The spatial and temporal distribution of dendrite fragmentation in solidifying Al-Cu alloys under different conditions

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Abstract

The directional columnar solidification of Al-Cu alloy dendrites was studied *in-situ* by synchrotron X-ray radiography to investigate the spatial and temporal distribution of dendrite fragmentation, without and with an applied pulsed electromagnetic field (PEMF) and in different solidification directions. The differing arrangements had a strong and reproducible influence on fragmentation behaviour that was rationalised using a model of solute-driven re-melting of dendrite arms in microstructural regions of high vulnerability. Although absolute rates of fragmentation varied, all the fragmentation distributions had a characteristic peak in fragmentation rate at a distance of 500 - 800 μm into the mushy zone. Consistent with the need for solute-rich liquid flow for dendrite root re-melting, this peak was explained to occur under conditions where there was both comparatively steep liquid solute concentration gradients, measured directly from the radiographs, and relatively high permeability of the dendrite network to liquid flow.

Keywords: Solidification, Synchrotron X-ray radiography, Dendrite fragmentation, Aluminium alloys, Pulsed electromagnetic field

1. Introduction

The mechanical properties of many complex shaped castings depend critically on the microstructure that develops during solidification because it is frequently impossible or expensive to manipulate the microstructure subsequently in the solid-state. Cast alloy microstructures often evolve as extended zones of elongated and inter-locking columnar, dendritic grains. As solidification progresses, these columnar, mushy zones become progressively less permeable

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to the flow of the residual liquid needed to feed any solidification shrinkage, and the interlocking grains have restricted ability to accommodate solidification strains. Consequently, in shaped castings, semi-continuous or continuous casting of slabs or billet, dendritic microstructures are more prone to macro-segregation and mechanical property anisotropy. Therefore it is commonplace in industrial practices to manipulate casting conditions to favour the formation and growth of refined, equiaxed dendritic grains rather than columnar grains. Equiaxed microstructures have better liquid feeding characteristics, minimise mechanical anisotropy, reduce casting variability and improve most mechanical properties. Many technologically important alloys cannot be cast with acceptable properties without the application of procedures to promote equiaxed grain formation.

For many alloys and processes, the most effective route to an equiaxed cast microstructure is through the addition of an extrinsic grain refiner to the melt shortly before casting, of which the best-known example is the addition of micron-sized TiB_2 particles to aluminium alloys. The resulting high number density of potent, microscopic solid particles in the melt ensures easy (low undercooling) nucleation of primary grains throughout the melt, at all stages of solidification, so that extended columnar zones do not develop. Alternatively or in addition, casting conditions can be contrived so that any evolving, extended columnar dendrites become prone to fragmentation. The resulting dendrite fragments are themselves then potent nucleation seeds and embryonic grains that are convected around the melt. These fragments provide *intrinsic* grain refinement and partial or complete suppression of extended columnar zones. Where potent extrinsic additions are either unavailable or prohibited by process practicalities or melt cleanliness considerations, intrinsic grain refinement increases in importance.

Several ideas and theories have been proposed to explain the fragmentation and detachment of dendrite arms during solidification, including: re-melting due to recalescence, curvature effects or solute pile-up¹⁻⁶, highly localized changes in free energy due to concentrated elastic and/or plastic strain under bending that leads to local melting⁷, induced grain boundary formation down which liquid can penetrate⁸, and exhaustive reviews on the topic can be found in^{9,10}. Amongst these theories, the re-melting of dendrite roots due to solute effects has the most support and experimental evidence, and likely represents the mechanism most prevalent under typical casting conditions. Following the ideas of Jackson *et al.*¹, Mathiesen *et al.*^{3,4,11} used X-ray synchrotron radiography to implicate strongly the effect of solute pile-up in fragmenta-

tion, and Ruvalcaba *et al.*¹² then showed direct evidence of the detachment of secondary arms due to solute enrichment within the mushy zone of Al-Cu alloys. Liu *et al.*² also suggested that the dynamics of solidification, such as slowing of dendrite growth, could increase the local solute concentration in the solid-liquid region of the dendrite growth front (the mushy zone), and consequently promote the tendency for fragmentation.

Dendrite fragmentation can be enhanced by the application of external fields to the melt during casting, such as electromagnetic forces or mechanical stirring^{2,9,13–19}. The effect of the external field is generally held to be indirect, arising from the action of the induced force on the *liquid*, leading to increased melt convection, which induces instabilities or fluctuations in the local liquid solute concentrations in contact with the evolving solid dendrites. Fleeting and before compositional equilibration can be re-established, there then arises a thermodynamic driving force for the dissolution of the relatively dilute solid in regions of favourable curvature, and the tendency for fragmentation is increased⁶. Recently, Liotti *et al.*^{5,6} used X-ray radiography combined with a controlled pulsed electromagnetic field (PEMF) technique to capture the dynamics of columnar fragmentation, and measured a reproducible increase in the fragmentation rate when a sinusoidal PEMF was applied and liquid solute distributions were disturbed. Nonetheless, some debate continues as to whether fragmentation might also be achieved by *mechanical* failure of dendrites due to the direct action of the externally imposed forces on the *solid* dendrites, perhaps under specific, relatively high load conditions^{9,10,13–15,20}.

