Dynamic evolution of liquid-liquid phase separation during continuous cooling

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Abstract

Solidification from a multiphase fluid involves many unknown quantities due to the difficulty of predicting the impact of fluid flow on chemical partitioning. Real-time x-ray radiography has been used to observe liquid-liquid phase separation in $\text{Al}_{90}\text{In}_{10}$ prior to solidification. Quantitative image analysis has been used to measure the motion and population characteristics of the dispersed indium-rich liquid phase during cooling. Here we determine that the droplet growth characteristics resemble well known steady-state coarsening laws with likely enhancement by concurrent growth due to supersaturation. Simplistic views of droplet motion are found to be insufficient until late in the reaction due to a hydrodynamic instability caused by the large density difference between the dispersed and matrix liquid phases.

I. Introduction

The interpretation of solidification reactions commonly begins with an initial assumption that the fluid being consumed by the growing crystals is homogeneous and only allowed to vary in composition or temperature in a continuous manner. For many situations this approach is valid, but the introduction of a multiphase flow, where discrete boundaries and transient local conditions dominate, significantly complicates transformation behavior. In systems which contain a monotectic reaction, such as aluminum-indium (Al-In)^{1,2} a miscibility gap exists, shown in Fig. 1, in which an initial phase separation reaction differentiates a single liquid phase into two distinct liquid phases ($L \rightarrow L_I + L_{II}$) at the binodal temperature, T_B . Upon cooling from the binodal to the monotectic temperature (T_{MO}), the two liquids form a microstructure involving a solute-lean solid phase and retained solute-rich second liquid phase ($L_I + L_{II} \rightarrow Al_{FCC} + L_{II}$). Continued cooling and further formation of solid aluminum results in progressively indium-enriched L_{II} liquid before the final freezing of nearly pure indium. The distribution of solute in the final microstructure is sensitive to changes in the liquid-liquid phase separation reaction.

The utilization of immiscible liquids and monotectic solidification is of interest to develop applications for self-healing properties³ in bulk materials or to obtain consistent properties in wear resistant bearings^{4,5}; it would be advantageous for these applications to create reproducible and homogeneous dispersions of the minority indium-rich phase within the aluminum matrix during solidification. However, due to the large density difference between the two liquids in the Al-In system some sedimentation is likely, the degree of which depends on factors such as the imposed cooling rate and temperature gradient.

During solidification of hypermonotectic $\text{Al}_{90}\text{In}_{10}$, indium-rich droplets may be suspended in the dispersal medium or as a boundary layer ahead of the $\text{Al}/(\text{L}_\text{I}, \text{L}_\text{II})$ interface. After very slow cooling in a shallow thermal gradient, settling of the dense indium-rich L_II droplets results in significant sedimentation and a layer of indium-rich solid will be present at the bottom of the sample; the upper portion of the sample will be enriched in aluminum.⁶ Fast cooling in a sharp thermal gradient would minimize sedimentation, and the excess indium would be incorporated into the solid aluminum matrix as fibers or droplets. At intermediate cooling rates, such as those studied here, a mixture between these extremes is anticipated.

While there are presently no closed form solutions to encompass all of the fine-scale details of liquid-liquid phase separation and multiphase convection during monotectic solidification, there have been numerous experimental studies^{7,8,9,10} and a wide range of theoretical¹¹ developments that have progressively improved predictions of key microstructural features, such as the final phase distribution. Recent work has directly investigated size-dependent behavior of single droplets, which has demonstrated the dynamic balance between thermo-capillary and buoyant forces in determining droplet interaction with a monotectic growth front.^{12,13,14,15} These studies have also determined that the dispersed phase is heavily influenced by solute gradients in the continuous phase, can show complex hydrodynamic behavior, and break common assumptions of droplet pushing or engulfment behavior during monotectic growth. Multiple liquids undergoing a sequence of reactions leads to complicating considerations that must be accounted for simultaneously making a truly complete description difficult. For instance, the partitioning of mass into regions of different densities changes the relative movement of the liquids in terms of both

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4 velocity and direction of motion. A change in the convection environment can upset
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7 assumptions such as the macroscopic homogeneity of a sample or the local solute
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10 environment of a growing phase.

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13 Fortunately, tools and techniques have been developed by various groups over
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15 multiple decades that take advantage of high brightness x-ray sources so that direct
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18 observation of phase transformations and dynamic events in metals is possible in real time.
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21 ^{16,17,18,19,20} Here, the dynamic evolution of the indium-rich liquid droplets and their motion are
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23 observed using high-brilliance synchrotron x-ray radiography. Using quantitative image
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25 analysis the ensemble characteristics of the L_{II} droplet population are quantified in terms of
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27 size, number density, and velocity while the sample is cooled from the single phase liquid
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29 through the phase separation reaction to a final temperature just above the monotectic
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31 reaction. These factors influence the time-dependent nature of the resulting structure.
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33 Specifically, droplet dynamics are interpreted using non-zero volume fraction Lifshitz-
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35 Slyozov-Wagner (LSW)-type steady state growth,^{21,22,23} precipitate growth from a
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37 supersaturated matrix,²⁴ coalescence,^{25,26} and the effect of convective motion on measured
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39 ensemble characteristics.^{27,28}
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48 **II. Methods**

