TIME-RESOLVED X-RAY IMAGING IN STUDIES OF ADVANCED ALLOY SOLIDIFICATION PROCESSES

Ragnvald H. Mathiesen¹ and Lars Arnberg²

¹SINTEF Materials and Chemistry, N-7465 Trondheim, Norway.
²Dept. of Materials Technology, NTNU, N-7491 Trondheim, Norway.

INTRODUCTION

During solidification of metallic alloys growth patterns form dynamically at the solid-liquid (s-l) interface as archetypes of self-organization in systems away from equilibrium and belong to non-linear physics. These self-assembly solidification structures evolve in complex processes determined by the transport of heat and mass to and from the different constituents. The transport processes are also influenced and complicated by interacting mechanisms such as convection, solid flow and melt segregation. Physics describing a full scale casting must account for phenomena occurring over lengths from the atomic (interface attachment kinetics, nucleation) to the macroscopic (macro segregation), over a typical time-scale from microseconds (diffusion-controlled growth) to minutes (coarsening), e.g. [1-7].

While numerical computer modeling for simulations covering the range from solidification fundamentals to full scale castings has advanced considerably over the last couple of decades, provision of new experimental data to guide theory and modeling has fallen behind. In the past in-situ studies of evolving solidification microstructures and process phenomena has been limited to work with optically transparent organic model systems [8-10], that display cellular and dendritic growth patterns analogous to those common to metals. Owing to a density shift across the s-l interface, model system growth can be monitored by video microscopy. Such studies have been extensive and contributed to promotion of consistent theory with provision of benchmark data for advancement in modeling [11-14]. However, despite their importance, the organic systems fail as full analogs to metals and alloys. Firstly, the variety in suitable systems is limited and far from complete as generic representatives for the multitude of growth patterns relevant to binary and multi component alloys. Also, since most physical properties decisive to the solidification processes are distinctively different between the models and their metal counterparts, e.g. heat conductivities and capacities, freezing temperatures, viscosities, solute/solvent mass ratios, etc, many fundamental aspects in solidification science are either inaccessible or impossible to scale from model observations to real systems of interest.

Metal transparency and interaction with X-rays constitute candidate principles from which methods for in-situ monitoring of solidification processes could be constructed. However, source brightness and detection efficiency has limited the practical impact of X-rays as a diagnostics tool for studies at physically relevant time- and length scales (ms, μm). The first X-ray investigations were based on radiography with conventional sources and used for in-situ studies of solute redistribution and boundary layer propagation[15,16]. The geometrical resolutions obtained, \( r_f > 50 \mu m \), prevented studies with curved fronts, but the resolution by contrast was adequate to verify proximity to conditions where solute diffusion in the solid can be neglected (Scheil-conditions). Already in their early work Stephenson and Beech [16] demonstrated the influence of buoyancy convection on the solute boundary layer by comparative measurements varying the growth direction relative to gravity. In the following years, however, little progress was made in this field. In the mid 90’s, micro focus sources were introduced in solidification science by a series of successive studies of striations, droplet formations and engulfment in...
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

This document is provided by ICDD in cooperation with the authors and presenters of the DXC for the express purpose of educating the scientific community.

All copyrights for the document are retained by ICDD.

Usage is restricted for the purposes of education and scientific research.

DXC Website  –  www.dxcicdd.com

ICDD Website  -  www.icdd.com
binary monotectics [17,18], reporting \( r_g \sim 30 \mu m \). About the same time a similar setup was used to study convection and solidification microstructures in Ga-In [19].

