ABSTRACT

Three-Dimensional Characterization and Real-Time Interface Dynamics of Aluminum-Copper Dendritic Microstructures

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The morphological evolution of initially equiaxed dendritic and directionally solidified Al-Cu microstructures are studied in three dimensions. Initially equiaxed dendritic Al-20wt%Cu and Al-14wt%Cu microstructures are analyzed \textit{ex–situ}, and data is collected using serial sections and X-ray tomography. Samples of the same composition, along with initially directionally solidified Al-26wt%Cu and Al-15wt%Cu samples, are coarsened \textit{in–situ}, and data is collected at temperature using X-ray tomography.

The \textit{ex–situ} studies show that the microstructures evolve into highly interconnected structures, where the inverse of specific surface area ($S_v^{-1}$) scales linearly with $t^{1/3}$. As the size scale of the microstructure increases, the interface shape distributions (ISDs) change only slightly. The distributions of interface normals indicate that the microstructures are approximately isotropic. The scaled genii are also independent of coarsening time within the error of the experiments. Thus, the microstructures evolve
self-similarly, both morphologically and topologically. The differences in scaled morphologies and topologies can be attributed to the difference in solid volume fraction, with the higher volume fraction sample exhibiting a more compact ISD and a smaller scaled genus.

The in – situ coarsened samples are analyzed using a new 4D characterization technique. Expanding on the idea of an ISD, the probability of finding any three characteristics of the interface in relation to one another is determined. This results in a plot of semi-transparent isosurfaces of constant probability. In order to connect the velocity of an interface to its morphology, the principal curvatures, $\kappa_1$ and $\kappa_2$, and velocity, $V$, are examined.

Comparing Al-26 wt% Cu (42% solid) and Al-15 wt% Cu (74% solid), as solid volume fraction increases, the diffusional distance, or distance in which shapes interact, decreases. In the 74% solid samples, specific interface shapes (e.g.-parabolic or hyperbolic) have equal and opposite velocities in close proximity to one another. There is no evidence of this in the 42% solid sample. Thus, there is more interaction between all shapes, which also indicates the diffusional distance is longer. Further, as the diffusional distance increases, the dispersion of velocities with respect to a specific pair of principal curvatures decreases. Thus, predicting how interface shapes evolve in these microstructures will be much more straightforward.
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CHAPTER 1

Introduction

The evolution of dendritic solid-liquid mixtures during coarsening has been studied for some time [1–8]. These investigations have led to significant advances in predicting the evolution of dendritic microstructures. However, most models employ strongly idealized geometries of the solid phase, and most of these experiments examine mushy zones using two-dimensional sections of three-dimensional microstructures. Thus, it is difficult to determine if the assumptions employed in these models are realistic. Finally, the coarsening process is driven by interfacial curvature, which is an inherently three-dimensional quantity. All of these factors make it difficult to completely determine the evolution of these structures when studied using two-dimensional sections. We thus analyze the morphology and topology of these structures in three dimensions using techniques that are valid regardless of the morphology and topology of the mixtures.

Dendrites are the general morphology observed for metal systems during solidification. Their growth and evolution lead to the formation of a mushy zone, a two-phase region where the solid phase has a dendritic, or tree-like, structure and the liquid phase forms the surrounding matrix. Holding this mixture for any length of time at a temperature that yields a mushy zone results in coarsening of the dendrites. The morphology and length scale of the microstructure can change significantly depending on the time spent in this region, which then affects the properties of the material. Thus, it is imperative we understand the coarsening process. To accomplish this, it is necessary to
focus on measuring, and perhaps predicting, changes in the dendrite morphology as
coarsening occurs.