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51 To make the Al-In alloy studied here, charges of 99.999+% pure aluminum and indium
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53 were loaded into small graphite crucibles which were then sealed into evacuated and Ar
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55 backfilled quartz tubes before being melted in a furnace. The cooled ingot was cold-rolled to
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57 a final thickness of 200 μm . Circular disks of the alloy were punched out of the rolled sheet,
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4 coated with boron nitride and sandwiched between two quartz slides. The edges of the
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7 quartz slide were melted together to form an airtight seal in order to limit oxidation during
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10 heating. A schematic cutaway of the encapsulated sample is shown in the inset of Fig. 2. The
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12 graphite layers help to support the graphite susceptors on each side of the sample and also
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14 provide additional thermal control across the sample when placed in the furnace rod.
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17 Additional details about the starting material can be found in the online supplementary
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20 material.
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23 A 12.7 mm diameter graphite rod, which held the encapsulated sample, was heated
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25 using two independently controlled induction coils centered above and below the sample
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27 position; the rod was instrumented with thermocouples to provide temperature monitoring
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29 and feedback control. Proportional integral derivative control of the power to each of the
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31 coils allowed for consistent control of the cooling rate and thermal gradient. The gradient
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33 across the sample is approximately 130K/cm. In this earlier version of the in situ furnace,
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36 gradient control could be challenging, but the drift in these experiments is not expected to
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39 be more than 10% since the applied cooling rate was held constant and the velocity of the
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41 bimodal reaction and the solidification reaction across the field of view were nearly
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44 constant. X-ray imaging was performed at the Sector 32-Insertion Device beamline at
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47 Argonne National Laboratory's Advanced Photon Source.; an 18keV monochromatic x-ray
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50 beam was used with an exposure time of 0.04 s and an approximate frame rate of 4.5 Hz.
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53 The total field of view (FOV) for the x-ray images was approximately 1.37 x 1.72 mm,
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56 corresponding to an approximate imaged volume of 0.47 mm³. X-ray absorption primarily
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4 produces the observed contrast, and the less dense aluminum-rich phases appear lighter
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7 than the denser, indium-rich L_{II} phase.
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10 A representative x-ray radiograph of the two-phase liquid structure is shown in Fig. 3.
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12 Images such as this were used to quantify the indium droplet population characteristics.
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14 With radiography, volume information must be inferred from contrast variations caused by
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16 different x-ray absorption characteristics of each phase and prior knowledge of probable
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18 feature shapes. Given the isotropic nature of the liquid indium and aluminum it was
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20 expected for the minority phase to form spheres; however, fluid flow results in shearing
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22 forces which may cause the spheres to deform. Measurements of droplet size were
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24 therefore obtained to ensure that both spheres and prolate ellipsoids (where two principal
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26 axes are equal and different from the third ($x=y \neq z$)) were properly counted. All image
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28 analysis was performed using ImageJ or associated plugins. Manual size determination
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30 involves tracing each droplet using image processing software, thresholding to leave only
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32 the outlines that can be automatically classified by size and shape statistics. To this end, the
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34 droplets were measured using their overall area to obtain an effective radius and were also
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36 measured using a major and minor axis length to determine the volume of a representative
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38 ellipsoid which could be converted to an effective radius. These methods never differed by
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40 more than 2% therefore the data from a spherical assumption is shown throughout.
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43 Additionally, the values reported for the number density include some projection driven
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45 error (e.g. when one droplet passes behind another). However, since the droplets move, the
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47 projection issue may be mitigated by counting those particles that are known to be
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49 temporarily hidden behind the projection of another. Manual velocity measurements utilize
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the ImageJ Manual Tracking²⁹ plugin to determine distance traveled between frames. Automated velocity measurements rely upon the ToAST³⁰ routine. A significant amount of scatter is present in the results from the automated measurements as well as misidentified particles moving with either zero speed or entire frame lengths. Therefore, these edge velocities were eliminated and average values are shown in the present work. The manual measurements were used to confirm that the automated algorithm is representative of true behavior.

III. Results

The rapid appearance of indium-rich L_{II} droplets during cooling ($>10^{13} \text{ m}^{-3}\text{s}^{-1}$) upsets the initially stable state. This sudden partitioning of density during the phase separation is also responsible for a complex momentum transfer that drives the relatively fast convective motion during continued cooling. When the droplets first nucleate they are small and their motion remains largely Brownian in nature for the first few seconds; reflecting the initially quiescent flow in the single phase liquid melt. Since a shallow temperature gradient is applied to the sample, the bottom of the images is cooler than the top. Therefore, the initial precipitation reaction sweeps upward through the FOV over the course of ~ 2.3 s. Because the temperature range over which droplet formation is possible sweeps through the field of view, it appears that droplets quickly move upward; however, tracking 50 droplets during the initial droplet nucleation stage shows that the average drift speed was less than $30 \text{ }\mu\text{m/s}$, with a uniform velocity/direction distribution ($0\text{-}360^\circ$). The dynamic progression of flow and droplet growth are highlighted in Movie 1³¹, where the images start shortly before the initiation of cooling and end just after the monotectic front sweeps through the FOV. Due to

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4 uneven thermal contact between the quartz crucible assembly and the graphite heater, the
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7 solidification direction is rotated 30 degrees counterclockwise from the vertical axis.
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10 For the purposes of the present analysis where the majority of the nucleation
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12 reaction occurs before data is sampled, the time scales presented here are set to originate
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14 when half of the FOV contains indium-rich droplets, 1.15 s after the first appearance of
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16 indium-rich droplets at the bottom of the FOV. By this definition of time, the first full-scale
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18 measurement of the particle distribution takes place after the nucleation reaction has
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20 occurred and indium-rich L_{II} droplets are present within the entire FOV, corresponding to
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22 $t=1.15$ s.
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29 The droplet population in the FOV was sampled regularly throughout the reaction.
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31 The time dependent particle size distributions may be compared directly, as in Fig. 4, where
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33 the size distributions from two representative times are plotted. A clear change in the
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35 particle size distribution is shown between the measurements made at $t=9$ s and $t=40$ s. The
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37 mean particle size increases with time from $5.5 \mu\text{m}$ to $8.2 \mu\text{m}$ and the shape of the
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39 distribution shifts and is increasingly weighted to large droplet sizes with increasing time.
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41 Fig. 4 also shows a histogram of the data collected 40 s after the initiation of droplet motion
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43 with a $1 \mu\text{m}$ bin size. Alternatively, the ensemble particle characteristics may be separated
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45 into specific statistics and resolved over the observed range of time. A summary of the time
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47 dependent droplet size and number density from $\sim 8 \times 10^3$ individual measurements is
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49 provided in Figs. 5(a, b), respectively.
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During initial growth of the droplets, the mean and maximum droplet radii rapidly increase with increasing time (Fig. 5(a)). The increase in particle size and decrease in number density continues until approximately $t=10$ s when the severity of the decline is reduced (Fig. 5(b)). Since measurements are made in a fixed viewing frame while the droplets are free to move in the sample, some amount of scatter is introduced to the droplet size and number data as droplets move in and out of the FOV. For example, several seconds after the droplets have nucleated, additional accelerations become prominent and the ensemble begins to move with increased velocity. At this stage, small droplets will tend to rise toward the hot side of the crucible (the top of the FOV) while larger droplets tend to sink toward the bottom. This antiparallel motion of the L_{II} droplets gives way to larger-scale convection fields, which are seen in Movie 1 and are reflected in the step-like size and number density change which occurs between 15 s and 20 s in Fig. 5(b) and are denoted by an arrow. The observed changes in both droplet size and number density during this period correlate to a specific plume of droplets that flow into the FOV from an adjacent region of the sample. Similarly, at $t=33$ s, a new current introduces a droplet population that is undersized compared to prior values of mean particle radius.