The major challenge with conventional sources was and still is to obtain adequately high flux at the sample to facilitate short acquisition times that limits contrast blurring by the temporal evolution of the system. Another problem is the substantially lower resolution obtained with curved fronts, e.g. close to or at dendrite tips, which due to their 3D curvature fade as absorption contrast objects. Improvements in X-ray detectors combined with the eminent brightness and collimation offered by 3rd generation synchrotron radiation (SR) sources has opened for the use of X-ray imaging based techniques to investigate the interface morphology evolution, solute transport and various process phenomena at spatiotemporal resolutions gradually approaching those of video microscopy. In general, there are three different viable imaging techniques for the real time investigation of solidification microstructures in alloys: i) 2D X-ray radiography, ii) 2D white-beam X-ray topography or iii) ultra fast 3D X-ray tomography. Ultra-fast SR X-ray tomography with approximately 10 s acquisition per tomogram and a \( \Delta r_g \sim 3 \mu m \) resolution limit has just recently been demonstrated as a very promising tool in solidification science [20]. However, a 10 s acquisition requires the microstructure to remain semi-stationary within resolution limits during exposure, and is therefore most suited for studies of phenomena deep in the mushy zone, evolving over timescales of several seconds to minutes, like ripening and low permeability melt feeding occurring at rather high solid fractions. White-beam topography has been used quite extensively to study solidification microstructures [21-24], its main advantage being supreme s-l interface contrast by phase specific diffraction from the solid. However, in-situ topography is limited by the output signal strength; typically obtainable spatiotemporal resolutions are of the order 20 \( \mu m \) and 2 s. Accordingly, the most viable and flexible technique for spatiotemporal imaging of evolving solidification microstructures is X-radiography provided that the alloy system under investigation contain segregates that can be resolved by transmission contrast. With 3rd generation SR sources, partial beam coherence can be obtained at high photon energies, facilitating the use of X-ray phase contrast [25] in addition to the more conventional photoelectric absorption contrast. In general, this leads to an enhancement of interface contrast, and can also open for studies of s-l interfaces between aggregates of similar atomic compositions. The first demonstration of in-situ SR-radiography in solidification science was carried out with various alloys from the Sn-Pb system [26]. Cellular, columnar and equiaxed dendritic microstructures were studied employing a high-resolution fast readout detector [27], equipped with specially developed components for high resolution time-resolved imaging. In successive applications of the setup, solidification microstructures and phenomena were studied in various alloys from the Al-Cu system [28-31], where nominal resolutions combined to an optimum \( r_g \sim 1.5 \mu m \) at the s-l interface. Recently, other groups have applied similar setups to study solidification in Sn-Bi [32,33] and Al-Ni [34].

EXPERIMENTS

This section focuses on the main aspects of the experimental setup and procedure. A more detailed description can be found elsewhere [28]. Samples with nominal compositions Al-30wt%Cu were prepared by melting 99.999 wt.% purity Al and Cu alloys in alumina crucibles and cast in an insulated, bottom-chilled mould to promote directional solidification. Low porosity regions located about 10 mm from the chill was cut into rectangular slices measuring \( 15 \times 30 \text{ mm}^2 \) (y\( xz \)) and polished down to thickness of 0.2 mm (x). After 2 hrs pre-oxidation at 720 K, followed by boron-nitride spray coating, the samples were concealed in containers made of two rectangular 100 \( \mu m \) thick quartz glass plates.
A Bridgman furnace system [35], operating at temperatures up to 1200 K was built for directional solidification (DS) of small samples with simultaneous X-ray monitoring of the microstructure evolution in a fixed field-of-view [28]. The system consists of two independently controlled furnaces with identical temperature ranges where the length of the adiabatic zone between the heater and cooler compartments can be varied by furnace translations along z, in combination serving to define a uniform imposed temperature gradient, G, over the sample. A sample translation device is constructed such that the Bridgman system can be operated with solidification direction both parallel and anti-parallel with gravity, \( \mathbf{g} \). However, the small sample size makes it difficult to operate the system with an adequate z-reproducibility of isotherms with low G (< 10 K/mm), presumably due to a slight sample-position dependency in the heat transfer that becomes more severe with increasing furnace spacing. A schematic illustration of the Bridgman system is presented in Figure 1.

