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# In-situ Synchrotron X-ray Observations at SPring-8 BL20XU of Solidification in Hypoeutectic Al-Si Alloys[1]

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This paper demonstrates how recent advances in synchrotron technology have allowed for the X-ray imaging of real-time solidification in Al-Si alloys, despite the small difference in atomic number of these elements. The experiments performed at the SPring-8 synchrotron, involved imaging the solidification of Al-1wt%Si and Al-4wt%Si alloys under a low-temperature gradient and a cooling rate of around 0.3°C/s. The nucleation and growth of the primary aluminium grains as well as the onset of eutectic solidification were clearly observed. In the alloys containing Al-4wt%Si, contrast was sufficient to characterise the nucleation rate and growth velocity of the aluminium grains. The importance of improving observation of solidification in the Al-Si system by increasing the time resolution during critical events is discussed.

**Keywords:** Solidification, Synchrotron X-ray imaging, Al-Si alloy

## 1. Introduction

Advances in understanding the solidification of metallic alloys have traditionally been limited by the intrinsic difficulties of direct observation. The analysis of solidification by metallographic characterisation of solid samples requires assumptions, which have often been supported by supplementary experiments such as thermal analysis or quenching along with observations in transparent organic systems. Advances in synchrotron analysis have provided the opportunity to use X-rays to directly view solidification processes in-situ, including the development of microstructure and the formation of defects. As these techniques become more sophisticated it is possible to make observations in systems that have previously shown insufficient difference in the contrast between solid and liquid phases. One such system is the Al-Si system, which as a binary system, has been the subject of only limited investigations using synchrotron techniques.

Alloys based on the Al-Si system are the most commonly used aluminium foundry alloys and account for 85-90% of all cast aluminium products [1]. They have a low density, excellent strength-to-weight ratio, good corrosion resistance, high electrical and thermal conductivity and are economical to recycle. There are two major solidification reactions that contribute to the microstructure of these alloys. The first is the solidification of primary aluminium grains and the second is the solidification of the aluminium-silicon eutectic. Although the system has been the subject of intensive research for many decades, in-situ solidification observations would make an important contribution to understanding how the cast microstructures develop during solidification. However, similarities in the atomic mass of Al and Si along with the liquid/solid density of Al-Si limit the contrast obtainable by synchrotron X-ray techniques.

The binary Al-Si system is a simple eutectic system containing no intermetallic compounds and is characterised by the eutectic reaction at approximately 12.5Si and 577 °C [2]. The density of Al-Si alloys in the liquid, ρl, and solid, ρs, varies with composition and temperature and is described by Equations 1 and 2 [3] where T is temperature and C, wt% Si. Using these equations and assuming infinite diffusion in the liquid and none in the solid, the density difference at the solid-liquid interface on initial solidification will vary between 5.5% and 7% in hypoeutectic Al-Si alloys.

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$$\rho l = 2559.1 - 0.2820\,T + 3.371\,C \qquad \text{Equation 1}$$

$$\rho s = 2688.6 - 0.1990\,T - 2.295\,C \qquad \text{Equation 2}$$

Owing to the similar atomic numbers of Al and Si, this alloy system is not suited for X-ray radiography studies. One approach to address this issue has been to make trace element additions to enhance visualization. For instance, Mathiesen et al. studied eutectic formation in Al-8Si and Al-9Si alloys with Cu added to enhance X-ray absorption contrast [4]. The precipitation of Fe bearing intermetallic phases in Al-Si-Cu alloys has also been successfully examined using synchrotron techniques [5]. Jung et al., in their study of dendrite fragmentation of columnar grains in Al-7Si binary alloys observed that the minimal difference in the atomic numbers of Al and Si causes “no contrast” between the solid and the liquid [6]. To circumvent the visualization problem, they subtracted the previous image from the current to obtain some contrast, based on the work by Nguyen et al [7]. Their experimental conditions included samples that were 150-300 µm thick samples, with an X-ray beam energy of 17.5 keV. The optics in their system were chosen so as to obtain a large enough field of view (15x15 mm) with a good resolution (7.46 µm) and they used a maximum image capturing rate of 0.3 Hz. Other attempts have been made to study in-situ Al-Si solidification phenomenon using synchrotron radiation. These include those of Faraji et al. in studies on the nucleation behavior of different grain refiners in commercial A356 alloy using 3DXRD [8]. Srirangam et al. [9] have studied the structure of the liquid in Al-Si alloys with and without Sr additions using XRD from a synchrotron source. Wang et al. studied the formation of Fe rich β-intermetallics in Al-7.5Si-3.5Cu-0.8Fe alloys using synchrotron radiation [10]. Likewise, Terzi et al. studied β-phase formation in Al-8Si-4Cu-0.8Fe using synchrotron radiation [11]. More generally, synchrotron techniques are becoming increasingly important in materials characterization, as outlined by Rowenhorst and Voorhees [12] in a review of the advantages of using 3D techniques for materials characterisation.

