Real-time synchrotron x-ray observations of equiaxed solidification of aluminium alloys and implications for modelling

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Abstract. Recently, in-situ observations were carried out by synchrotron X-ray radiography to observe the nucleation and growth in Al alloys during solidification. The nucleation and grain formation of a range of Al-Si and Al-Cu binary alloys were studied. When grain refiner was added to the alloys, the location of the nucleation events was readily observed. Once nucleation began it continued to occur in a wave of events with the movement of the temperature gradient across the field of view due to cooling. Other features observed were the settling of the primary phase grains in the Al-Si alloys and floating in the Al-Cu alloys, the effects of convection with marked fluctuation of the growth rate of the solid-liquid interface in the Al-Si alloys, and an absence of fragmentation. The microstructures are typical of those produced in the equiaxed zone of actual castings. These observations are compared with predictions arising from the Interdependence model. The results from this comparison have implications for further refinement of the model and simulation and modelling approaches in general. These implications will be discussed.

1. Introduction

The results of two studies of equiaxed solidification observed by synchrotron real-time X-ray experiments are presented. One study was undertaken on a range of Al-Si alloys at the Spring-8 (Japan) synchrotron and the other on Al-Cu alloys at the Diamond Light Source (UK) synchrotron. Although experiments were undertaken on both unrefined and refined alloys, this paper only focuses on alloys that have been refined by an AlTiB master alloy. The purpose of these studies was to observe the nucleation events and the grain formation processes occurring during the formation of the equiaxed zone in a casting environment similar to that of gravity and low pressure die casting methods. As expected the solidification processes at this early stage of solidification are complex and dynamic. However, a number of features are clearly observed that provide a picture of the key factors affecting the final as-cast grain size.
The following sections describe the main observations and present images taken from the X-ray videos to illustrate the important features occurring during nucleation and grain formation including the effect of gravity and convection on grain growth and movement. The final section discusses the implications of these observations on the development of models for the prediction of as-cast grain size and the simulation of the nucleation stage and subsequent development of the equiaxed grains.

2. Experimental Methods

2.1. Real-time x-ray of Al-Si alloys
The Spring-8 experiments consisted of performing real time in-situ solidification experiments on Al - 1, 4, 7 and 9 wt%Si refined with 0.1 wt%Ti from the Al3Ti1B master alloy. Samples of a given alloy sandwiched between Al₂O₃ plates 100 µm apart were inserted into a furnace and underwent a heating and cooling cycle designed to capture melting and solidification of the sample while being exposed to the X-ray beam. The experiments were performed in low-resolution as well as high-resolution beam lines. Detailed procedures for selecting radiation energy, image processing algorithm, experimental set-up etc., have been described previously in a number of articles [1-4]. A low thermal gradient was present, although not deliberately controlled in all experiments [2, 5]. The cooling rate was set to 20 K/min for all cases. Note that there is a lack of contrast between the liquid and solid phases due to there being little difference in X-ray absorption and, therefore, the X-ray energy was set as low as 16 keV to enhance the contrast between solid and liquid phases. The energy of 16keV enabled the detection of solidifying dendrites in the liquid phase by absorption contrast. As discussed in previous work [1], phase contrast also enhances the contrast at the solid - liquid interface. As a result the contrast is not as good as that usually observed in Al-Cu alloys and some of the images can be difficult to see clearly.

2.2. Real-time x-ray of Al-Cu alloys
In-situ X-ray radiography studies of the solidification of Al -15 wt%Cu refined by 0.1 wt%Ti from a Al5Ti1B master alloy were carried out at the B16 beamline at the Diamond Light Source using a specially designed solidification rig. The rig consisted of a small Bridgman furnace for directional solidification composed of two independently controlled plate heaters separated by a small gap. Thin foil samples 200 µm thick were encapsulated within 100 µm quartz coverslips and their solidification was imaged by recording the transmitted X-ray signal. Details about the furnace and the experimental set up can be found in [6]. Experiments were carried out with and without the presence of a controlled temperature gradient parallel to gravity. Initially the temperature of both heaters was increased above the melting point of the alloy until the sample was fully melted. When a thermal gradient was needed during solidification it was imposed by decreasing the temperature of one of the two heaters while remaining above the melting point. When thermal stability was reached the cooling of the sample was initiated by lowering the temperature of both heaters at a constant rate until the entire field of view was solid.