The experiments were performed at beam line ID22 at the European Synchrotron Radiation Facility (ESRF). Monochromatic X-rays at 15 KeV gave an incident beam flux at the sample varying between 2 - 5 \( \times \) \( 10^{12} \) photons/(mm\(^2\)•s) with the storage ring current between each refill. The beam size applied gave a full field-of-view of 1.35 x 1.35 mm\(^2\) of the sample. Transverse beam coherency lengths were about \( l_x \sim 50 \) μm vertically, and \( l_y \leq 5 \) μm horizontally [36]. Accordingly, phase contrast could be obtained, at least along z, and in addition to regular absorption contrast, contribute to the visual appearance of phase boundaries. Data acquisition was carried out using a dedicated Fast Readout Low Noise (FReLoN II) high-resolution X-ray microscope [27, 28]. The microscope consists of a thin transparent Te or Eu doped Lu\(_{1-\delta}\)Al\(_{\delta}\)Sc\(_{0.6}\)O\(_{12}\) absorptive-emissive screen, placed in the X-ray beam in the front focal plane of a lens system. The microscope rear focal plane falls onto a custom made 4.2 Mpixel CCD with a physical pixel size of 14 μm and a dynamical range of 14 bits, i.e. 16384 grey levels. The CCD can be read out as four separate channels and transferred via optical fibres directly to computer memory. The highest nominal spatial resolution of the system, \( r_x \sim 0.6 \) μm with a readout dead time, \( t_{ro} \cdot 400 \) ms. For time-resolved imaging, a 2 × 2 hardware binning of the CCD allows both for shorter exposures and readout at the cost of a poorer spatial resolution; nominal features for the binned read out are: \( r_x \cdot 1.2 \) μm with \( t_{ro} \cdot 150 \) ms in the highest spatial resolution mode employing a 3.5 μm thin luminescent screen and the largest magnification available. In this study, a 12 μm thick screen with higher efficiency was employed together with a lower magnification to have better photon statistics at short exposure times. The thicker screen introduces a slight aberration, but since steady-state growth was not realised in the experiment, the spatial resolution was limited by the temporal blurring, \( r_t = t_{exp} v_s \), where \( t_{exp} \) is the exposure time, and \( v_s \) the local propagation velocity of the solid relative to the imaging system.

DS experiments were carried out either by moving the sample with a constant pulling or pushing velocity, \( v_{sp} \), from a position with a semi-equilibrated (T \( _f \) ± T) s-l front established in the camera, or by moving a fully molten sample into the cold furnace compartment. Keeping these alloys in a two-phase state for a long time in order to establish equilibrium temperature, T \( _f \), at the interface was prevented by sample life time. The direction of solidification was varied between the two approaches bottom-up (anti parallel \( \mathbf{g} \)) and top-down (parallel \( \mathbf{g} \)). G was varied between 12-55 K/mm, while \( |v_{sp}| \) was varied from 5 to 50.0 μm/s. The low detector system noise and a vanishing scintillator after glow permit exposure times as
low as $t_{\text{exp}} \approx 50$ ms, but visible 20 Hz source fluctuations, presumably induced by water cooling pumps on the optical elements, limited the minimum useful exposure time to 100 ms. Typically, the samples survived 10-20 consecutive series of solidification and remelting before contrast became too deteriorated by the numerous, highly transparent micro pores formed during cycles of solidification-melting. This problem accumulated with the number of cycles since pores filling the entire spacing between container walls partly encapsulates in oxide/BN upon thermal shrinkage, preventing the liquid from re-entering these voids upon remelting. The assessment of a melt protective and low contrast coating has been tedious [28], and even with the most appropriate method a significant variation has been encountered in the amount of unwanted coating contrast from one sample to the other.