In the casting of metals it is desirable to refine the grain size, often through the addition of inoculants. While some progress has been made in understanding the role of inoculants, the challenge facing the casting industry is the fact that >90% of added inoculants do not take part in the nucleation phenomena. Recently, one of the authors of this paper, StJohn, [13] proposed the Interdependence Theory which predicts the formation of a Nucleation Free Zone (NFZ) ahead of a growing grain. This NFZ is predicted to exist even in the presence of inoculants. Thus, the theory predicts the presence of unused inoculants. A greater understanding of the Interdependence theory could be obtained through the in-situ observation of solidification phenomena and synchrotron X-ray experiments are one of the main techniques capable of obtaining this data. This paper investigates the feasibility of observing the nucleation and growth of Al grains in binary Al-Si alloys.

## 2. Materials and Methods

Alloys were prepared by melting appropriate quantities in an induction furnace and both alloys had an addition of 0.1% (nominal) Ti added in the form of an Al-3Ti-1B master alloy. Thermal analysis samples were taken from the melt using a procedure described in detail elsewhere [14].

Synchrotron X-ray radiography experiments were performed on beam line BL20XU of the SPring-8 synchrotron (see Figure 1) with an energy of 16keV, using an experimental technique that was developed in previous research [15]. A planar undulator was used as a light source and the radiation was monochromatised with a Si double crystal monochromator. An image detector consisting of a single crystal phosphor screen and a CCD camera was used. The sample detector distance was less than 1 m. A graphite heater was used and BN plates shielded radiation from the heater, creating a window (roughly 10 mm×10 mm) at the centre for the X-ray beam.

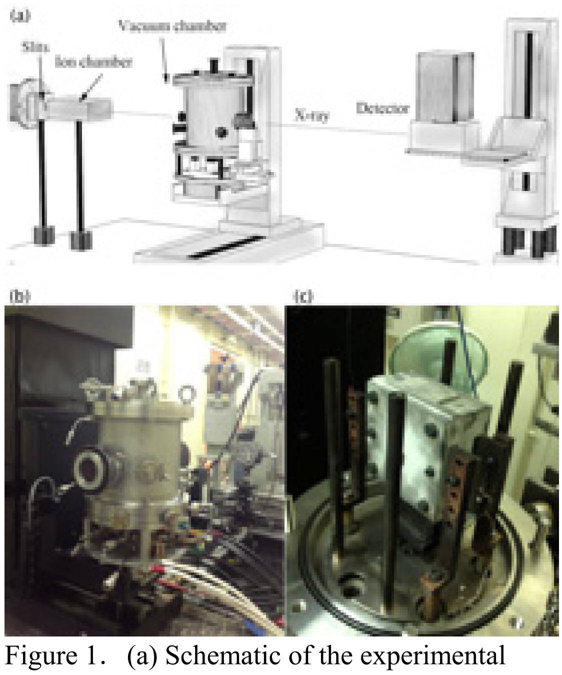


Figure 1. (a) Schematic of the experimental setup for the real-time observation of solidification [16], (b) vacuum chamber and (c) furnace at the SPring-8 BL20XU beam line.

Specimen cells were made of $Al_2O_3$ window plates and BN retainer plates. Al-Si samples of composition shown in Table 1, with dimensions of 7 mm×7 mm×0.1 mm were placed between the two $Al_2O_3$ window plates with a thickness of 0.15 mm. The specimen and the window plates were retained by the BN plates. Specimens were inserted into the furnace and melted at around 20°C superheat for the Al-1Si sample and around 40°C superheat for the Al-4Si sample. The imposed thermal gradient led to a temperature difference of ~1 K across the field of view and the cooling rate was approximately 0.3°C/min. Images were captured at a frame rate of approximately 1Hz and the pixel size of the measurement is around 1 μm x 1 μm.

Since the X-ray absorption coefficients of Al and Si are nearly the same, the solute rejection at the solidifying front does not cause any clear contrast between the solid / liquid interface. Thus, it is required to detect the contrast induced by the density difference between the solid and the liquid phases. Polished Al-Si specimens, with no coating and a thickness of 100μm were inserted into the specimen cell. Observation was performed under a vacuum (10-3 torr). Although a thin oxide film was produced on the specimen surface, the melt flow compensated for the solidification shrinkage. Consequently, the thickness of the specimen was kept constant throughout solidification. The constant thickness was advantageous for detecting the solid / liquid interface.

