizing the reaction between the cast iron and the quartz. The reaction between the crucible and enclosed sample was further minimized by holding the alloy for only a few seconds in the molten state, as shown in the temperature profile in Supplementary Fig. S2.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.actamat.2018.06.007.

The assembly was mounted on an alumina ceramic ram and the heating was performed using a bespoke environmental cell. The design details of the environmental cell and sample module are provided elsewhere [17]. During tomography experiment, the sample was first heated to 1167 ± 0.5 °C at a rate of 0.5 °Cs$^{-1}$, briefly held in liquid state and then cooled at a rate of 0.03 °Cs$^{-1}$. Tomographic acquisition was performed using a 70 keV monochromatic beam. In total, 62 tomograms were acquired with 360 projections per tomogram and exposure time of 0.11 s was used per projection (or 40 s per tomogram). Algorithms previously published by Raven [28] and Paganin et al. [29] were used for ring removal, and to enhance the contrast of the 2D projections respectively, before using filtered back-projection for reconstruction.

## 3. Results and discussion

The chemistry of the alloy used in this investigation is specifically chosen such that the formation of nodules is promoted. It consists of ~2 and 0.07 wt% Si and Mg respectively, Si stabilizes the graphite [12] and Mg promotes the formation of nodules [11,12,15]. The multitude of graphite morphologies revealed at high temperature just after solidification by the in situ setup is shown in Fig. 2a. The dark phase in the 2D superimposed *XY*, *XZ* and *YZ* slices are (solid) graphite and the bright region is comprised of liquid and solid austenite dendrites, they are indistinguishable due to similar X-ray attenuation. The outer, region of this Ø 2 mm cylindrical specimen contains compacted graphite (also known as vermicular graphite), it is a variant of flaky graphite with thicker features and blunt tips. In a metallic matrix, the presence of sharp incoherent features reduces ductility as a result of accelerated crack initiation in the matrix during mechanical loading. The diverse graphite morphologies in the entire 8 mm tall specimen are shown in Fig. 2b.

The overview image provided in Fig. 2b shows the final graphite morphology through the entire sample after it has solidified. The central region of the sample is nodular graphite (see Fig. 2a). However, there is a thin peripheral region where compacted graphite has formed. This is due to the loss of Mg from the exterior of the sample to the inert atmosphere in the capsule, depleting the Mg level for a few hundred microns from the sample edge. As shown in supplementary movie M1, the graphite forms first in the thin peripheral region via the nucleation of compacted graphite and austenite dendrite ($\gamma$). The growth morphology of the dendrites is governed by constitutional undercooling resulting from

**Table 1**
Composition (in wt. %) of the cast iron alloy used.

| C | Si | Mg | P | Cu | Mn | S |
|---|---|---|---|---|---|---|
| 3.6 | 1.91 | 0.075 | 0.017 | 0.012 | 0.099 | 0.001 |