3. Nucleation
Figures 1 and 2 show the solidification sequence of an Al-7wt.%Si alloy and an Al-15wt.%Cu alloy, respectively. From the X-ray videos the progress of nucleation can be readily observed. Figures 1 and 2 show selected images to illustrate the features of nucleation observed in the videos. In Figure 1 the temperature gradient is positive from the bottom left to the top right of the field of view. New grains are progressively nucleated as the temperature gradient moves through the melt due to cooling. The arrows marked on Figure 1 highlight the position of the most recent wave of nucleation. In Figure 2 the temperature gradient is very low and close to isothermal in the field of view and nucleation progresses from the top of the field of view. The reason for this observation is that Cu-rich liquid segregates to the bottom due to having a higher density. The liquid of lower Cu content has a higher
liquidus temperature and thus begins to solidify first. It can be clearly seen that nucleation occurs in waves of events similar to the Al-Si alloy. The wave-like nature is particularly obvious in the 12.5s image in Figure 2. What cannot be observed easily in Figure 2 but is clearly visible in the videos is that once nucleation of grains occurs they then begin to float upwards. The effect of gravity and density differences between phases is discussed in section 5.

Figure 1. Images showing the time-sequence of wave-like grain nucleation in an Al-7wt%Si alloy with 0.1% Ti from an Al3Ti1B master alloy. The formation of grains starts at the bottom left hand corner and proceeds towards the top right hand corner of the field of view. The arrows show the demarcation between nucleated and non-nucleated areas. The time of 0 s is taken from the image prior to the image where the first grains are observed.

Figure 2. Image sequence of the solidification of an Al-15wt%Cu containing Al5Ti1B master alloy in close to isothermal conditions (G < 1.5 K/mm) with a cooling rate of 20 K/min. Grains are seen appearing in a wave from the top of the sample towards the bottom. Nucleation began at the top of the field of view due to solute (Cu) segregation in the bottom of the sample. The final frame (t = 150 s) shows the final microstructure of the fully solid sample.

4. Grain Formation

Once nucleation occurs the grains grow with a dendritic morphology. The growth of the Al-Si primary dendrite arms was measured for the Al-Si alloys and it was found that the growth rate fluctuates with a periodicity between 0.2 and 0.4 s where the growth rate changes from a low rate to several 100 µm/s and then back again as apparent in Figure 3. Fluctuations in the rate of growth have previously been observed by Mathiesen et. al. in an Al-15wt.%Cu alloy [7].
Figure 3. The fluctuation of the growth rate of dendrite tips in the Ti refined Al-7wt%Si alloy. A grid has been superimposed to help view the relative dendrite tip movements. The images are taken at 0.2 s intervals beginning at 66.4 s after the start of recording. In the centre grain, along the +x direction, there is negligible tip growth between (A) and (B), which accelerates in (C), and continues to grow in (D). Along the +y direction there seems to be no growth between (A)-(C), but rapid growth in (D). In the −y direction there appears to be some growth between (A)-(C), which seems to decelerate in (D). These differences in the amount of growth manifest as tip growth rate fluctuations.