RESULTS

The experiments with Al-Cu have produced in-situ observations of different growth modes that can occur in binary hypoeutectics and moreover provided unprecedented results on important solidification phenomena such as columnar dendrite fragmentation [31] and micro porosity formation [28]. Solidification of hypoeutectic Al-Cu alloys with bulk liquid constitutions, $C_0 = 30\%\text{wtCu}$, is generally associated with considerable micro segregation phenomena, both between $C_0$ and free dendrites, $C(T) \leq C(T_{\text{eut}}) = 5.6\%\text{wtCu}$, and between $C_0$ and the enriched mush liquid that due to the rejection of solute at the s-l interface builds up to a maximum $C = C_e = 33.1\%\text{wtCu}$. Here, $C$ symbolizes solid solution Cu in the $\delta$-Al primary phase, with maximum at the eutectic temperature $T_{\text{eut}} = 821$ K where the remaining liquid solidifies into alternating lamellas of $\delta$-Al/ $\alpha$-Cu.

Figure 2 presents an overview of some of the different growth patterns studied with the $C_0 = 30\%\text{wtCu}$ alloys. These are only $3.1\%\text{wtCu}$ off-eutectic causing the temperature difference between dendritic and eutectic fronts, or the actual alloy freezing range, $\Delta T_s$, to be compressed. $\Delta T_s = T_f(C_0) - \Delta T - T_e(C_e) = T_0 - \Delta T$, where $m = -4.9 \text{ K}/\%\text{wtCu}$ is the liquidus slope, $\Delta T_0 = m(C_0 - C_e)$ $15.2$ K the equilibrium freezing range, and $\Delta T$ the undercooling at the primary phase front, with eventual eutectic front undercooling neglected. More specifically, the freezing range, or the mush extension length can be expressed as $l(\Delta T_s) = l(\Delta T_0) = \Delta T_0/G \times 560 \mu\text{m}$. Accordingly, for the external cooling rates employed, $(dT/dt) = Gv_s$, the entire alloy freezing range and the simultaneous growth of $\delta$-Al and interdendritic eutectic can be studied within the same field of view. The eutectic front is in part made apparent by phase contrast due to the density difference, $\Delta \rho$, between the liquid and the eutectic solid, both with average compositions $C_e$. The eutectic fronts appearing in Fig. 2a), b) and c) display characteristic interference fringes. There are also contrast contributions from absorption due to the solid micro segregation pattern caused by the alternating lamellae eutectic microstructure, apparent as transmission image projections causing the internal eutectic contrasts seen in Fig. 2b), c) and d). In the following, focus will be given to a case similar to the one in Fig. 2a), but with DS $\cdot g$.  

Figure 2. Observed growth modes in Al-30%wtCu: a) columnar $\delta$-Al dendritic and planar eutectic, b) equiaxed $\alpha$-Al dendritic and planar eutectic, c) planar eutectic, and d) cellular eutectic.
In general, top down directional solidification is, due to thermo-solutally driven convection, less stable than the more conventional opposite, antiparallel with \( g \). An approach to predict the source for macroscopic buoyancy driven flow by heat and mass gradients parallel to \( g \) is

\[
Ra_n = \frac{(\Delta \rho / \rho)_n g L^3}{v D_n},
\]

where \( Ra_n \) is the Rayleigh number, with the subscript \( n = \{C, T\} \), for distinguishing between solute and temperature driven flow, respectively. \( g = 9.81 \text{ m/s}^2 \), and \( L \) is a critical length. \( D_n \) is the liquid diffusivity which take values \( D_C \cdot 3.1 \cdot 10^8 \text{ m}^2/\text{s} \), and \( D_T \cdot 4 \cdot 10^4 \text{ m}^2/\text{s} \), respectively. The kinematic viscosity, \( \nu = 6 \cdot 10^{-7} \text{ m}^2/\text{s} \). In conventional hydrodynamics, the critical length would be half of the confined dimension, i.e., \( L \sim 100 \mu\text{m} \). \( (\Delta / \rho) \) represents the segregated quantity, i.e. the liquid density gradient relative to the bulk liquid density. In the solutal case with \( e \) as the eutectic constitution liquid density and \( \rho_0 \) as the density at 30\%wtCu, we get \( (\Delta / \rho)_C = (e - \rho_0) / \rho_0 = 4.2 \cdot 10^{-2} \). For the thermal equivalent, \( (\Delta / \rho)_T = GL \), where \( G = - (1/ \rho)(\partial / \partial t) \) is the thermal expansion coefficient of the liquid. -values for Alx\%wtCu liquids has not been found but as a first order approximation the value for pure Al suffices, i.e., \( -1.1 \cdot 10^{-4} \text{ K}^{-1} \) [37]. Employing G from the experiment, numeric evaluation of eqn. (1) yields \( Ra_C \sim 10^4 \), and likewise \( Ra_T \sim 200 \). Apparently, transport of heat over the critical length is too rapid to cause any convection, whereas the tendency for buoyancy driven flow due to solute diffusion, should be severely reduced by the tight confinement of the crucible. Nevertheless, it was found in experiments and subsequent analysis that substantial flow was present. The apparent misprediction of \( Ra_n \) as calculated by eqn. (1) can be ascribed to negligence of the solid network and how that influences the critical lengths. A more sophisticated calculation can be carried out along the lines suggested by Beckermann et al. [38], leading to a replacement of \( L^3 \) in eqn. (1),