In this paper we investigate the fragmentation of Al-Cu alloy columnar grains using X-ray radiography without and with an applied PEMF of different strengths during upwards and downwards directional solidification, with multiple repeat experiments of every experimental condition. We quantify fragmentation behaviour as a function of position in the mushy zone to form a large data set that allows meaningful identification of common fragmentation features between all experiments, as well as differences that depend on specific conditions. For the first time, a comprehensive explanation of the spatial and temporal distribution of fragmentation behaviour is presented that accounts for all the key observations, based on the extension of solute pile-up models combined with fine-scale spatially resolved measurements of liquid solute concentration gradients deep in the inter-dendritic channels.

Figure 1: The upper and lower heater temperatures and pulsed electromagnetic field (PEMF) signal (on/off) profiles during a typical solidification experiment, in the case from bottom to top (B2T) and with a PEMF applied at $t = 0$ s.

2. Experimental methods

2.1. Dendrite fragmentation

In-situ synchrotron X-ray radiography studies of the solidification of an Al-15wt.%Cu alloy were carried out at the B16 beamline at the Diamond Light Source (UK) using a bespoke solidification rig. A comprehensive description of the equipment and sample preparation is given by Liotti *et al.*⁶. Videos of the formation of a dendritic array and the subsequent evolution of the mushy zone were recorded without and with the application of a pulsed electro-magnetic field (PEMF). All fragmentation measurements were obtained under quasi-static conditions in the mushy zone in a fixed thermal gradient i.e. without pulling (Bridgman growth) of the sample through the temperature gradient.

The experiments were divided into three steps, as shown in Fig. 1. First, the temperature of both heaters was increased above the melting point of the alloy until the sample was fully melted, then a temperature gradient was imposed in the liquid by decreasing the temperature of one of the two heaters (region 1). Second, when a stable gradient was reached, sample cooling was initiated by lowering the temperature of both heaters at a constant rate until

Experiment	Growth direction	Gradient (K/mm)	PEMF force (mN)	No. of repeats
B2T	Upwards	48	-	11
B2T PEMF = ± 0.3 mN	Upwards	48	0.3	10
T2B	Downwards	48	-	8
T2B PEMF = ± 0.3 mN	Downwards	48	0.3	4
T2B PEMF = ± 0.9 mN	Downwards	48	0.9	6

Table 1: Experimental parameters summary for the 39 fragmentation experiments on Al-15wt.%Cu samples.

dendrites appeared in the field of view and reached approximately the centre (region 2). At this point the dendrite front was usually approximately flat across the field of view. Third, cooling was stopped, the temperatures and the thermal gradient were kept constant, and after a few seconds the PEMF was switched on (region 3).

The solidification rig was controlled remotely by National Instruments hardware and software (LabView) and the heater temperatures controlled by a carefully calibrated PID algorithm. The achievable cooling rate ranged between $0.05^{\circ}\text{C s}^{-1}$ to 2°C s^{-1} . The overall temperature stability of the heaters was investigated in detail at various stages of multiple experiments and was $\pm 0.5^{\circ}\text{C}$.

Dendrites were grown both upwards, from bottom-to-top (B2T) and downwards, top-to-bottom (T2B). All PEMF experiments used a pulse frequency of 1 Hz, a sine-wave form with peak-to-peak amplitude of 30 V, and a mean amplitude of 0, inserted into a $50\ \Omega$ circuit corresponding to a current of $I = \pm 300$ mA. Two ring magnets, a ferrite type and a samarium-cobalt type, with different magnetic field strengths were used. The magnetic field B of the two magnet types at 3 mm from the magnet surface was estimated to be 0.1 T and 0.3 T respectively. Magnets were air cooled and replaced frequently to mitigate any loss of magnetism because of overheating due to their proximity to the sample heaters. The Lorentz force F applied to the sample was estimated as ± 0.3 and ± 0.9 mN for the two magnet types respectively. A total of 39 experiments were carried out under the experimental conditions summarized in Table 1.

2.2. Solute measurement experiments

Additional in-situ synchrotron X-ray radiography experiments to characterize the spatial distribution of solute concentration within the mushy zone of an Al-25wt.%Cu alloy were carried out on the ID19 beamline at ESRF (France), using the same solidification rig and experimental methods described for the Diamond B16 experiments. The undulator X-ray source of ID19 provided brightness and stability conditions better suited to the quantification of solute concentrations in the liquid. White-beam mode was used i.e. only a gold-coated diamond absorber and the mandatory Be exit window were in the X-ray path. The single-harmonic undulator (U17.6, gap 16 mm) provided a peak photon energy of 19 keV. To acquire high-resolution radiographic images, a $\times 10$ Olympus objective (0.3 numerical aperture) projected the luminescence image formed on a 10 μm thick GGG:Eu scintillator via a mirror and a tube lens (periscope configuration) onto the CMOS chip of a pco.DIMAX camera (PCO AG, Germany, 2011 $\times$ 2011 pixels, 11 μm pixel size). The resulting spatial resolution was 1.1 μm /pixel with a field of view of 2.2 mm $\times$ 2.2 mm recorded at 6.7 Hz, which was the highest frame rate achievable in continuous recording mode. In total 24 solidification sequences across the range of conditions shown in Table 1 were recorded.