Images from the synchrotron video were analyzed for the rate of increase of the number of grains. Individual grains were manually counted on each frame as a function of time for refined alloys of all compositions (Al-1, 4, 7 and 9 wt%Si). The grain count is presented as a function of time in Figure 4(a). The maximum number of grains was observed for 1 wt%Si, steadily decreasing with the increasing Si composition. The maximum grain count was converted to grain number density by dividing the grain count by the area of the field of view. As expected, the grain density decreases with increasing composition. There is more than an order of magnitude difference in grain number density between the 1 and 9wt%Si alloys. This observation is important when analyzing the effect of solute concentration in grain refined alloys. Clearly, in Al-Si alloys, there is a marked difference in inoculant efficiency with change in Si concentration. This information is often obscured in grain size data (see figure 5) which is the more widely used parameter.

Figure 4. (a) The number of grains as a function of time in refined Al-Si alloys and (b) the maximum grain count from (a) converted to grain number density per unit area (m²).

The grain size of the Al-Si alloys is plotted as a function of Si concentration in Figure 5. For the synchrotron experiments the maximum grain number (Figure 4) for a given alloy composition was converted into grain size by assuming a perfect spherical shape for the grains occupying the sample volume. The data for refined and unrefined alloys show a clear difference with data for the unrefined
alloys showing larger grain sizes as expected. The data obtained from the synchrotron experiments fit well with those from the casting experiments of previous researchers. Irrespective of the presence of refining agents, the data shows an increase in grain size beyond ~3 wt%Si. Below this concentration, unrefined alloys show a decrease in grain size as the Si composition increases. The refined alloys tend to show the same grain size for Si compositions lower than 3%. The higher growth restriction factor with increasing solute content is expected to result in smaller grain sizes at higher compositions. However, Al-Si alloys show an opposite trend and the increase in grain size with Si content is known as Silicon poisoning [8].

Figure 5. Grain size as a function of Si composition from casting and synchrotron experiments for both unrefined and refined alloys.

5. Effect of Gravity and Convection

It was observed that the relative movement of grains in Al-Cu alloys compared to Al-Si alloys was reversed. In the Al-Cu alloys the upward movement of grains is illustrated in Figure 6 over a time interval of 3 seconds. This upward drift of grains, also observed in other research on similar Al-Cu compositions [9], can have a significant effect with the newly nucleated grains moving from their nucleation sites up into the semisolid region assisting the packing of grains.

Figure 6. (a) The location of the grains at time $t_0 = 0$ s, (b) differential images between four frames taken at 1 s intervals ($t_1 = 1$ s, $t_2 = 2$ s, $t_3 = 3$ s) showing the floating of the four dendrites in the center of the field of view (highlighted in magenta).

On the other hand, the primary Al dendritic grains in the Al-Si alloys have a tendency to sink. This is more noticeable when the grains are small. As both the Al-Si and Al-Cu primary phases grow they begin to interact with each other preventing further sinking or floating. Figure 7 illustrates the degree of movement of the primary grains in the refined Al-4 wt%Si alloy over a period of 5 seconds. Note
that some grains do not move over this time period (identified by dashed lines) while others sink (solid lines). This maybe because these grains remain stuck between the Al$_2$O$_3$ plates as the grains are already the same size as the thickness of the sample.

Figure 7. Primary Al grains in a refined Al-4 wt%Si alloy growing and sinking simultaneously with time. The change in the location of the center of the grain is marked by the ends of the red solid lines, with the movement shown as a downward arrow. Not all grains move as indicated by the dotted white lines. Images are from the high-resolution synchrotron experiments.

The relative difference in grain motion between the Al-Si and Al-Cu alloys can be understood with reference to Figure 8. This figure shows the density difference between the solid and liquid phases at the point of initial nucleation (fraction solid approaching zero) for a range of hypoeutectic Al-Cu and Al-Si compositions. Data for the Al-Cu alloys are taken directly from [10] while those for the Al-Si alloys come from the equations provided in [11] with the required temperatures taken from the equilibrium liquidus temperature for that composition. For all hypoeutectic Al-Si compositions the density of the newly nucleated solid grains is greater than that of the liquid. For the Al-Cu alloys a similar condition holds when the Cu concentration is less than around 10.5 wt%. However, as the concentration of Cu exceeds this level (as in the experimental alloys of this paper) the density of the newly nucleated grains is less than that of the liquid. As discussed in [9] the velocity of the grains will depend on the relative contribution of the buoyancy forces and the drag due to interaction with the sample walls, which is a function of viscosity, grain size and mould dimensions. The effect of the grain motion on microstructure development will also depend on the direction of travel relative to the thermal gradient.