\[
L^3 = F(f_s) \lambda_1 l(\Delta T_0) \Delta x,
\]

with \( \Delta x \) as the sample thickness, \( F(f_s) \) as a function of the fraction solid accounting for reduction of the mush permeability due to solidification [38], that has been modified here to the confined geometry handling permeability drop only in one dimension. \( \lambda_1 \) is the spacing between primary dendrite arms, and \( l(\Delta T_0) \) as the characteristic mush extension length. Numerical evaluation of eqn. (1) now requires a practical example for assignment of the microstructure characteristics. Nevertheless, some general remarks can be made. From eqn.’s (1) and (2) it is clear that the tendency for flow is further increased by lowering of \( C_0 \) due to the increase in \( l(\Delta T_0) \). Also, a low G promotes flow, both by its influence on \( l(\Delta T_0) \), and since it results in a coarsening of the microstructure, i.e. larger \( \lambda_1 \) [29], which is reasonable since coarser microstructures should correspond to a coarser micro segregation.

Figure 3 presents a selection of frames from a sequence of DS•g in a 30\%wtCu alloy. The applied exposure, \( t_{\text{exp}} = 0.3 \text{ s/frame} \). The sample was solidified from the melt, initially positioned with its upper edge just below the cold furnace at \( T= 748 \text{ K} \) in contact only with the hot furnace at \( T= 882 \text{ K} \). Pushing the sample at constant velocity, \( v_w = -22.5 \mu\text{m/s} \), opposite to \( G \), multiple nuclei form and evolve into a columnar front, originating from one nucleus selected by competing kinetics, propagating closely parallel to \( G \). The sample was monitored online at a pre-calibrated position, with acquisition of images started as the solidification front appeared in the field of view, at \( t = - 9.0 \text{ s} \). Computer memory configuration allowed collection of 120 consecutive frames. Figure 3 shows a part of the sequence where solute rejected at the interface piles up between the leftmost and the central primary trunk. The solute enriched layer builds to a critical thickness, upon which a settling flow of this denser melt is initiated, directed down to the left. In addition to the adapted image coloring, the images have been stretched in contrast to preserve most of the range to display constitutional gradients in the melt.
A challenge for quantitative image analysis is the relatively low amount of transmission contrast available to quantify solute gradients. If we for simplicity assume the solid to expand the full crucible thickness, a linear stretch would preserve 92% of the 15 KeV X-ray transmission contrast to the range between the primary solid, \( C_s(T) \cdot C_s(T_f) = kC_0 = 5.1\%\text{wtCu} \) and the \( C_0 \) bulk liquid, leaving only about 8% contrast for liquid analysis. Accordingly, an extremely low-noise detector system is required. By custom made routines, it has been possible to assign a binary masking algorithm that separates the pixels in two classes; one containing all solid-free pixels and the other containing all solid pixels plus those corresponding to a mix of solid and liquid. It is fair to assume the liquid phase to fill the entire crucible allowing for 2D projected quantitative constitutional analysis to be made. For the other class however, constitutional analysis will be dubious since some of the pixels correspond to X-ray transmission through an unknown combination of solid and liquid, and also for the fully solid two-phase - Al dendrite + eutectic region, inhomogeneous thermal contraction can give rise to thickness variations. From gradient operations on the binary mask, 2D projected coordinates of the s-l interface can