3. Data analysis

3.1. Dendrite fragmentation analysis

Raw radiographic images were often affected by illumination variations originating from the X-ray optics as well as occasional surface defects on the samples, as shown in Fig. 2(a). Raw image processing and then dendrite fragmentation analyses were performed using scripts written in Matlab language. First, the images were flat field corrected: the raw images were divided by a flat image recorded when the sample was fully liquid (Fig. 2(b)) to remove intensity variations. Second, a band structure due to uneven illumination generated by the multi-layer monochromator²¹ (Fig. 2(c)) was corrected by dividing images by their own background derived from a spatial filter applied to each image (typically gaussian) with a large rectangular kernel of approximately 5 $\times$ 200 pixels. Finally, a spatio-temporal gaussian filter with a small square kernel was applied to smooth high frequency noise and to adjust the pixel intensity to maximize the contrast between solid and liquid (Fig. 2(d)). The filter was typically 3 $\times$ 3 $\times$ 5 (pixel height $\times$ pixel width $\times$ number of frames) to provide a compromise between smoothing

Figure 2: Example of image processing steps for the data collected at Diamond B16 and used for the fragmentation analysis. (a) raw image, (b) image after flat field correction, (c) image (b) after applying the de-banding code, (d) image (c) after smoothing the noise using a spatio-temporal gaussian filter and equalizing the pixel intensity to emphasize the contrast between solid and liquid.

and potential loss of detail.

The videos were analysed using a semi-automatic approach involving a series of Matlab scripts to record the manual identification of a fragmentation event location and other relevant information i.e. depth into the mushy zone. Data was analyzed to obtain the fragmentation rate, cumulative fragmentation number, and the distribution of fragments as a function of the mushy depth and solid fraction. These are defined as follows:

- Fragmentation number - the raw total number of detached arms, of every order (primary, secondary, etc), detected in each experiment and not normalised by volume or time.
- Cumulative fragmentation - cumulative sum of the total number of detached dendrite arms for each experiment divided by the volume of the mushy zone within the field of view (number of fragments/ m^3).
- Fragmentation rate - total number of measured arm detachments over a time interval of typically 10 s divided by the time interval and the volume of the mushy zone in the field of view (number of fragments/ (m^3s)).
- Mushy depth - the depth at which a fragmentation event occurred, measured as the

vertical distance (i.e. in the y direction) from the tip of the longest dendrite to the fragment event (μm).

Several approaches were investigated to measure the local solid fraction as a function of depth into the mushy zone. However the errors in the solid fraction estimates were considered unacceptable e.g. accounting for the constrained geometry of the sample²². Therefore, although solid fraction always increased with increasing mushy depth, the use of measured solid fraction data is generally avoided in the subsequent analysis.

3.2. Solute analysis

Solute concentrations in the liquid were estimated from radiographs collected at ID19. The raw images were processed to transform pixel intensities to solute concentration using the Beer-Lambert law²². The gradient of solute (Cu) concentration in the liquid in the interdendritic channels was obtained by calculating the numerical gradient of the solute map using Matlab's built in gradient function. The gradient along the x and y directions of a solute map $S(x, y)$ are defined as $(dS/dx)_y = [S(x + 1, y) - S(x - 1, y)]/(2\Delta x)$ and $(dS/dy)_x = [S(x, y + 1) - S(x, y - 1)]/(2\Delta y)$ where Δx and Δy are the pixel width and height respectively. Section S.1 in the supplementary material gives more information about image processing and solute map generation. The error in the Cu solute concentrations in the liquid within a single sequence was estimated as $\pm 0.05 \text{ wt\%Cu}$. Sample to sample variations were likely larger, but most of the subsequent analysis relies only on relative changes in Cu concentrations in an image or a sequence, rather than absolute concentrations.

4. Results

4.1. Fragmentation rate

Figure 3 shows side by side two fragmentation map sequences of Al-15wt.%Cu samples for experiments with a PEMF applied and solidifying downwards top-to-bottom (T2B, left paired image) and upwards bottom-to-top (B2T, right paired image). Readers are invited to view the corresponding videos at Video1. The experiments were carried out under nominally identical conditions, differing only in the direction of the thermal gradient. Time was set at $t = 0 \text{ s}$ when dendrites were considered stationary in the field of the view and the PEMF turned

Figure 3: Fragmentation maps from two sequences during the solidification of Al-15 wt%Cu with thermal gradient $G = \pm 48 K mm^{-1}$ and PEMF ($F = \pm 0.3 mN$). In each image pair the location of a fragmentation event that occurred within the 30 s time segment is identified by a yellow circle.

on. Each image has superimposed yellow circles that indicate the location of a fragmentation event manually identified by eye that occurred within the 30 s period; each subsequent map represents a successive 30 s period. Although the two arrays were qualitatively similar (inclined at approximately 22.5° to the vertical with a primary arm spacing of $254\text{ }\mu\text{m}\pm 91\text{ }\mu\text{m}$ and $278\text{ }\mu\text{m}\pm 97\text{ }\mu\text{m}$ for B2T and T2B respectively) there was a significant difference in the number of fragmentation events in each of the observation periods. In the B2T arrangement, the fragmentation rate was relatively low in the first 30 s, but rapidly increased to a peak after 60 s to 90 s, then slowed to a rate similar to the self-fragmentation rate before the PEMF was applied⁶. In the T2B arrangement, the number of fragmentation events was significantly lower, with no significant increase even after a long period of applied PEMF. In both sequences, fragmentation events were concentrated comparatively deep into the mushy zone.