The coarsening process in isothermal alloys proceeds by the diffusion of mass from
one region of the interface to another. This mass flow is a result of the relationship
between the composition of the liquid at the interface and the mean curvature of the
interface as given by the Gibbs-Thomson equation. Thus, variations in interfacial
curvature lead to concentration gradients. The resulting flux decreases regions of high
curvature and increases regions of low curvature, leading to a decrease in the total
interfacial area over time. Thus, the coarsening process decreases the total interfacial
free energy by increasing the overall size scale of the system.

Traditionally, the length scale of a dendritic solid-liquid mixture undergoing coars-
ening has has been characterized using the secondary dendrite arm spacing, a quantity
easily measured using two-dimensional sections, and one that increases as $t^{1/3}$ during
coarsening [3]. However, a transition to spherical solid particles during coarsening [8]
as well as other topological changes are possible; thus, the inverse surface area per unit
volume, $S^{-1}_v$, is used. It is easily measured in three dimensions and first utilized to
characterize dendritic structures undergoing coarsening by Marsh and Glicksman [8].

Although $S_v$ describes the kinetics of the coarsening process, it provides no informa-
tion on the details of the microstructure. Thus, the interfacial curvature is measured
to quantify the morphology of the dendritic mixtures and its changes with coarsen-
ing time. The curvature of a patch of interface is defined by its principal curvatures,$\kappa_1$ and $\kappa_2$, which are the diagonal elements of the curvature tensor. Since curvature
varies spatially in these mixtures, the probability of finding a patch of interface with a
given pair of principle curvatures is determined and then displayed as a contour plot, or interface shape distribution (ISD), to quantify the morphology of the interface. In systems composed of spherical particles, the curvature of each particle is related to the radius. Thus, by measuring the distribution of radii in the system, the distribution of interfacial curvature is also determined. Therefore, the ISD is a generalization of the classical particle size distribution for systems of spherical particles.

We characterize the directionality of the structures by determining the probability of finding an interfacial normal, \( \mathbf{n} \), pointing in a given direction [9]. This probability is determined by projecting a unit interface normal, originating at the center of a sphere and ending on the surface of the sphere onto a plane tangent to the sphere and perpendicular to the axis along which the projection is made. The data is binned in three dimensions before it is projected onto the sphere, which removes potential artifacts from the projections; these artifacts are seen in two-dimensional polar plots when the data is binned after the projection is complete. Thus, each bin encompasses the same three-dimensional area of the unit sphere. We then create a contour plot, or interface normal distribution (IND), of the probability distribution of the interface normal orientations.

We characterize the topology of the mixtures by measuring the genus, \( g \), which quantifies the complexity of the microstructure, see DeHoff et. al. [10]. The genus of an object is one less than the number of cuts necessary to sever the object from itself. A closed surface, such as a sphere, has a genus of zero. When a handle or loop is added to the sphere, or a hole is cut through the sphere, as in a torus, the genus is increased
by one. Thus, when a structure is fully interconnected, the genus is a measure of the number of loops present in a specified phase of the structure.

Finally, the interface dynamics of the Al-Cu system is studied using in-situ, or real-time, X-ray tomography and a new three-dimensional characterization technique. Expanding from the idea of an ISD, a third dimension is added to these probability contour plots. Thus, the resulting probability of finding any three characteristics in relation to one another can be represented as isosurfaces of constant probability. The plot is semi-transparent such that each of the isosurfaces can be seen. The first test of these plots examines the principal curvatures, $\kappa_1$ and $\kappa_2$, and velocity, $V$ in an effort to connect the velocity of an interface to its morphology. Thus, the most probable interface shapes in the microstructure and how they move with coarsening time are identified.

The new 3D semi-transparent probability plot is general, one that can be used to compare any three features of the microstructure and the correlation of those specific features to one another. Thus, the interface dynamics of coarsening can be characterized in depth. This will elucidate many aspects of the coarsening process that were undetermined and not able to be calculated using ex-situ measurements, and this characterization technique will also play a vital role in creating accurate phase-field models of these complex systems.
CHAPTER 2

Dendritic Coarsening

In two-phase, topologically complex microstructures, coarsening is still not well understood. Dendrite formation is the common crystallization method in metals and alloys, especially in cast microstructures, but it can also be observed during the crystallization of vapors and solutions of salts and organic compounds [11]. Dendritic solid-liquid mixtures are ideal for studying coarsening. This is because the microstructure is on a size scale that can be analyzed experimentally, and the thermophysical properties of many alloy systems are relatively well-known and understood.