Aside from the convection-induced changes in the measured droplet ensemble characteristics, continuous underlying trends appear to dominate both the droplet size and number density during the first 40 s of observation. This initial stage of particle growth in a continually decreasing droplet population is termed Stage 1 behavior. By fitting the average droplet radius, $\langle R \rangle$, and number density, N , it is found that LSW-type coarsening kinetics appear to be capable of explaining the majority of the initial trend. Least squares fits are

given in Eqs. (1) and (2). This finding is corroborated by the shape of the droplet size distributions such as that obtained at $t=40$ s in Fig 4.

$$\langle R \rangle [\text{m}] = \left(2.0 \times 10^{-6} \pm 0.2 \times 10^{-6} \left[\text{m s}^{-1/3} \right] \right) t^{1/3} \quad (1)$$

$$\frac{N[\text{m}^{-3}]}{10^{13}} = \frac{5.4 \pm 0.1 [\text{m}^{-3}\text{s}]}{t} \quad (2)$$

A dramatic change in the number density and size trends occurs 40 s after the start of the phase separation reaction, which marks the second stage of the reaction. As stage 2 of the reaction progresses, both the droplet radius and number density rapidly decrease. During this time, both the radius and the number density as functions of time are described well by linear fits.

$$\langle R \rangle [\text{m}] = \left(-1.75 \times 10^{-7} \pm 1 \times 10^{-7} [\text{m}] \right) (t - 40\text{s}) + 6.62 \times 10^{-6} \text{m} \quad (3)$$

$$\frac{N[\text{m}^{-3}]}{10^{11}} = (55 \pm 2 \text{ m}^{-3}) - (0.89 \pm 0.03 \text{ m}^{-3}) (t - 40\text{s}) \quad (4)$$

The pronounced change in behavior of both the droplet radius and number density approximately 40 s after the start of the liquid phase separation reaction suggests that droplet motion during Stage 2 of the transformation is dominated by different forces than at the beginning. Additionally, the change in behavior can be clearly seen in the droplet motion in Movie 1, where the droplets change their direction of motion and collectively move downward at $t=40$ s. Fig. 6 presents the quantification of the direction and velocity of the droplet motion to provide insight into the change in behavior. The direction-independent droplet velocity as a function of reaction time is plotted in Fig. 6(a) and the relative speed and direction of the droplets are plotted together versus time in Fig. 6(b). In Fig. 6(a) the

red circles indicate data from automated tracking and the blue points represent manually tracked droplet motion.

First, comparing the speed of droplet travel between the two regimes shows that the droplets during first 40 s of the transformation are characterized by an initial sharp increase in travel speed that then progressively decreases. At the onset of the second stage of the transformation the speed of the droplets increases again and some of the highest droplet velocities are recorded just before the monotectic transformation front reaches the image FOV.

The data in Fig. 6(b) extend the insight into the driving forces for droplet motion by considering the speed and angle of droplet motion with respect to the horizontal axis independently. To generate the plot in Fig. 6(b) a two dimensional probability distribution is constructed at each time step with angle and speed as the independent variables. Points that define the 90th percentile contour are selected and plotted as a function of time. It is important to note that the angle axis in Fig. 6(b) is flipped (positive to the right) in order to clearly show the trend (upward motion corresponds to angles with negative values and downward motion is represented by positive values). The initial average angular dispersion of particle motion is centered near zero, indicating no net change in position, and the corresponding travel speed is also quite low ($\sim 40\text{-}50\text{ }\mu\text{m/s}$). With increasing reaction time the particles begin to change both speed and direction, increasing speed to between $\sim 160\text{-}180\text{ }\mu\text{m/s}$ and descending at an angle approximately 60° from horizontal. Since the final

monotectic was aligned approximately 30° counterclockwise from vertical the particles are moving approximately normal to the monotectic front.

IV. Discussion

The distinct changes that occur in the observed droplet motion, size, and number density between Stage 1 and Stage 2 of the transformation at approximately $t=40$ s necessitate that these two stages be considered separately. This dramatic shift in the measured trends is likely influenced by the start of the $L_I + L_{II} \rightarrow Al_{fcc} + L_{II}$ reaction at the bottom of the sample. Although the initial solid formation at the bottom of the sample is not in the field of view, the front velocity and applied cooling rate are consistent with this assumption. One consequence of solid formation is that the fluid velocity in the frame of reference will include a contribution from the shrinkage that occurs when Al_{fcc} replaces the L_I liquid phase.