be extracted. Accordingly, mush constitutions, solutal undercooling at the interface, local interface morphologies, propagation velocities and other solidification characteristics can be extracted [29]. In Figure 4 the columnar dendrite tip, \( v_{sl,n}(t) \), eutectic front velocities, \( v_{sl,e}(t) \), and the corresponding solutal tip undercoolings, \( \Delta T_{c,n}(t) \), are shown for parts of the full image sequence represented by selected frames in Figure 3, where \( n=1-3 \) corresponds to the three columnar tips enumerated from left to right. While velocities have been calculated from the extracted interface coordinates, \( \Delta T_{c}(t) \) is deduced from X-ray absorption analysis of the liquid and therefore semi-independent on the interface. These and other relevant quantities fluctuate in a manner that reflects a transient situation at the front. The primary arm spacing, however, adapts more slowly to transient conditions, and between tips 1 and 2 it remains fairly constant through the selected part of the sequence at \( 1^{1/2} = 238 \mu\text{m} \). Applying this in eqns. (2) and (1), give \( Ra_c \sim 1650 \). Hence, the driving force for solute flow at the micro-meso length scale is substantial, just below the verge of where self-sustainable convective rolls could start to form. Transient behavior at the growth front is consistent with the local liquid flows and occurs since the solute boundary layer builds to a critical thickness/density upon which the enriched melt layer settles, altering the tip undercoolings and consequentially the growth dynamics, and leaves behind an evacuated mush in which a new local solute boundary builds up again [29]. Later, this behavior has been confirmed by microstructure phase field modeling in a simplified system, operating with two columnar dendrites and liquid flow out of the mush at \( C_e = 11.2\%\text{wtCu} \), where the eutectic reaction can be neglected [39]. The results of this simulation show the same type of temporal sinusoidal variations for the relevant parameters, with a direct relation to the buoyancy driven liquid velocity field. There are, however, a few subtle differences that deserve particular attention.
For columnar dendritic growth in alloys like Al-Cu it is reasonable to assume Scheil-conditions, i.e., neglecting diffusion in the solid, since \( D_{dc} \approx 3 \cdot 10^{-13} \text{ m}^2/\text{s} \) or four orders of magnitude less than \( D_{lc} \). Likewise, thermal diffusion is fast, and normally regarded as complete at any time. Therefore in absence of liquid flow, dendrite morphology and propagation is determined explicitly by solute diffusion and capillarity effects. Capillarity scales with the s-l surface tension, and is in general anisotropic as the crystalline solid. However, this anisotropy is weak and can be neglected for the purpose here. The capillarity contribution to the interface undercooling is given by \( \Delta T_c = \left( \frac{1}{r_1} + \frac{1}{r_2} \right)^{-1} \), where the Gibbs-Thomson coefficient, \( = 2.4 \cdot 10^{-7} \text{ K m}^{-1} \), for Al-Cu, with \( r_1 \) and \( r_2 \) as the local radii of curvature. Comparison with \( \Delta T_c \) in Figure 4b) immediately shows that \( \Delta T_c \) can be neglected unless \( r_1 \) and \( r_2 \) become very small, typically of the order of 1 – 2 \( \mu \text{m} \) or less. In growth fully controlled by solute diffusion, the concept of local equilibrium must hold at the sl-interface [3], and a direct coupling should exist between \( v_{sl} \) and \( \Delta T_c \). The coupling relation can be expressed with the following solute conservation equation

\[
D_c \nabla C = v_{sl} C_l^* (k - 1), \tag{3}
\]