The coarsening process proceeds by the diffusion of mass from one region of the interface to another, as described by the Gibbs-Thomson equation,

\[
C_L = C_\infty + l_c H
\]

where \( C_L \) is the liquid composition at a curved interface, \( C_\infty \) is the liquid composition at a flat interface, \( l_c \) is the capillary length, which is a function of the solid-liquid interfacial energy, and \( H \) is the mean interfacial curvature, given by:

\[
H = \frac{\kappa_1 + \kappa_2}{2}
\]

where \( \kappa_1 \) and \( \kappa_2 \) are the minimum and maximum principal curvatures of the interface, respectively. Thus, variations in interfacial curvature lead to concentration gradients.
The resulting flux decreases regions of high curvature and increases regions of low curvature, leading to a decrease in the total interfacial area over time. Thus, the coarsening process decreases the total interfacial free energy by increasing the overall size scale of the system.

Dendritic coarsening was first described by Papapetrou in 1935 [12]. Since then, several models, mostly two-dimensional, have been proposed to explain dendritic coarsening. Although the curvature of a dendrite arm varies with position, most models assume the arm is cylindrical. Kattamis et. al. [4] considered all arms the same cylindrical shape except one, which is thinner than the rest. Thus, as time increases, the flux of solute proceeds from the thinner arm, where curvature is higher, to the thicker arms, where the curvature is lower, at a rate that is proportional to the difference in the radius of the dendrite arms. Eventually, the thinner arm radially re-melts into the matrix.

Kahlweit [5] examined dendritic coarsening in \( NH_4Cl \) and postulated that the arm of a dendrite axially re-melts into the primary stalk of the dendrite without the radius of the arm changing. He considered the tip of the dendrite to be a sphere while the arms are cylindrical. Thus, the tip has twice the mean curvature of the arm. When one of the arms is thinner than the rest, the flux of solute moves away from the tip of the thinner dendrite arm, causing the arm to dissolve from tip to root.

Other models describe one of the dendrite arms as tear-shaped [1,2], see Fig. 2.1(a), where one radius of curvature is at the base of the primary stalk and the other radius of curvature is at the tip of the secondary arm, while the surrounding arms are cylindrical. The radius at the tip is greater than the radius at the base, and thus, material is
transported away from the base and into the arm. This eventually causes the dendrite arm to detach from the primary stem of the dendrite. Although this theory has been seen in experimentation, it is not entirely accurate. While the secondary arm detaches due to the curvature difference, the effects of the radius of curvature perpendicular to the axis of the dendrite are not clear. Thus, the kinetics for detachment described by this model are incomplete.

Young and Kirkwood [13] used a similar tear-shaped model to examine the interactions between secondary dendrite arms, see Fig. 2.1(b). Two dendrite arms are tear-shaped instead of one. The flux of solute still proceeds from the base of the primary stalk toward the tip of the secondary arm, but it concentrates at the cylindrical region of the arm near the tip. This decreases the distance between the two tear-shaped dendrite arms. Over time, this space disappears and the secondary arms coalesce.
Figure 2.2. Four different models for isothermal coarsening: (1) radial remelting, (2) axial remelting, (3) arm detachment, (4) arm coalescence.

Figure 2.2 summarizes the historical models for dendritic coarsening. It is evident that each of these models describes only part of the dendritic coarsening process. Perhaps what is most important is that they demonstrate the dependence of the evolution of the microstructure on the actual curvatures of the dendrite arms. In addition, it is possible that in mushy zones, the microstructure is too complex to be described by the evolution of a single dendrite arm. Thus, none of these models would yield a predictive theory for the evolution of the complex solid-liquid mixtures found in mushy zones.