**3. Results and Discussion**

The X-ray images of solidification as captured during the experiments are shown in Figure 2 (a) – (e) for both alloys. The labeled times in Figure 2 are measured from the time at which nucleation was first observed (tN=0) and would roughly correspond to the liquidus temperature of the given alloy. Although times could be recorded accurately, due to the small sample size it was not practical to embed a thermocouple in the samples and exact temperatures cannot be reported. Very rapidly after grain nucleation (within a few seconds), the total number of grains for each sample is fixed and no further nucleation was observed. It was noted that the number of grains was slightly higher in the Al-1Si sample and this may relate to the higher concentrations of Ti and B. For the first few seconds the newly formed grains are highly mobile and some rotation and drifting of the grain location under gravity is observed. Around five seconds after nucleation, the grains had formed a coherent network and no further grain movement was noted. The effect of solute segregation in halting grain growth was apparent in many instances where the growth of adjacent dendrite arms appeared to slow before impingement on their immediate neighbours. The commencement of eutectic solidification was observed as a clear increase in contrast (bright white region) between dendrite arms and adjacent grains as seen in Figure 2(e). It is noted that the time of eutectic solidification commencement is different for these alloys due to the larger non-equilibrium freezing range in the alloy with lower silicon concentration. Between the onset of nucleation, just prior to Figure 2(a) and eutectic solidification, Figure 2 (e), significant coarsening of the secondary dendrite arm spacing occurs, although the rate of coarsening is faster earlier in solidification.

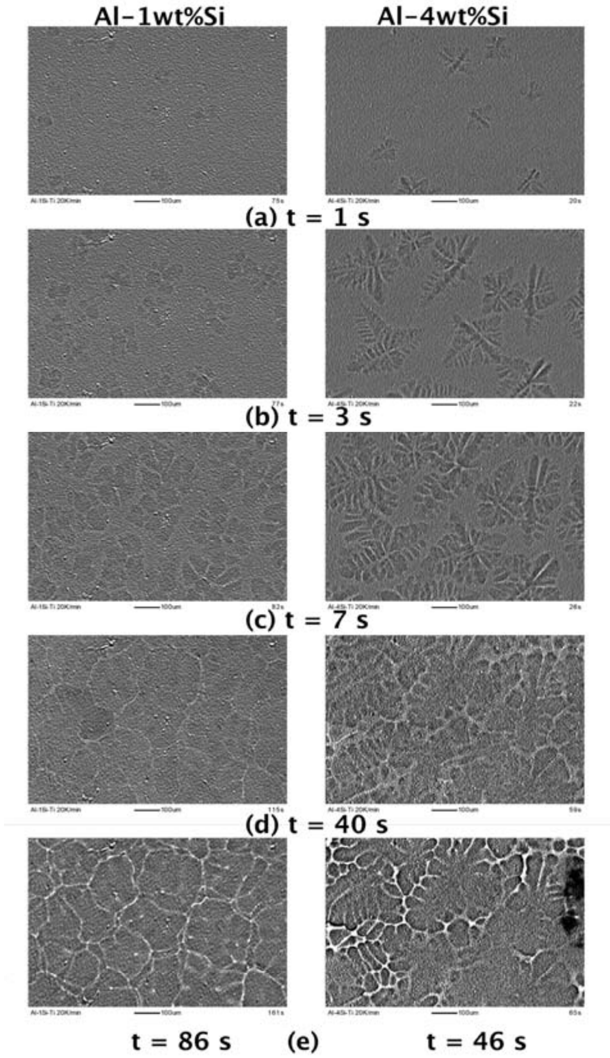


Figure 2. Selected X-ray stills of solidification for the Al-1Si alloy, left, and the Al-4Si alloy, right. Time measurements are relative to the first observation of nucleation.

## 4. Conclusions

This research was performed to determine the feasibility of using synchrotron based X-radiographic techniques to directly observe the nucleation and growth of primary Al grains in binary Al-Si alloys. We have demonstrated the successful capture of solidification events including grain nucleation, coarsening, and the onset of eutectic solidification. The growth interface was detected by the density difference between the solid and liquid. The resolution that was obtained should be possible for most aluminium alloys. Quantitative measurements from the images can be used to obtain nucleation frequency and dendrite tip velocities. It is apparent from the results that the use of synchrotron X-ray techniques must be tailored to the phenomena of most interest. For research into grain nucleation and refinement, the timing of nucleation and the spatial distribution of grains is critical and this would benefit from a large field of view and a high data collection rate around the primary reaction when the microstructure evolves rapidly, even in samples cooled relatively slowly. On the contrary if eutectic solidification is the main focus, then a higher magnification is required. The results of this research will be used in the ongoing development of grain refiners for Al-Si alloys and also contribute to improved synchrotron observation techniques.

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