where \( \nabla C \) is the solute concentration gradient at the sl-interface, and \( C_l^* \) the interface solute concentration. Eqn. (3) explicitly states that the solute rejected at the interface must diffuse into the liquid. For simplicity, assume the columnar dendrite to be represented satisfactorily as a cylinder with a hemispherical needle tip with curvature \( R \), for which eqn. (3) can be transformed to [40]

\[
\frac{(C_l^* - C_b)}{C_l^*(1 - k)} = \frac{v_{sl} R}{2D_c}, \tag{4}
\]

where the LHS is normally referred to as the solutal supersaturation, \( C_b \), and relates the tip solutal undercooling to the amount of solute rejection. RHS is the so-called solutal Péclet number, \( P_c \), which merely scales the solute diffusion distance, \( 2D_c/v_{sl} \), with a characteristic length, \( R \). It should also be noted that eqns. (3) and (4) should hold at the interface even if liquid flow is present, since liquid velocities must terminate at the boundary. Eqn. (4) also relates the independent velocity and solute undercooling estimates in Fig. 4 to one another via assignment of a third quantity, the dendrite tip curvatures \( R(t) \), which have been estimated by fitting weighted least squares parabolas to the columnar tips. Therefore, if \( (P_{c/l} \cdot c) \) is plotted against time, as in Figure 5, internal consistency of estimates at the interface should yield \( (P_{c/l} \cdot c) \approx 1 \). As seen in Fig. 5 this holds reasonably well for tip \( n = 3 \), which is not as severely affected by the mush solute plume ejection as the two others. For tip \( n = 2 \), \( P_{c/l} \) exceeds \( c \) after \( t \approx 2 \text{ s} \), and remains substantially larger until \( t \approx 8 \text{ s} \). This can be explained by the insufficient physical resolution at high interface velocities, i.e. at \( t = 6.5 \text{ s} \), \( v_{sl,2} \approx 80 \mu\text{m/s} \), which from eqn. (3) corresponds to \( \nabla C \approx -0.8 \text{ wt}\% \text{Cu/\mu m} \) at the interface. Velocities in the liquid must at least match that of the interface, so the corresponding temporal smearing of the n=2 tip and its adjacent liquid limits the local geometrical resolution to \( \Delta r = (v_{sl,2} - v_{sp}) t_{exp} \approx 17 \text{ \mu m} \), hence solute gradients at the interface become inaccessible at
high $v_s/v_p$ ratios. The same arguments apply for the overshoot of $(P_c/C)$ for $n=1$ after $t \sim 6$ s. Obviously, since the liquid pixels are of finite size they represent a volume extending into the liquid and will accordingly be affected by buoyancy driven flow, yet continuity requires flow velocities to be damped toward the interface [39], and presumably the primary concern is the coarse local resolutions at high interface velocities. The latter causes a systematic underestimation of the solute concentration profile decaying exponentially from the tip. Also at high $v_s$, $R$ approaches the nominal resolution limit, and tends to be systematically overestimated with enhancement of $P_c$ as a result. Nevertheless, liquid flow is the responsible driving force for interface acceleration, since the solute ejection sweeps away enriched melt further ahead of the tip, replacing it with a melt at $C_0$ constitution. Consequently $VC$ becomes steeper, with s-l interface acceleration as a result.