The mean fragmentation rates, averaged over all the experiments with same conditions and binned into 10 s periods are shown in Fig. 4. The shaded area represents the 10% and 90% quantile bounds for the data at each condition. In the cases where there was no applied PEMF the fragmentation rate was always below $0.5 \times 10^9 \text{ fragments m}^{-3} \text{ s}^{-1}$ for both solidification directions and the total number of fragments at a given time was similar. For B2T and no PEMF, the rate rose slowly to approximately $0.45 \times 10^9 \text{ fragments m}^{-3} \text{ s}^{-1}$ in the first 100 s and then began to slowly decrease again, with some fragmentation continuing beyond 400 s; for T2B and no PEMF, the trend was similar with a fragmentation peak after approximately 100 s and the subsequent decrease in rate almost reached zero after approximately 250 s. The differences are more evident in Fig. 5(a) that shows the T2B to B2T fragmentation rate ratio in 30 s segments. The T2B fragmentation rate was on average 60% lower than B2T.

The very low fragmentation rate in the T2B orientation when compared with the B2T orientation was consistent with dendrite fragmentation behaviour in Al-Cu alloys during Bridgman growth in similar orientations^{3,4}. The slightly higher absolute number of fragmentation events in the T2B orientation in the present work was ascribed to the larger, constant field of view, and the much longer observation times of the quasi-steady arrangement compared with earlier work.

The fragmentation increased, especially in the B2T arrangement, soon after the PEMF was applied, and then decreased slowly to the self-fragmentation rate. Fig. 5(b) shows the PEMF to no PEMF fragmentation rate ratio in 30 s segments. For B2T, the largest difference was 30 s

Figure 4: The average fragmentation rate of Al-15wt.%Cu calculated in 10 s steps for the different solidification arrangements listed in Table 1. Time $t = 0$ s was set as the time when the dendrites were considered stationary and, in the case of the experiment with PEMF, the time at which the PEMF was initiated. The filled symbols are mean values, while the shaded area represents the experimental variability (10% and 90% quantile). The zoomed area shows detail of the low fragmentation rate region.

Figure 5: (a) The T2B to B2T fragmentation rate ratio, and (b) the PEMF to no PEMF fragmentation rate ratio for various B2T and T2B conditions listed in Table 1. All data calculated in 30 s bins.

after the PEMF was applied, when the fragmentation rate with $F = \pm 0.3$ mN was approximately $\times 6$ than without PEMF. For T2B, the application $F = \pm 0.3$ mN had a slight effect on increasing fragmentation rate and only with $F = \pm 0.9$ mN was there an appreciable increase in the fragmentation rate. At both field strengths in the T2B orientation, the application of the PEMF took up to 200s to reach its peak effect of $\times 4.2$ and $\times 15$ for $F = \pm 0.3$ and ± 0.9 mN respectively. The application of the PEMF increased the experiment-to-experiment variation in the fragmentation rate, as shown in Fig. 4, suggesting that multiple experiments and averaging were particularly useful in revealing underlying trends reliably.

The significant difference in fragmentation behaviour with solidification direction suggested that in cases where PEMF was applied and fragmentation rate increased, it was not the direct mechanical action of the Lorentz force that increased fragmentation (or at least it was not a first order effect) since direct mechanical fragmentation can be expected to be little influenced by the solidification direction.

Figure 6: Normalized total number of fragments as a function of y -distance measured from the tip of the longest dendrite for four different experimental arrangements in Al-15wt.%Cu. The bar colours correspond to the relative contribution of an individual experiment to the overall distribution.

4.2. Dendrite fragmentation distribution

Considering all experiments, the normalised number fraction of fragments as a function of distance away from the dendrite tip front and into the mushy zone is shown in Fig. 6, sub-divided into plots for B2T, T2B, B2T with PEMF, and T2B with PEMF cases. Ignoring differences between the conditions already discussed above, it is striking that the normalised shape of the four distributions were similar. The distribution shape was similar to the fragmentation distributions recently reported for a Sn-Bi alloy²³.

If a gaussian distribution is fitted to the data in Fig. 6, then the best-fit mean of the distribution corresponded to the position of maximum fragmentation number, and occurred at distances into the mushy zone in the range 500 μm to 800 μm . Other subtleties may lie in

the data, such as bi-modality or systematic differences in the position of peak fragmentation, but even with this comparatively large data set, further inferences were not supported safely by the data. Considering the present work and other recent comparable studies²³, it is clear that a peak in fragmentation rate hundreds of microns into the mushy zone is a characteristic feature of quasi-static columnar dendritic arrays, independent of solidification direction or the presence or strength of an applied external field.

4.3. Solute gradients in the liquid

Since earlier work⁶ had suggested that movement or perturbation of the solute-rich liquid drives dendrite fragmentation, the solute distribution in the inter-dendritic channels was measured directly from radiographic videos of solidification of an Al-25wt%Cu alloy. This relatively concentrated alloy was chosen to maximise X-ray absorption contrast due to spatial differences in the solute (Cu) distribution. As an example, Fig. 7(a) shows a number of horizontal lines superimposed across the inter-dendritic channels of a quasi-static dendrite array. Note that although the applied PEMF in the experimental arrangement acted in the horizontal direction, along these lines, due to the complex inter-dendritic geometry, induced flows can be expected to be more complex, in local eddies or recirculating patterns²⁴. The liquid concentration profiles, left to right, along each of the horizontal lines in zones A and B are shown in Figs. 7(b) and (c) respectively. The colour of the profile provides an indication of its vertical position: blue is nearest the tips and progressively more yellow is deeper into the dendrite array. Because the inter-dendritic channels get narrower further into the mushy zone, the profiles became progressively shorter. The average solute concentration over the length of each profile increased with depth i.e. the average liquid concentration increased with solid fraction as expected for hypo-eutectic Al-Cu alloys with an equilibrium partition coefficient $k \approx 0.17$. For a given profile, there was a peak in the liquid concentration that became progressively pronounced with increasing depth, and occurred approximately half-way across the inter-dendritic channel for both zones A and B (and all others studied). This type of distribution has also been measured by *in-situ* radiography in the inter-dendritic channels of Ga-In alloys²⁵.