IV.i Stage 1, Droplet Growth and Coarsening

In order to interpret the large amount of data captured during imaging and post-processing, it is useful to consider the potential growth mechanisms which may be active during the liquid-liquid phase separation reaction. Three contributing modes of droplet growth and coarsening are considered here: growth in a supersaturated matrix, LSW-type coarsening, and droplet coalescence. First, for the selected $Al_{90}In_{10}$ composition the formation of L_{II} droplets likely necessitates nucleation of new droplets as opposed to spinodal decomposition. Nucleation requires enough undercooling to overcome the development of a new interface, and at least some portion of the early stage growth would

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4 resemble diffusional growth into a supersaturated matrix. During the course of cooling, the
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7 tie lines predict a greater equilibrium volume fraction of L_{II} to be stable, potentially leading
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10 to larger supersaturations with time that would make pure diffusional growth dominant.
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12 However, the kinetics of diffusional growth in a liquid can be fast therefore the local
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14 environment near the droplets may maintain a relatively small supersaturation which would
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16 allow coarsening kinetics to play an active role. Finally, droplet-droplet collisions,
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19 coalescence, can result in an increase in particle size at the expense of overall number
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22 density of particles.
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26 Each of these growth modes results in characteristic time dependent changes in the
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28 droplet size, illustrated schematically in Fig. 7, in which an initial Gaussian population is used
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31 to represent the product of the nucleation reaction. For each of the three growth
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33 mechanisms considered here, the growth rate, number density, and the time-dependent
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35 characteristic distribution, are provided for comparison with the experimentally measured
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38 data.
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42 Growth from a supersaturated matrix, following the simplest case³², results in an
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44 increase in size for all particles with a growth rate given in Eq. (5) that depends upon the
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46 amount of supersaturation (S_o) and the diffusion coefficient (D). At constant
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49 supersaturation, growth proceeds in a parabolic manner; inclusion of other effects such as
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52 droplet motion can vary the power law dependence depending upon the chosen bounding
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54 conditions. By using reduced dimensions of $z_g=r/\langle r \rangle$ and $\tau_g=K_g t/\langle r \rangle$, where K_g is a rate
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57 constant, an initial size distribution, $f_{o,g}(z_g, \tau_g)$, may be used to solve for the distribution for a
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range of times. The general solution for the size distribution with time is given in Eq. (6). In this case, the average particle size displays inverse square root time dependence (i.e. $t^{-1/2}$). As a consequence of the available supersaturation in the continuous phase, the particle size can increase while the number density remains equal to or larger than the initial number density.

$$\frac{dr}{dt} = \frac{DS_0}{r} \quad (5)$$

$$f_g(z_g, \tau_g) = \frac{z_g}{\sqrt{z_g - 2\tau_g}} f_{0,g}(\sqrt{z_g - 2\tau_g}) \quad (6)$$

For constant volume fraction coarsening, the growth rate of any individual particle is dependent upon the entire distribution of particles. In this case, a critical radius (r_c) is defined so that droplets with $r > r_c$ grow while droplets with $r < r_c$ shrink. In a dilute solution, where the volume fraction of the dispersed phase is small, the critical radius is the geometric mean and an individual particle growth rate may be described by Eq. (7) where B' is a constant which includes the interfacial energy, supersaturation, and diffusion coefficient.

^{21,22,23,33} During normal operation of this growth mode, the supersaturation in the matrix is negligible, prohibiting further nucleation. Since there is always a population of particles smaller than the critical radius that shrink and no new particles being developed, the number density continually decreases with time, the number density of particles is proportional to t^{-1} . Constant volume fraction coarsening results in a steady state shape of the size distribution which has a maximum cut-off size when scaled to the critical radius, which evolves with a $t^{1/3}$ dependence. The dilute solution holds the majority of the key features of this type of growth process, however a more complex iterative solution is given by Marqusee and Ross³³, where

more detailed descriptions of the terms may be found, that applies to finite volume fractions and has been used to analyze the data. Following the conclusions of Marquess and Ross, the scaled distribution function $f(z)$, is given by Eq. (8). In Eq. (8), c_0 is a mass balance normalization constant, z is the time-scaled and normalized size, and z_0 is the normalized cut-off size³³. The impact of a finite volume fraction is captured by the values of α , β , and δ , which must be solved numerically. In the dilute limit, these constants yield the same values consistent with the standard LSW theory.^{21,22,23}

$$\left. \frac{dr}{dt} \right|_{r_c} = \frac{B^*}{r} \left(\frac{1}{r_c} - \frac{1}{r} \right) \quad (7)$$

$$f(z) = \frac{c_0}{(z_0 - z)^\alpha} \frac{1}{(z + 3/z_0^2)^\beta} \exp\left(\frac{-\delta}{z_0 - z}\right) \quad (8)$$

Population changes due to coalescence are bounded by an initial²⁵ rate of interaction that depend upon the starting distribution and a long time steady state rate.³⁴ Like coarsening, this growth mode generally obeys self-similar scaling laws^{34,35} which depend upon the type of interactions in the system; e.g. the frequency of aggregation may change with changes in total number density, fluid flow characteristics, and surface properties between the dispersed and matrix phases. The general signature for the long term steady state population is an exponentially increasing mean droplet volume, $\langle V \rangle$, and exponentially decreasing droplet number density.³⁶ It can be shown that the average particle size, $\langle r \rangle$, has a complex time dependence as shown in Eq. (9), but that the distribution obeys the general scaling spectra³⁴ given in Eq. (10) when the volume of the particle is used in the scaling

factor such that $z=V/\langle V \rangle$. In each of these cases, m and α are parameters related to the interactions between particles and externally applied conditions.

$$\frac{d\langle r \rangle}{dt} \propto \left(\frac{4\pi}{3^4} \right)^{1/3} t^{\left(\frac{1}{3m-3} - 1 \right)} \quad (9)$$

$$f(z) \approx z^{m+1} \exp(-\alpha z) \quad (10)$$

In prior studies of droplets near the monotectic growth front, coalescence of droplets was observed. However, during the present analysis there was no significant evidence for coalescence. Additionally, the number density trend, while decreasing did not resemble the expected exponential decay which the theory suggests. While this mechanism may still be active, the fits to the data represented by Eqs. (1) and (2) initially suggest that a coarsening mode may dominate, but concurrent growth due to supersaturation cannot be discounted easily. Additionally, the particle size distributions through time, as shown in Fig. 8(a) share features common to Eq. (8), rather than Eq. (10).