More recently, the study of coarsening in dendritic microstructures has moved into three dimensions. The methodology is discussed in detail below, but the significant advancements are summarized here. Alkemper, Mendoza, and Kammer [9,14–19] have
explored coarsening using alloys that have been directionally-solidified prior to coarsen-
ing. They employed aluminum-copper and lead-tin binary systems at various volume
fractions over various coarsening times. All studies have observed eventual cylinder
and cylindrical-like shape formation parallel to the initial solidification direction and a
lack of self-similar growth in the system, even after sufficiently long coarsening times.
There has been no observation of the microstructure breaking up into spherical shapes.
The consensus of these studies is that initial solidification processes have a significant
impact on the evolution of the microstructure throughout coarsening, which is why
cylindrical shapes remain even after significant coarsening has occurred.

In quantifying dendritic coarsening, studies of coarsening using two-dimensional
sections have placed significant focus on the secondary arm spacing, $\lambda_2$. This is because
it is a relatively easy feature to measure, and it increases during coarsening similarly
to average particle size in spherical systems. Fig. 2.3 and Eq. 2.3 show the relationship
between secondary arm spacing and local solidification time, $t_f$ [3].

\begin{equation}
\lambda_2 \sim t_f^{1/3}
\end{equation}

However, measuring $\lambda_2$ after substantial coarsening poses a significant problem. It
has been shown experimentally that initially dendritic microstructures can evolve into
spheroidal solid particles where secondary arms do not exist, see Fig. 2.4 [8].

Therefore, a morphologically independent quantity that provides a measure of the
length scale of the structure is necessary. The inverse of the specific surface area, $1/S_v$, a
three-dimensional quantity, is thus employed. The relationship between specific surface

area, $S_v$, and time, $t$, is displayed in equation 2.4, and it is analogous to equation 2.3.

$$S_v^{-3}(t) - S_v^{-3}(0) = Kt$$

Specific surface area remains a valid measure of the characteristic length of the microstructure through such changes as arm detachment, arm coalescence, break-up into spherical particles, and other topological changes. Thus, it adequately represents the kinetics of the coarsening process. It is an inadequate measure, however, for characterizing the morphological changes in the microstructure. This is because it is an average over the system, and it cannot account for any detailed evolution of the microstructure. Therefore, the interfacial curvature must also be measured, which will be discussed in Chapter 4.
Figure 2.4. Two-dimensional micrographs showing Sn-40 wt% Bi coarsened for (A) $t = 0$, (B) $t = 10\ min$, (C) $t = 2.5\ hr$, (D) $t = 240\ hr$.

The $t^{1/3}$ power law is observed in many systems, from spinodally decomposing alloys to systems with spherical particles. In most cases, it is associated with a microstructural self-similarity. Self-similarity is an important feature of a microstructure that is undergoing coarsening. If a microstructure is evolving self-similarly, it can be rendered time-independent when scaled by a time-dependent length scale, such as $S_v$. In particular, the presence of self-similarity implies that even though the structure is coarsening via a very complex mass-transport process, the system self-organizes into a unique scaled microstructure, e.g., a unique particle size distribution in systems with
spherical particles \cite{20, 21}. For systems that have complicated bicontinuous, or inter-connected, structures, interface shape distributions have also been observed to scale during coarsening \cite{22}.