From the solute concentration profiles, the local solute gradient can be readily obtained and using the image in Fig. 7, Fig. 8(a) shows the resulting contours of local solute gradient, superimposed on the radiograph. Using the same data, Fig. 8(b) then shows the relationship

Figure 7: Line profiles measured within the mushy zone during solidification of a Al-25wt%Cu alloy (a) location of all the lines along which solute concentration was measured, and (b) and (c) the corresponding solute profiles from zones A and B respectively. The radiograph colormap was set to inverse gray scale to enhance visual clarity.

between the *maximum* solute concentration gradient of each profile as a function of the y -distance into the dendrite array. Solute gradients were lowest in the dendrite tip region and increased progressively with distance in the y -direction into the dendrite array. Local solute gradients also depended on the inter-dendritic channel geometry. For example, Fig. 8(a) shows a localized region of relatively high solute gradients in the bottom left corner of the image. By comparison with the corresponding image in Fig. 7(a), this region of high solute gradient was clearly correlated with the fragmentation of a primary dendrite. The reader is again invited to view the video sequence, which is particularly instructive (Video2).

To explore if the tendency for fragmentation was promoted by relatively high local solute gradients, as implied by Figs. 8(a) and (b), held more generally, the same sequence was analysed further as follows. The field of view was first divided into a two-dimensional grid of $550\text{ }\mu\text{m} \times 550\text{ }\mu\text{m}$ sub-domains. Then, over a period of 20 s, the number of fragmentation events was recorded within each of these sub-domains, along with the maximum solute concentration gradient within each sub-domain. Fig. 9 plots the resulting local fragmentation rate as a function of the local maximum solute gradient for each sub-domain over the full sequence. Fig. 9 suggests that fragmentation broadly increases with local solute gradient.

5. Discussion

While the overall fragmentation magnitude was affected both by the growth direction and the application of a PEMF and its strength (Figs. 4 and 5), there was little influence on the overall spatial distribution of fragmentation events (Fig. 6). Our earlier work suggested that fragmentation arises from solute-driven re-melting caused by the destabilization of the equilibrium solute field at the solid-liquid interface, and that this re-melting is preferred in local regions of high curvature; this vulnerability to re-melting is summarised in Fig. 10(a)⁶. Under these assumptions it was proposed that the local re-melting behaviour could be described by:

$$m\Delta C_L^* = \Gamma \Delta \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (1)$$

where m is the slope of the liquidus (K/wt.%), ΔC_L^* is the change in the liquid composition at the interface (wt.%) due to liquid flow (convection, external field, etc), Γ is the Gibbs-Thomson coefficient (mK) and r_1 and r_2 are the dendrite root radii of curvature as shown

Figure 8: (a) Horizontal solute gradient contour map within inter-dendritic channels for the same experiment shown in Fig. 7. The bar legend indicates the magnitude of the gradient. The radiograph colormap is an inverted gray scale of Fig. 7 to enhance the visibility of the solute gradient contours. (b) the relationship between local solute gradient and distance in the y -direction into the mushy zone. The best linear fit to the data points is shown by the dashed red line.

Figure 9: The local dendrite fragmentation rate as a function of the maximum in the local inter-dendritic solute gradient in the liquid as measured for the same experiment shown in Fig.7. The best linear fit to the data points is shown by the dashed red line.

in Fig. 10(a). A sudden change in the interfacial liquid solute concentration will cause an adjustment of two curvature radius r_1 and r_2 . If the left hand side term is positive (an increase in solute concentration) then either r_1 will decrease and/or r_2 will increase, both of which will increase the tendency for detachment of the arm by dendrite root re-melting. We now extend this model to explain the *spatial distribution* of dendrite fragmentation for the first time, linking all observations such as the effect of solidification direction, application of an external field and its strength, etc.

Consider three scenarios for the liquid solute concentration profile along a horizontal line across an inter-dendritic channel, as shown schematically in Fig. 10(b). If the solute distribution is flat (case 1) then any perturbation that induces horizontal flow will have no effect on interfacial conditions at the dendrite root ($\Delta C_L^* = 0$) and curvature will remain unchanged. If the solute distribution is weak with distance (case 2) then some destabilization might occur with the onset of liquid flow ($\Delta C_L^* > 0$); the profile in case 3 provides the strongest destabilization ($\Delta C_L^* \gg 0$), and promotion of fragmentation. The consistency of our experimental observations with this model of the factors controlling fragmentation is now discussed.

Figure 10: (a) schematic arrangement of two secondary dendrite arms attached to a primary trunk showing regions that are more vulnerable to re-melting due to their local curvature, and (b) different possible scenarios for the distribution of solute in the liquid across an inter-dendritic channel.