The most intriguing feature of Fig 5., however, is the appearance of $(P_c/C)$ for tip $n=1$ from $t=0 - 6$s. Here, the growth velocity and curvature does not adapt to the apparent tip undercooling. During this time $v_{s,1}$ is similar or even smaller than $v_p$, and consequentially temporal blurring will be small, $\Delta T \cdot v_p \cdot t_{exp} \sim 6.5$ μm, resulting in reliable estimates for $C_0$ and $R$. One explanation for this behaviour is that eqn. (4) neglects a solutal disturbance for the undercooling at dendrite tip $n=1$ due to solute pileup in the bulk liquid ahead of this tip arising from the solute plume and further increased by solute advection from neighbouring dendrites further ahead. The typical solute diffusion length, $1_c = 2D_c/\langle v_s \rangle \cdot 170$ μm. If the liquid constitution this far into the bulk liquid exceeds $C_0$, a reduced supersaturation is felt at the tip. This effect is taken care of by replacing $C_0$ in eqn. (4) with $C_0$ being the temporary bulk liquid constitution at a distance $1_c$ ahead of the tip. The temporary increase of the bulk solute concentration could, if more severe, cause interface propagation to terminate. Solutal blocking of columnar fronts has recently been demonstrated both by simulations [5] and experiments [31] to be one of the key mechanisms for promoting so-called columnar to equiaxed transitions. The effects obtained by correcting $\Delta T_c$ and $C$ for bulk solute enhancement is shown by the dashed curves in Figs. 4b and 5. Evidently, the correction only in part explains the particular $P_c/C$ discrepancy. Apparently there is a slight time lag between $C$ and the corresponding $v_{s,1}$, $R$, suggesting a departure from purely solutally controlled conditions at the interface. Indeed, if we consider tip growth during this period, its maximum undercooling is tedious; it has a thermal contribution which involves a two-way heat transport through three different phases: eutectic, $-\text{Al}$ and liquid. In addition liquid undercoolings due to curvatures and solute transport between the eutectic lamellae are inevitably present. Therefore, arguments made here will be qualitative only. The external heat extraction rate through the Bridgman system is $Gv_p$, while $(dT/dt)_e$, the cooling rate required at the eutectic front is roughly $Gv_{f_e}$ with $f_e$ as the fraction eutectic. With undercooling neglected, $f_e=f(T_e)$, i.e., the fraction liquid remaining at eutectic equilibrium temperature, that with Scheil-conditions for $-\text{Al}$, yields $f_e \cdot 0.84$. The difference between the two cooling rates must be balanced by volumetric recalescence due to the release of latent heat by solidification of the eutectic, i.e. $\Delta l/c = G(v_{f_e} - v_p) \cdot 0.3$ K/s $\sim 1.5$ $Gv_p$. Hence, due to the high fraction
eutectic, recalescence corresponds to about 50% of the heat extracted externally. Hence, the eutectic front acts as a local heat source for the liquid, and even though heat diffuses rapidly, influence on the dendritic network at mush depths similar to the n=1 tip position, about $\Delta z \cdot 0.5 \Delta T_0/G = 280 \mu m$ ahead of the eutectic front can occur. This has been demonstrated in other studies, where recalescence has been shown as a potent source for detachment of dendrite fragments by remelting of network roots [41, 42]. The latter study was done with DS in Al-30%wtCu under similar conditions. Accordingly, due to the near eutectic composition and the influence of gravity on the rejected solute, there is a potential for local interactions between the eutectic and the dendritic front, as well as amongst neighbouring dendrites, and consequently a full model incorporating a larger dendritic array as well as a nearby eutectic reaction is necessary to fully explain the spatiotemporal behaviour of the system.

CONCLUSIONS
Herein, a potential for time-resolved X-radiography as a tool for in-situ studies of advanced non-equilibrium alloy solidification processes has been demonstrated. The experimental technique developed is already well-suited for collection of benchmark data to further advance modeling and theory, and to clarify the importance of gravity on the spatiotemporal evolution of solidification microstructures, transport processes and segregation phenomena. With further development of such experiments, photon sources and detectors, X-ray imaging techniques can become invaluable tools in future solidification science.

ACKNOWLEDGEMENTS
The European Synchrotron Radiation Facility is acknowledged for granting beam time to experiment HS-1332. This work has been funded by the project NorLight Shaped Castings, with the following partners: Alcoa Automotive Castings, Scandinavian Casting Center ANS; Elkem Aluminium ANS; Fundo Wheels AS; Hydro Aluminium Metal Products; Hydro SA, Hydro Magnesium; the Netherlands Institute for Metals Research; NTNU; and SINTEF. The authors thank the industrial partners and the Norwegian Research Council for financial support.

REFERENCES