However, such scaling has not been observed in previous studies of coarsening in dendritic solid-liquid mixtures where the dendrites are produced by a directional solidification process, even though the microstructures are evolving according to the $S_{v}^{-1} \propto t^{1/3}$ relationship. Mendoza et. al. \cite{16, 18} and Kammer et. al. \cite{9, 19} found that the interface shape distributions and genus do not scale when the dendrites are produced by a directional solidification process in Al-Cu and Pb-Sn alloys, respectively. The lack of self-similarity is due to the directionality that remains in the structure throughout the coarsening process. Thus, it is not possible to use the powerful unifying ideas of self-similarity to understand coarsening in these systems.
CHAPTER 3

Experiment

3.1. Aluminum-Copper System

Figure 3.1. Aluminum-Copper phase diagram.

Binary Aluminum-Copper is the alloy system of choice for these studies. The phase diagram for the Al-Cu system is seen in Fig. 3.1. Four different weight fractions are
examined, and two different initial solidification techniques are used. Samples of Al-15 wt% Cu and Al-26 wt% Cu (< 99.99% purity, provided by Ames Laboratory) were directionally solidified as in [16]. These structures are only used for the in-situ X-ray tomography studies.

Samples of Al-14 wt% Cu and Al-20 wt% Cu were initially solidified in an equiaxed manner by Dr. Markus Rettenmayr at the University of Jena in Germany. This is one of the first studies of Al-Cu microstructures that were formed using equiaxed techniques. The equiaxed microstructures are unique because they should have no directionality; they should be, on average, isotropic in all directions. A two-dimensional micrograph of the initial structure, prior to coarsening is seen in Fig. 3.2.

Figure 3.2. Initial microstructure of Al-20 wt% Cu prior to coarsening. The Al-rich dendrites are white and the Al-Cu eutectic is black.
Since these are solidified structures, microsegregation may be present in the un-coarsened samples, which could create composition gradients in the Al-rich dendritic phase during the initial stages of coarsening. Thus, the following calculation is completed to investigate if (and when) compositional homogeneity is reached. The diffusion distance, $x$, is

\begin{equation}
    x = \sqrt{D_s t}
\end{equation}

where $D_s$ is the solid diffusion coefficient for Al-Cu, and $t$ is the time (sec). Using $D_s = 0.3 \, \mu m^2/sec$, and $t = 150 \, sec$ (the minimum time it takes to reach the coarsening temperature), $x = 6.7 \, \mu m$. The initial average length scale of the microstructure, dependent on the weight fraction of Cu, ranges from $10 – 25 \, \mu m$. Thus, there could be some microsegregation present, affecting the initial coarsening of the structure. After 10 minutes of coarsening, however, the average length scale of the system ranges from $29 – 43 \, \mu m$. Thus, most of the Al-rich dendritic phase has coarsened sufficiently enough that it is compositionally uniform, and microsegregation is no longer a factor.

### 3.2. Coarsening Furnace

Three cylindrical ingots (diameter of ca. 7.62 mm) of Al-20 wt% Cu and three samples (diameter of ca. 7.62 mm) of Al-14 wt% Cu are prepared for coarsening by cutting off the bottom portion of the sample; this includes a hole in the ingot where the thermocouple used for solidification of the sample was placed. The diameter of the samples is reduced using sandpaper such that the ingot closely fits within the hole of the small coarsening furnace.
Figure 3.3. The coarsening setup.

The small coarsening furnace is composed of ceramic, hot-pressed Boron Nitride. The BN holder is resistance-heated, by the wires woven through its walls in order to control potential thermal gradients during coarsening. It also positions the small furnace in the center of the large furnace. The wires leading up through the top of
the large furnace are encased by Alumina rods to insulate them from the ambient temperature. The schematic of the coarsening furnace and wiring diagram as well as the picture of the coarsening furnace inside of the larger furnace is seen in Fig. 3.3.