5.1. Effect of distance into the mushy zone

With reference to the experimental data in Figs. 7(b) and 8(b), dendrite fragmentation should increase with increasing distance into the mushy zone because we have shown that solute gradients increase, and this was indeed shown in the fragmentation distributions in Fig. 6, but only up to the point of peak fragmentation. Fragmentation by re-melting also requires movement of the liquid, which is now considered in terms of buoyancy effects in the inter-dendritic channels, and the permeability of the channels to flow.

Fig. 11 plots the liquid solute concentration C_L as a function of solid fraction f_S for an Al-Cu alloy, where the relationship between C_L and f_S is given by the well-known Scheil equation. The incremental change in liquid solute concentration for an incremental change in solid fraction $\frac{\Delta C_L}{\Delta f_S}$ is also shown for Al-15wt%Cu and Al-25wt%Cu. As solid fraction increases i.e. further into the mushy zone, incremental increases in the solid fraction correspond to progres-

Figure 11: Equilibrium solute concentration in the liquid from the Scheil equation for Al-15wt%Cu and Al-25wt%Cu alloys, and its rate of change, using an assumed constant equilibrium partition coefficient $k = 0.17$.

sively larger incremental changes in the liquid solute concentration (dotted lines). Given the large difference in density between Al and Cu (2.7 and 8.9 g cm^{-3} respectively), the arising spatial differences in liquid density encourages buoyancy driven convection, the tendency for which will increase with depth into the mushy zone. Thus, the initial increase in fragmentation rate with increasing depth into the mushy zone can be explained by (1) the interaction of steepening solute concentration gradients in the inter-dendritic liquid combined with (2) an increasing tendency for buoyancy driven movement of this liquid.

If this explanation held at all locations, the fragmentation rate should increase steadily up to the solid fraction (or depth into the mushy zone) at which eutectic solidification begins. However the robustly reproducible profiles in Fig. 6 showed that while fragmentation rates rose as predicted, they reached a peak and then decreased with further distance into mushy zone. Given that the liquid flow required for dendrite root destabilisation will depend on the local permeability of the dendrite network, the decrease in fragmentation rate after a peak at a depth of 500 to $800 \text{ }\mu\text{m}$ is suggested to arise because although the tendency for buoyancy driven flow and the solute gradients in the liquid are increasing, the ability to realise this flow becomes progressively more difficult as permeability decreases both with increasing solid fraction and decreasing primary arm spacing. Liquid viscosity may also increase at lower temperature and higher solute content. Restricted flow gradually dominates as the solid fraction

increases stabilising the dendrite network and suppressing the tendency for fragmentation.

5.2. Effect of solidification direction

Although most previous work has concentrated on the upwards, B2T solidification direction, there have been some studies of the downwards, T2B arrangement, and most have concluded that the inter-dendritic liquid should be comparatively dilute in alloys where the solute is denser than the solvent, as is the case here, because the solute-rich, dense liquid “drains” from between the dendrites. It should also be noted that buoyancy effects will give rise to a compressive stabilizing stress in primary dendrites oriented towards the vertical in the T2B case compared with tensile de-stabilizing stresses in similar dendrites in the B2T case, and that these will act simultaneously with any solute-movement destabilization. To investigate solute effects, the local concentration from positions within the inter-dendritic channels in typical T2B and B2T Al-25wt.%Cu sequences was measured, as shown by points P_n in Figs. 12(a) and (b) respectively, where n is the point number. The points were chosen to be always in an inter-dendritic channel as the dendrites grew, and solute concentration with time was recorded as shown in Figs. 12(c) and (d).

Surprisingly, the T2B arrangement showed the evolution of more concentrated inter-dendritic liquid compared with the B2T arrangement, and that the solute environment in the T2B arrangement was significantly more dynamic. These conditions arose because cooler, more concentrated and therefore denser liquid from above the field of view was continuously draining downwards through the inter-dendritic channels. As the solute-rich liquid descended against the imposed temperature gradient, it was too concentrated for the slightly hotter temperatures encountered and a thermodynamic driving force for solid re-melting in order to dilute this meta-stable liquid was established. This dynamic adjustment of the microstructure occurred continuously during growth as the dense liquid drained through the dendrite array, preferentially re-melting and eliminating any vulnerable regions of curvature. Thus, when the quasi-static arrangement in which fragmentation rates were measured was reached, fragmentation rates were always relatively low because the population of vulnerable regions required for fragmentation rate was relatively small - the dynamic solute environment during growth ensured a significant population of vulnerable regions could not be established.

Figure 12(e) shows that the normalised distributions of maximum solute concentration gradient were approximately the same for the T2B and B2T arrangements, supporting the conclusion that differences in fragmentation rate did not arise from differences in the local solute environment in the quasi-static arrangement, but instead were due to an inherently more stable starting microstructure.

5.3. Effect of a pulsed electromagnetic field

The effect of a pulsed magnetic field on fragmentation is through the enhancement of the movement of solute-rich liquid. Over the range studied, for the first time it is shown directly (rather than from post-solidification grain size measurements) that the stronger the field, the greater the induced flow and the higher the fragmentation rate. There was no compelling evidence for any change in fragmentation mechanism or the distribution of fragmentation events when the PEMF was applied.