In order to help separate the relative contributions of growth and coarsening, a comparison is made between the fitted experimental curves and ideal coarsening growth. The comparison is made using the ratios of the key population statistics of measured droplet cutoff radius (as represented by the maximum), the critical radius (as approximated here by the 71st percentile), and the average droplet sizes. Complimentary numbers from ideal coarsening behavior are obtained from Eq. (8). The ratios are plotted as a function of time in Fig. 9 and it is shown that all three measured values are consistently larger than unity, maintaining a constant offset factor of approximately 1.5 after initial droplet formation. Exceptions to this rule occur at the very earliest stages of the reaction, where the measured

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4 values are greater than 1.5 times size predicted from pure coarsening. It is expected that the
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7 initial deviation stems from a significant contribution of diffusion controlled growth from
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10 the supersaturated matrix. The constant offset factor of 1.5 over most of the transformation
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13 is an indication that other possible growth modes are influencing the actualized distribution
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15 of sizes, especially at early times.
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18 Normally analytical models are applied in a growth regime where it is correct to
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21 assume that a single growth mechanism is acting (e.g. growth and coarsening are mutually
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24 exclusive). When the conditions lie in certain parameter ranges, each mechanism can
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27 contribute to the total change in size and number density of the growing phase. However, a
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30 theoretical framework for interpreting the combined action of coarsening and growth has
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33 been provided by Ratke and Beckerman²⁴ where this middle ground is identified. When both
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36 mechanisms contribute to the changes in droplet population behavior, the nucleation and
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39 growth of particles due to a constant heat extraction rate can mitigate the loss of particles
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42 from coarsening (resulting in no net dissolution of particles). This superposition of
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45 coarsening and growth occurs when the growth rate is 1.89 times larger than that for pure
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48 coarsening behavior.
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51 The measured growth ratio in the present work is ~ 1.5 and coincides with a
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54 decreasing droplet number density, supporting the transition as reported by Ratke and
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57 Beckerman. The data from Stage 1 are, therefore, consistent with combined action of
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60 growth and coarsening kinetics where the coarsening plays a significant role. However, it is
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63 critical to note that neither the work by Ratke and Beckerman, nor the simple growth
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models provided in Eqs. (6) and (8), strictly capture the complexities of moving phase boundaries or particle motion. Additional factors to incorporate particle motion or dynamic boundary solutions may need to be considered to determine an accurate model to comprehensively describe the growth of second phase liquid droplets in the matrix liquid.

IV.ii Stage 2, Droplet Number Density and Size Reduction

The later portion of the L_{II} droplet behavior is characterized by significantly different trends in observed droplet velocity, size, and number density. Measurements of the angle of motion captured in Fig. 6(b) would suggest that velocity due to solidification shrinkage and/or gravity become the dominant mechanisms affecting droplet motion. A simplistic analysis of solidification front velocity and the approximate position of the field of view relative to the sample lead to the conclusion that solidification initiates very close to the time when Stage 2 also begins. With a front velocity of $\sim 145 \mu\text{m/s}$, we may ascribe a component of the velocity vector between 7 and $15 \mu\text{m/s}$ of downward motion to solidification shrinkage, however, this constant value applied across droplets of all sizes would not account for the measured gradual shift in velocity angle or the droplet acceleration of $15 \mu\text{m/s}^2$. Therefore, it is believed that the constant force of gravity is involved in the decay of velocity in all non-downward directions.

Concomitant with the velocity changes, there is also a very sharp change in the particle size and number density trends. There is also a change in the distribution shape with time as shown by Fig. 8(b). Simulation of monotectic structures elsewhere has indicated that the size dependent acceleration due to gravity could lead to removal of large droplets

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4 from the field of view, leaving only smaller particles to be counted.⁹ To separate size driven
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6 sedimentation from global influences on all the entire droplet population, numerical
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8 predictions were used to provide a set of particle population distribution outcomes based
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10 upon measured size distributions and the size dependent sedimentation due to gravity.
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12 These numerical predictions rely upon simple assignments of representative velocities and a
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14 change in that velocity due to particle size (i.e. Stokes settling and Marangoni force) and not
15
16 any type of in depth flow calculation. The measured size distribution was paired with the
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18 measured velocity distribution data to create a starting point at which the effect of particle
19
20 removal from the field of view could be tested.
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29 A simulated box was constructed with the real sample dimensions and a droplet
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31 number density of $1.85 \times 10^{12} \text{ m}^{-3}$ (~7000 droplets) to replicate the conditions observed at
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33 $t=40 \text{ s}$. The particles were each randomly assigned a vertical position and a vertical
34
35 component of velocity. Then gravitational and Marangoni forces are applied to each particle
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37 and the evolution of any given field of view due to this type of motion. The results of these
38
39 predictions are shown by the data points in Fig. 10, where the predicted droplet radii in the
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41 FOV are plotted in Fig. 10(a) and the droplet number density values are plotted in Fig. 10(b).
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43 Also plotted in Fig. 10 are the fit curves from Fig. 5 and Eq. (4).
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51 Depending on where in the sample the field of view is placed, a longer or shorter
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53 incubation time is observed where there is little change in either the average radius or the
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55 number density. Upon reaching the end of the incubation time, the number density and
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57 average size of droplets begins to decrease. The number density and radii trends resulting
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from 100 iterations of the simulation is shown by bands of points in Figs. 10(a,b) where time is plotted so that the population matches the experiment at $t=40s$. In both cases, the size and number density predictions correspond very well to the fitted curves replotted from Fig. 5, suggesting that particle removal via sedimentation may accurately describe the number and size of particles in a given field of view.