Figure 8. The density of solid and liquid phases early in solidification for a range of Al-Si and Al-Cu alloys. Data from [10, 11].
Of interest for the study of casting quality is the ability of real-time synchrotron studies to observe how the growing grains pack together to form the final as-cast macrostructure. In Figure 2 and more readily observed in the video, the grains appear to rotate to fit into the spaces formed by the previous layer of grains and sometimes vertical channels of liquid between the grains seem to form. The channels most probably form as the intergranular liquid is displaced by the rising lighter Al grains. This movement of the liquid would in turn assist the rotation of the grains. This process may affect the formation of casting defects such as hot tearing and porosity formation.

6. Other observations

In addition to the wave-like nature of nucleation shown in Figures 1 and 2 it was noted that once nucleation occurs no further nucleation is observed to occur between adjacent grains. This process of nucleation supports the predictions of the Interdependence model which was further validated by numerical modelling [12]. It can also be observed that once the grains nucleate they do not remelt even when they move considerable distances from the point of nucleation particularly in the Al-Cu alloys. This survival is due to the low applied temperature gradients allowing the formation of constitutional supercooling throughout much of the liquid which protects the grains from remelting. A significant observation from viewing the videos is that there is no evidence of fragmentation in either of the alloy systems studied; implying fragmentation may not be favoured during equiaxed solidification compared with directional solidification where much evidence of fragmentation has been reported in the literature.

7. Implications for Modelling and Simulation

The modelling of grain nucleation is difficult and many models simply set a matrix of nucleant locations which can trigger nucleation when the liquidus is reached during cooling. However, the nucleant particles, in this case TiB₂ particles, usually have a broad range of particle sizes and thus potencies that is difficult to model [13]. Because the observations of this research indicate that nucleation occurs on the most potent particles, most of the smaller particles can be ignored as they are unlikely to ever nucleate a grain [13]. The observation of fluctuating growth rates in the Al-Si alloys show just how complex the casting environment is. To be able to predict fluctuations thermal and solutal convection needs to be modeled. Recent modelling research is attempting to deal with the effects of convection during solidification [14, 15]. The thermo-solutal convection may also affect the local undercooling ahead of the dendrite tips which in turn may affect the size of the nucleation free zone [2, 13] and the subsequent nucleation rates. Add the effect of relative changes in density within the semisolid melt and the physics becomes complicated. Thus, analytical models would be inadequate for the accurate prediction of as-cast grain size and its variation throughout the macrostructure compared to sophisticated numerical models such as reported in [16]. However, the Interdependence model which is an analytical model, is remarkably effective as an indicator of relative, if not actual, grains size [13].

8. Concluding remarks

As shown in this work the grain size outcomes of these real-time synchrotron studies correspond to that of actual castings. Therefore, from observations of the solidification of the alloys studied, information on nucleation and grain formation provide useful data that improves our understanding of the solidification mechanisms in actual commercial castings. Not only are we now able to quantify the rate and progress of nucleation events but also gain information on the role of density differences and convection in affecting the final as-cast grain structure. These studies allow us to test the established theories of nucleation and grain growth and also analytical and numerical models with regard to their
validity and weaknesses providing avenues for their improvement. The complexity of the modelling task in providing accurate simulations has been highlighted by the observed interaction between alloy chemistry and the changing thermal, relative phase density and fluid states in facilitating solidification and the arrangement of grains within the final as-cast macrostructure. Further real-time synchrotron studies will be undertaken to gain quantitative information to improve our knowledge and validate the analytical and numerical models used by the authors.

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