5.4. Effect of time

All the fragmentation data for an applied PEMF showed that after a peak in the fragmentation rate, the rate reduced progressively as observations continued. This arose because on application the PEMF increased liquid movement and previously stable regions became de-stabilized. The most vulnerable regions re-melted most readily, and those marginally more stable a little later, and so on. Because a quasi-steady arrangement was used, the population of remaining vulnerable regions continuously reduced with time⁶.

One last reproducible feature of all the fragmentation rate variations with time that should be explained is the delay in the fragmentation rate increase, after the PEMF was applied. It is suggested that this delay arose because the complete re-melting of dendrite roots under the induced flow conditions used in this study took several cycles to complete, and that the number of cycles required for re-melting and fragmentation will depend on the relative stability of the dendrite array. Support for this explanation is provided by the much longer time for the fragmentation rate increase to become measurable in the T2B (≈ 200 s) than B2T (≈ 30 s) arrangement: as described earlier, there was a lower starting population of vulnerable regions

Figure 12: Local solute concentration measurements within the inter-dendritic channels for the T2B and B2T arrangements in Al-25wt.%Cu alloy: (a) and (b) location of points from which the solute concentration was measured as a function of time ; (c) and (d) the corresponding liquid solute concentration histories ($t = 0\text{ s}$ is when dendrites first appeared in the field of view); and (e) comparison of the normalised distribution of maximum solute gradient in the two orientations.

in the T2B compared with B2T arrangement, so that when the PEMF was applied, any re-melting and fragmentation took more cycles to achieve, and thus more time.

5.5. *Summary*

A solute-driven model of dendrite root re-melting that accounts for all the observations in the present work, and which is consistent with earlier reports of dendrite fragmentation, has been described^{1-4,6,11,12}. The key features are:

1. Steep liquid solute concentration gradients encourage dendrite fragmentation. Solidification orientations that promote solute build-up in the inter-dendritic channels promote the tendency for dendrite fragmentation e.g. upwards solidification in an Al-Cu alloy.
2. Vulnerable regions in the dendrite array, characterised by small radii of curvature, are prone to fragmentation by re-melting. The total number of fragmentation events will be in proportion to the number of these regions. Arrays grown under conditions that promote vulnerable regions will be more prone to subsequent fragmentation e.g. unsteady growth; growth conditions that remove vulnerable regions will be more stable e.g. solute draining effects.
3. Inter-dendritic liquid flow encourages dendrite fragmentation due to re-melting. Flow may be due to buoyancy effects from density differences in the solute-rich liquid, or due to the application of an external field. The extent to which induced flows are realised, and thus fragmentation promoted, depends on the local permeability of the dendrite network.
4. Under quasi-steady conditions, perturbation of the liquid destabilises and fragments the most vulnerable regions first and the fragmentation rate then reduces progressively.

Within the range of solidification conditions studied here, the dendrite fragmentation rate with distance into the mushy zone had a characteristic shape that was suggested to relate to the spatial distribution of liquid solute concentration gradient and how easily this liquid can move in the inter-dendritic channels. For the first time we have successfully measured the solute gradient distribution directly from radiographs, which showed a strong correlation with the measured spatial distribution of dendrite fragmentation events. Although requiring some improvements in spatial resolution of radiographs, continuing improvements in beamline optics and detectors suggests that eventually time-resolved acquisition of images of sufficient fidelity

to directly map curvature and permeability, alongside concentration gradient, from experiment may be possible. In this way, a comprehensive model of the spatial distribution of dendrite fragmentation, extendable to 3D and to industrial conditions, may be realised.

6. Conclusions

Dendrite fragmentation in the mushy zone during directional solidification of Al-Cu alloys, both upwards and downwards and without and with the application of a pulsed electromagnetic field (PEMF) has been studied *in-situ* by synchrotron X-ray radiography. Many videos of fragmentation were analyzed systematically to quantify the effects of growth direction and PEMF strength on fragmentation rates and their position. Although solidification direction and the application of a PEMF affected the extent of dendrite fragmentation, the overall spatial distributions of fragmentation events in the mushy zone were similar. A qualitative model of dendrite fragmentation that suggested solute induced dendrite root re-melting as the primary mechanism was extended to explain all the observed effects, in which solute concentration gradients, which were measured directly from X-ray radiographs, were suggested to be critical.