IV.iii Flow and Hydrodynamic Instability

One unique aspect of the constant gradient furnace and sample shape used here is that the observed convection appears to produce a highly complex flow that is not well correlated to simple gravitational and Marangoni force arguments alone. This is in contrast to previous work in Bridgman-type solidification experiments^{13,14} as well as simulations of monotectic solidification³⁷, where the same flow behaviors can typically be correlated to gravitational or Marangoni movement patterns. Additionally, the thermal gradient imposed in the current study is small enough that significant thermosolutal driven convection is not expected to lead to the observed velocity and directional instability. However, as noted by Ruzicka and Thomas³⁸ in reference to buoyancy-driven flow patterns in multi-phase bubble columns; while dispersed and thermal convection are related, there is a critical difference in that dispersed particles act as individuals with their own inertia. Therefore, while there is coherency of motion in the vertical direction, imposed by gravity or the interfacial energy gradient, coherency can be disturbed by inertial interactions between particles and the backflow of fluid through the pseudo-random arrangement of droplets.

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4 During Stage 1 growth rapid churning of the two liquids was observed immediately
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6 after the onset of droplet formation. In addition, plumes of droplets can be seen in Movie 1
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8 sweeping in and out of the field of view. These two events signify the onset of complex
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10 hydrodynamic instability in the observed flow patterns during the first 15 s of cooling and
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12 droplet growth which can be qualitatively explained by the findings of Rothman and
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14 Kadanoff³⁹. In the work by Rothman and Kadanoff, the flow of bubbles with buoyant forces
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16 of opposite sign tended to develop larger-scale fingers of cooperatively moving groups that
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18 move independently of other regions; these fingers resemble thermal plumes. The bubble
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20 plumes are analogous to the current identification of plumes of droplets sweeping in and
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22 out of the field of view. It would also follow that since these groupings are distinct in their
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24 flow behavior, that they may also be distinct in their size at any given time, leading to the
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26 step-like shifts in number density shown in Fig. 5. Fortunately, some of the lost coherent
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28 “bulk motion,” such as overall droplet velocity, can be recaptured from statistical sampling.
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30 In the current case, the entire volume is not viewed, but a section is sampled for the entire
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32 lifetime of the reaction.
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43 The rapid increase in droplet velocity in Fig. 6(a) show the initial hydrodynamic
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45 instability occurring several seconds into the reaction which then damps out over the course
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47 of the next 30-40 seconds. Immediately after droplets are visible the droplet speed is low,
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49 around 30 $\mu\text{m/s}$. The droplets then rapidly accelerated to a maximum speed, $>200 \mu\text{m/s}$, due
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51 to density driven momentum transfer between the L_I and L_{II} phases. After the rapid
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53 momentum transfer however, an exponential type of decay in droplet speed is observed,
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55 consistent with damping due to the lack of additional perturbations. The shaded grey band
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in Fig. 6(a) emphasizes the transition between velocity regimes during Stage 1 motion. The nature of the damping may be quantified by $v=v_0\exp(-t/\tau_v)$ where v_0 is the maximum droplet speed of 244 $\mu\text{m/s}$ and τ_v is the decay time constant of ~ 32 s. A plot of this fit is shown in by the green line overlaid on the data in Fig. 6(a). The damping of the particle speed is well fit by the simple exponential model. Momentum transfer between the two liquids during coarsening and growth of the droplets does not appear to result in the pronounced hydrodynamic instability as was observed during the rapid formation of the initial droplet population. A measurement early in the reaction has been used to pin the low velocity nature of the droplets just after nucleation.

During Stage 2 of the transformation, the angular dispersion of the droplet directions narrows and crosses zero, as shown in Fig. 6(b), such that the majority of the particles begin to move downward. The average speed of the droplets initially decreases, since the droplets that were moving upward must switch direction. During continued cooling there is an acceleration of a typical particle by $\sim 15.5 \mu\text{m/s}^2$. Given the average size of the particles, the buoyant force, Marangoni action, and Stokes drag, the calculated terminal settling velocity, in the absence of convection, should be less than 300 $\mu\text{m/s}$, consistent with the observed maximum value of $\sim 200 \mu\text{m/s}$ and the fact that the particles were still accelerating. It should be noted that the constrained dimensions, which would tend to limit fluid velocity, were not included as a factor.

Finally, the combination of these observations provides some guidance to explain the microstructural changes in monotectics after changes in processing history. It is known that

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4 solidification velocity and thermal gradient affect the microstructural outcome in terms of
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6 the final indium distribution. The effect of thermal gradient is relatively straightforward,
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8 precipitation of the second liquid phase at a short distance from the solidification front
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10 determines the maximum distance that the droplets could fall before being engulfed by the
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12 interface, resulting in systematic changes in the distribution of the second phase liquid in the
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14 solid. When considering the solidification velocity in an arbitrary gradient, the consequences
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16 are less clear. Certainly, the current results indicate that quenching the liquid while the
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18 droplets are small and less susceptible to agglomeration at the monotectic interface would
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20 result in less sedimentation. However, these results indicate that there is an optimal
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22 processing time during which the naturally induced hydrodynamic instability may be utilized
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24 to promote random mixing of the droplets while simultaneously maintaining the ability to
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26 coarsen the microstructure to the desired droplet size and number density.
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36 **V. Conclusions**

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39 We have utilized real-time data during cooling of hypermonotectic Al-In in order to
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41 study droplet dynamics in the liquid. Measurements from $\sim 8 \times 10^3$ particles (non-unique) have
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43 allowed for specific trends in droplet size and number density to be identified and
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45 interpreted within the context of several possible mechanisms. Convective motion plays a
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47 large role in the local statistics, but the combined action of LSW-type coarsening and
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49 supersaturated growth appear to be the dominant growth mechanisms during the first
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51 portion of the reaction. A sharp change in the population behavior occurs in the later stage
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53 of the phase separation reaction and it appears to initiate approximately when the
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55 monotectic reaction begins at the bottom of the sample. Particle removal from the field of
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4 view due to sedimentation is consistent with numerical simulations of the droplet size and
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6 number density in the later stage of droplet evolution. Finally, it is apparent that simplified
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8 and generalized models of growth may be appropriate for modeling these reactions on a
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10 larger scale, but that special attention must be given to the complex fluid flow instabilities
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12 which may change the spatial distribution of phases.
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References