![Figure 3.4. The heating profile for the coarsening furnace.](image)

The large furnace is heated to just below the eutectic temperature, 813K, in order to minimize radiative heat loss from the smaller furnace. The samples are then isothermally coarsened at 826K, five kelvin above the eutectic temperature, for 10, 1060, and 6566 minutes (for the Al-20wt%Cu samples) and 10, 1190, and 6960 minutes (for the Al-14wt%Cu samples). A PID temperature controller monitors the temperature through a thermocouple located in the wall of the BN holder and dynamically adjusts the applied power in order to keep the temperature of the small BN furnace constant. The heating profile for the BN holder is seen in Fig. 3.4. Because of the oscillations about the desired temperature, a minimum coarsening time of 10 minutes
can be employed. Once the desired coarsening time is reached, the sample is quenched in water to assure a fully-formed eutectic.

### 3.3. Serial Sectioning

There are two data collection techniques used for these samples, serial sectioning and X-ray tomography.

The Al-20\textit{wt\%}Cu samples are serial sectioned using a recently developed, virtually fully-automated serial sectioning technique [23], see Fig. 3.5. The \textit{z}-spacing between sections is 4.75\textit{µm} for the 10 minute sample and 9.5\textit{µm} between sections for the 1060 and 6566 minute samples. The \textit{x-y} resolution is set by the magnification used for the light microscope. A 10x objective (0.507\textit{µm/pixel}) for the 10 minute sample and a 5x objective (1.03\textit{µm/pixel}) for the 1060 and 6566 minute samples are utilized. The newly cut sample surface is cleaned with ethanol and then photographed. A linear variable differential transformer (LVDT) records the horizontal position of the sample when the picture is taken, and then the sample proceeds back to the start position where the procedure begins again. Figure 3.6 presents a schematic illustration of the sectioning process with the coordinate system specified.

### 3.4. X-Ray Tomography

#### 3.4.1. X-Ray Tomography at Argonne National Laboratory

The already-coarsened Al-14\textit{wt\%}Cu samples are prepared for X-ray tomography by machining them into 2 mm diameter ingots. The X-ray tomography is then conducted at the Advanced Photon Source (APS), at the DND-CAT 5-BM-C beamline at Argonne
(a) Front view of the serial sectioner.

(b) Back view of the serial sectioner.

Figure 3.5. Pictures of the serial sectioner.
The in-situ X-ray tomography is carried out at the TOMCAT beamline at the Swiss Light Source located at the Paul Scherrer Institut in Villigen, Switzerland. There are two important parts of this process: (1) the coarsening setup and (2) the actual tomography setup. Both will be discussed in detail below.
3.4.2. Coarsening Setup for X-Ray Tomography

Samples of directionally solidified Al-15\textit{wt}\%Cu and Al-26\textit{wt}\%Cu along with samples of Al-14\textit{wt}\%Cu and Al-20\textit{wt}\%Cu with equiaxed dendritic microstructures were cut into 1 mm and 2 mm diameter specimens in preparation for in-situ X-ray tomography. The energy needed to penetrate the samples is dependent on the diameter of the sample being analyzed; thus two sample sizes are created to provide flexibility.

A custom made furnace, developed with Erik M. Lauridsen at Risø National Laboratory, was used to coarsen the samples at 826 K, 5 K above the eutectic temperature. The goal was to create a furnace-within-a-furnace setup similar to what was used for the \textit{x-situ} coarsening. Therefore, there is an ambient temperature furnace, necessary to control radiative heat loss from the smaller furnace, and then a BN sample holder for the actual samples. Photos of the ambient temperature furnace can be seen in Fig 3.7.
Figure 3.8. Photo of the thin-walled BN holder, atop the alumina rod, mounted on the rotating stage at the SLS.