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8. Appendix

References

- [1] K. A. Jackson, J. D. Hunt, D. R. Uhlmann, and T. P. Seward. On origin of equiaxed zone in castings. *Transactions of the Metallurgical Society of Aime*, 236(2):149–158, 1966.
- [2] S. Liu, S. Z. Lu, and A. Hellawell. Dendritic array growth in the systems $\text{NH}_4\text{Cl-H}_2\text{O}$ and $[\text{CH}_2\text{CN}]_{(2)}\text{-H}_2\text{O}$: the detachment of dendrite side arms induced by deceleration. *Journal of Crystal Growth*, 234(4):740–750, 2002.
- [3] R. H. Mathiesen and L. Arnberg. Stray crystal formation in Al-20wtCu studied by synchrotron x-ray video microscopy. *Materials Science and Engineering A - Structural Materials Properties Microstructure and Processing*, 413:283–287, 2005.
- [4] R. H. Mathiesen, L. Arnberg, P. Bleuet, and A. Somogyi. Crystal fragmentation and columnar-to-equiaxed transitions in Al-Cu studied by synchrotron x-ray video microscopy. *Metallurgical and Materials Transactions A - Physical Metallurgy and Materials Science*, 37A(8):2515–2524, 2006.
- [5] E. Liotti, A. Lui, R. Vincent, S. Kumar, Z. Guo, T. Connolley, M. Hart, L. Arnberg, R. H. Mathiesen, and P. S. Grant. A synchrotron x-ray radiography investigation of induced dendrite fragmentation in Al-15wtCu. *Light Metals Technology 2013*, 765:210–214, 2013.
- [6] E. Liotti, A. Lui, R. Vincent, S. Kumar, Z. Guo, T. Connolley, I.P. Dolbnya, M. Hart, R.H. Arnberg, L.and Mathiesen, and P.S. Grant. A synchrotron x-ray radiography study of dendrite fragmentation induced by a pulsed electromagnetic field in an Al15Cu alloy. *Acta Materialia*, 70:228–239, 2014.
- [7] S. Ananiev, P. Nikrityuk, and K. Eckert. Dendrite fragmentation by catastrophic elastic remelting. *Acta Materialia*, 57(3):657–665, 2009.
- [8] R. D. Doherty, H. I. Lee, and E. A. Feest. Microstructure of stir-cast metals. *Materials Science and Engineering*, 65(1):181–189, 1984.
- [9] J. A. Spittle. Columnar to equiaxed grain transition in as solidified alloys. *International Materials Reviews*, 51(4):247–269, 2006.
- [10] J. Hutt and D. StJohn. The origin of the equiaxed zone - review of theoretical and experimental work. *Int. J. Cast Metals Res.*, 11:13–22, 1998.

- [11] R. H. Mathiesen and L. Arnberg. X-ray radiography observations of columnar dendritic growth and constitutional undercooling in an Al-30wtCu alloy. *Acta Materialia*, 53(4):947–956, 2005.
- [12] D. Ruvalcaba, R. H. Mathiesen, D. G. Eskin, L. Arnberg, and L. Katgerman. In situ observations of dendritic fragmentation due to local solute-enrichment during directional solidification of an aluminum alloy. *Acta Materialia*, 55(13):4287–4292, 2007.
- [13] J. Pilling and A. Hellawell. Mechanical deformation of dendrites by fluid flow. *Metallurgical and Materials Transactions A - Physical Metallurgy and Materials Science*, 27(1):229–232, 1996.
- [14] C. J. Paradies, R. N. Smith, and M. E. Glicksman. The influence of convection during solidification on fragmentation of the mushy zone of a model alloy. *Metallurgical and Materials Transactions A - Physical Metallurgy and Materials Science*, 28(3A):875–883, 1997.
- [15] Z. Fan. Semisolid metal processing. *International Materials Reviews*, 47(2):49–85, 2002.
- [16] M. C. Flemings. Behavior of metal-alloys in the semisolid state. *Metallurgical Transactions A - Physical Metallurgy and Materials Science*, 22(5):957–981, 1991.
- [17] D. Brabazon, D. J. Browne, and A. J. Carr. Mechanical stir casting of aluminium alloys from the mushy state: process, microstructure and mechanical properties. *Materials Science and Engineering A - Structural Materials Properties Microstructure and Processing*, 326(2):370–381, 2002.
- [18] H. K. Moffatt. Electromagnetic stirring. *Physics of Fluids A - Fluid Dynamics*, 3(5):1336–1343, 1991.
- [19] P. A. Davidson. Magnetohydrodynamics in materials processing. *Annual Review of Fluid Mechanics*, 31:273–300, 1999.
- [20] D. Shu, B. Sun, J. Mi, and P.S Grant. A high-speed imaging and modeling study of dendrite fragmentation caused by ultrasonic cavitation. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 43(10):3755–3766, 2012.
- [21] R. Dietsch, A. Rack, T. Weitkamp, M. Riotte, T. Rack, T. Holz, M. Kremer, D. Weissbach, C. Morawe, F. Siewert, M. Meduna, P. Cloetens, and E. Ziegler. Performance of

multilayer monochromators for hard x-ray imaging with coherent synchrotron radiation. *10th International Conference on X-Ray Microscopy*, 1365:77–80, 2011.

- [22] W.U. Mirihanage, K.V. Falch, I. Snigireva, a. Snigirev, Y.J. Li, L. Arnberg, and R.H. Mathiesen. Retrieval of three-dimensional spatial information from fast in situ two-dimensional synchrotron radiography of solidification microstructure evolution. *Acta Materialia*, 81:241–247, 2014.
- [23] J.W. Gibbs, D. Turret, P.J. Gibbs, S.D. Imhoff, M.J. Gibbs, B.A. Walker, K. Fezzaa, and A.J. Clarke. In Situ X-Ray Observations of Dendritic Fragmentation During Directional Solidification of a Sn-Bi Alloy. *JOM*, 68(1):170–177, 2016.
- [24] Z. Guo, J. Mi, S. Xiong, and P. S. Grant. Phase field simulation of binary alloy dendrite growth under thermal- and forced-flow fields: An implementation of the parallel-multigrid approach. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 44(4):924–937, 2013.
- [25] N Shevchenko, S Boden, G Gerbeth, and S Eckert. Chimney Formation in Solidifying Ga-25wt pct In Alloys Under the Influence of Thermosolutal Melt Convection. *Metallurgical and Materials Transactions A - Physical Metallurgy and Materials Science*, 44A(8):3797–3808, 2013.