- ¹ F. Sommer, H.-G. Krull and S. Yu, in L. Ratke (ed.), *Immiscible Liquid Metals and Organics*, DGM-Informationsgesellschaft, Oberursel, 1993, p. 79.
- ² I. Kaban, S. Curiotto, D. Chatain, W. Hoyer, *Surfaces, interfaces and phase transitions in Al-In monotectic alloys*. *Acta Materialia* **58** (2010) 3406-3414.
- ³ B.J. Blaiszik, S.L.B. Kramer, M.E. Grady, D.A. McIlroy, J.S. Moore, N.R. Sottos, and S.R. White, *Autonomic restoration of electrical conductivity*, *Advanced Materials* **24** (2012) 398-401. Doi: 10.1002/adma.201102888
- ⁴ L. Ratke (ed.), *Immiscible liquid metals and organics*, DGM-Informationsgesellschaft, Oberursel, 1993.
- ⁵ T. Berrenberg, I. Steinbach, M. Rommerskirchen, and R. Mergen, *Proc. Of the Winter Annual Meeting of the American Society of Mechanical Engineers, ASME, Atlanta, GA, 1991, Vol. HTD-175*, p. 103.
- ⁶ R.N. Grugel, and A. Hellawell, *Alloy solidification in systems containing a miscibility gap*. *Metallurgical Transactions A* **12** (1981) 669-681.
- ⁷ P.A. Curreri, and W.F. Kaukler, *Real-time x-ray transmission microscopy of Al-In Alloys*, *Metallurgical and Materials Transactions A* **27** (1996) 801-808.
- ⁸ L. Ratke, and S. Diefenbach, *Liquid immiscible alloys*, *Materials Science and Engineering R* **15** (1995) 263-347.
- ⁹ J.Z. Zhao, and L. Ratke, *A model describing the microstructure evolution during a cooling of immiscible alloys in the miscibility gap*. *Scripta Materialia* **50** (2004) 543-546.
- ¹⁰ W. F. Kaukler, and P.A. Curreri, *In-situ x-ray microscopy of phase and composition distributions in metal alloys during solidification*, *Proc. SPIE 3782, Materials Research in Low Gravity II* (ed. N. Ramachandran) 302 (July 6, 1999); doi: 10.1117/12.351290.
- ¹¹ C. Beckermann, and R. Viskanta, *Mathematical modeling of transport phenomena during alloy solidification*, *Applied Mechanics Reviews*, **46** (1993) 1-27.
- ¹² P.L. Schaffer, R.H. Mathiesen, L. Arnberg, M. Di Sabatino, and A. Snigirev, *In situ investigation of spinodal decomposition in hypermonotectic Al-Bi and Al-Bi-Zn alloys*. *New Journal of Physics* **10** (2008) 053001.
- ¹³ P.L. Schaffer, R.H. Mathiesen, and L. Arnberg, *In-situ investigation of liquid-liquid phase separation in hypermonotectic alloys*. *Materials Science Forum* **649** (2010) 149-158.
- ¹⁴ P.L. Schaffer, R.H. Mathiesen, and L. Arnberg, *L₂ droplet interaction with α -Al during solidification of hypermonotectic Al-8 wt.% Bi alloys*, *Acta Materialia* **57** (2009) 2887-2895.
- ¹⁵ P.L. Schaffer, R.H. Mathiesen, and L. Arnberg, *In-situ X-ray investigation of immiscible phases in Al-Bi alloys*, *Modeling of Casting, Welding and Advanced Solidification Processes XI* (ed C.-A. Gandin and M. Bellet), TMS, Warrendale, PA, USA (2006) 383-389.
- ¹⁶ D.J. Rowenhorst, and P.W. Voorhees, *Measurement of interfacial evolution in three dimensions*. *Annual Review of Materials Research* **42** (2012) 105-124.
- ¹⁷ W.F. Kaukler, and P.A. Curreri, *Advancement of x-ray microscopy technology and its application to metal solidification studies*, *Proc. SPIE 2809, Space Processing of Materials* (ed. N. Ramachandran) 34 (July 12, 1996) 34-44 ; doi:10.1117/12.244353.
- ¹⁸ K.A. Nugent, *Coherent methods in the X-ray sciences*, *Advances in Physics* **59** (2010) 1-99.
- ¹⁹ J. Forstén, and H.M. Miettinen, *Radiographic observations of the solidification of metals*, *Journal of the Institute of Metals* **95** (1967) 143-145.
- ²⁰ R.H. Mathiesen, L. Arnberg, F. Mo, T. Weitkamp, A. Snigirev, *Time resolved x-ray imaging of dendritic growth in binary alloys*, *Physical Review Letters* **83** (1999) 5062-5065.
- ²¹ J.A. Marqusee, and J. Ross, *Theory of Ostwald ripening: Competitive growth and its dependence on volume fraction*. *Journal of Chemical Physics* **80** (1984) 536-543.
- ²² I.M. Lifshitz, and V.V. Slyozov, *The kinetics of precipitation from supersaturated solid solutions*. *Journal of Physics and Chemistry of Solids* **19** (1961) 35-50.
- ²³ C. Wagner, *Theorie der alterung von niederschlägen durch Umlösen (Ostwald-Reifung)*. *Zeitschrift für Elektrochemie*, **65** (1961) 581-591.

- 1
- 2
- 3
- 4
- 5
- 6²⁴ L. Ratke, and C. Beckermann, *Concurrent growth and coarsening of spheres*. *Acta Materialia* **49** (2001) 4041-4054.
- 7
- 8²⁵ I.M. Klink, R.J. Phillips, and S.R. Dungan, *Effect of emulsion drop-size distribution upon coalescence in simple shear flow: A population balance study*. *Journal of Colloid and Interface Science* **353** (2011) 467-475.
- 9
- 10²⁶ P.G.J. van Dongen, and M.H. Ernst, *Tail distribution of large clusters from the coagulation equation*. *Journal of Colloid and Interface Science* **115** (1987) 27-35.
- 11
- 12²⁷ L. Ratke, and W. Thieringer, *The influence of particle motion on Ostwald ripening in liquids*, *Acta Metallurgica* **33** (1985) 1793-1802.
- 13
- 14²⁸ G. Feingold, I. Koren, H. Wang, H. Xue, and Wm.A. Brewer, *Precipitation-generated oscillations in open cellular cloud fields*. *Nature* **466** (2010) 849-852.
- 15
- 16²⁹ F.P. Cordelieres, *Manual Tracking* [computer software]. (2005) Orsay, France. Available: http://imagej.nih.gov/ij/plugins/track/Manual_Tracking.java
- 17
- 18³⁰ S. Hegge, M. Kudryashev, A. Smith, F. Frischknecht, *Biotechnology Journal* **4** (2009) 903-913.
- 19
- 20³¹ Supplementary online material
- 21³² C. Zener, *Theory of growth of spherical precipitates from solid solution*. *Journal of Applied Physics* **20** (1949) 950-953.
- 22
- 23³³ J.A. Marqusee, and J. Ross, *Kinetics of phase transitions: Theory of Ostwald ripening*. *Journal of Chemical Physics* **79** (1983) 373-378.
- 24
- 25³⁴ P.G.J. van Dongen, and M.H. Ernst, *Scaling solutions of Smoluchowski's coagulation equation*, *Journal of Statistical Physics* **50** (1988) 295-329.
- 26
- 27³⁵ P.G.J. van Dongen and M.H. Ernst, *Dynamic scaling in the kinetics of clustering*. *Physical Review Letters* **54** (1985) 1396-1399.
- 28
- 29³⁶ T. Tobin, R. Muralidhar, H. Wright, and D. Ramkrishna, *Determination of coalescence frequencies in liquid-liquid dispersions: effect of drop size dependence*. *Chemical Engineering Science* **45** (1990) 3491-3504.
- 30
- 31³⁷ A. Ludwig, M. Wu, M. Abondano, and L. Ratke, *Gravity-induced convection during directional solidification of hypermonotectic alloys*, *Materials Science Forum* **508** (2006) 193-198.
- 32
- 33³⁸ M.C. Ruzicka, and N.H. Thomas, *Buoyancy-driven instability of bubbly layers: analogy with thermal convection*, *International Journal of Multiphase Flow* **29** (2003) 249-279.
- 34
- 35³⁹ D.H. Rothman, and L.P. Kadanoff, *Bubble, bubble, boil, and trouble*, *Computers in Physics* **8** (1994) 199-204.
- 36
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Figures and Tables

Fig. 1: A selected portion of the Al-In phase diagram depicting the miscibility gap in the liquid phase. The dashed curve is the chemical spinodal boundary. The red vertical arrow highlights the $\text{Al}_{90}\text{In}_{10}$ composition studied here with the binodal ($T_B=1016$ K) and monotectic ($T_M=910$ K) shown. All phase boundaries are solved from parameters provided in Sommer et. al. [1].

Fig. 2: A schematic of the furnace and sample configuration showing the sample position relative to the inductively heated ends.

Fig. 3: A background subtracted section of a single frame during cooling. The dark features are mobile droplets of indium-rich liquid within the aluminum-rich liquid. The dynamic droplet flow behavior is emphasized in Movie 1.

Fig. 4: Plots of indium-rich L_{II} droplet size distribution functions (lines) and a histogram of the droplet sizes for during early L_I/L_{II} phase separation. The histogram corresponds to the 40 s data set while the times for the curves are labeled in the figure.

Fig. 5: Plots of the L_{II} droplet (a) maximum and mean size and (b) number density as a function of time from the initiation of the phase separation reaction. The solid lines are fits through the data; the dotted and dashed lines in (b) are 90% prediction intervals.

Fig. 6: (a) Computed values for direction-independent droplet speed as a function of time. The open red circles correspond to automated measurements while the blue squares correspond to manual measurements. The green line is an exponential fit to the data for $10 < t < 40$ s, while the gray area illustrates the presumed trend in droplet speed. (b) A three dimensional depiction of droplet speed and direction of motion which shows the highest probability combination of values from $t=40$ s until the end of the monotectic reaction. The droplets start with a low velocity and largely random motion, but eventually a downward acceleration dominates.

Fig. 7: Qualitative features of populations undergoing (a) growth into a supersaturated matrix, (b) diffusion controlled coarsening, and (c) coarsening by droplet coalescence. The curves moving generally to the right are at longer times. General time dependent features of each are given in the figure, where n is the number density, r is the radius, and v is the total volume.

Fig. 8: Droplet size distributions are shown over time during (a) stage 1 where $0 < t < 40$ and (b) stage 2 $t > 40$. The color of each curve goes from light blue to red as time increases. The size distribution first spreads out and is skewed toward larger sizes, then retreats again toward smaller sizes during stage 2 of the reaction.

Fig. 9: The extracted statistics from the experimental distributions are compared to the theoretical values from a pure coarsening model by taking their ratio over time.

Fig. 10: A comparison between experimental fits (lines) and 100 numerical outcomes of size dependent settling (purple) for (a) the number density and (b) the average size of droplets during the last stage of the reaction. Both of the time axes are scaled so that $t=40$ in the experiment is at origin.

Figure 1

Figure 2
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Figure 6

Figure 7 - revised

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Figure 10