Because the sample is on a rotating stage, no wires or electrically-controlled heater can be used to minimize thermal gradients. Thus, the system is not a furnace-within-a-furnace, but instead we attempt to insulate the space between the walls of the ambient temperature furnace and the BN holder encasing the sample. A custom made BN piece is created to fill the air gap between the furnace coils and the actual sample, with the
goal being to reduce convective heat loss. There must be a gap in the BN insert in order for the X-rays to adequately penetrate the sample. The sample is placed inside a thin-walled BN holder because the holder itself must be X-ray transparent, and the sample needs to sit within an insulated holder. It is then glued atop an alumina rod, and mounted on the rotating stage. Thus, only the small BN holder and the sample are rotating during the experiments. This setup can be seen in Fig 3.8

### 3.4.3. X-ray Tomography at the Swiss Light Source

The tomography experiments were conducted on the TOMCAT beamline located at the X02DA port of the Swiss Light Source (SLS) at the Paul Scherrer Institut (Villigen, Switzerland). Information about the TOMCAT beamline can be found in [24]. X-ray photon energy of 20-30 keV was used, with exposure times ranging from 80-400 ms, and 721 projections captured over the 180° of rotation. The detector consisted of a Ce-doped YAG scintillator with a thickness of 20 µm, and a 2048 x 2048 pixel CCD camera with a 280c digital/analog converter and a 10MHz read-out speed. A total of 1024 slices, with voxels measuring 1.4 µm per side, were collected in times ranging from 2.5 min–6 min per scan. The setup can be seen in Fig 3.9.
Figure 3.9. Photo of the full setup at the SLS. The liquid nitrogen spray inhibits heat from the furnace from traveling down to the rotation stage.
CHAPTER 4

Analysis

4.1. Segmentation and Three-Dimensional Reconstructions

4.1.1. Segmentation

Segmentation is the division of an image into useful portions. This could be in terms of structural units of interest or enhancing specific objects of interest in the image. Ultimately, it is the separation of the foreground from the background. Thus, in terms of this research, it is the process of converting raw images collected from the experiments to binary, or black and white, images. The process is specific to the images, but there are general filters used to enhance contrast between the two phases. Because no etchant is used with the Al-Cu system, this process is done solely through manipulation of the images with Adobe Photoshop or Interactive Data Language (IDL), a language by Research Systems Inc. Fig. 4.1 shows various stages of the segmentation process, from the raw image collected from the serial sectioner, Fig. 4.1(a), to the grayscale, filtered image, Fig. 4.1(b), to the finished binary images, Fig. 4.1(d).

One way to measure the separation of the foreground from the background is to look at the histogram, see Fig. 4.1(c), of the grayscale image. The histogram, a measure of the number of pixels at each grayscale location over of full spectrum of black, at zero, and white, at 255, should have two distinguishable peaks with a local minimum
Figure 4.1. Two-dimensional images of Al-20 wt% Cu coarsened for 1060 minutes during the course of segmentation. (a) the raw image, (b) the grayscale, filtered image, (c) the histogram of the grayscale image, (d) the finished binary image.
between them. The most useful measure of the histogram is the distance between the peaks; the further they are from another, the better the contrast.

In order to increase contrast, the most important filter used is the high pass filter. The uneven illumination caused by the light microscope makes it difficult to level the background. The high pass filter removes these low frequencies, or gradual variations of the overall background, from the image. Once this filter has been applied, a leveling filter adjusts the pure white and pure black levels to the lightest and darkest pixels in the image itself and readjusts the grayscale accordingly. In essence, this filter expands the histogram over only the applicable gray levels in the image.

Once contrast has been enhanced, noise-reducing filters are used to change dissimilar pixels to match their surrounding area. There are two adjustments made within the filter to tailor it to the user’s needs. The radius feature determines how far away from the pixel of interest the filter looks for dissimilarities, and the threshold feature controls which pixels are examined. At a threshold of zero, all pixels are examined, and as the threshold increases, only pixels above the specified value are affected. Because this filter is, in essence, smoothing the interface between black and white, it has the possibility of significantly distorting the image if used improperly.

With the use of the serial sectioner, the segmentation process is done manually on each image. Because X-ray tomography is better suited for the Al-Cu system, contrast is enhanced just by the data collection process. Thus, the same filtering scheme could be used on every image. Further, the segmentation process could then be automated in IDL. Fig. 4.2 shows an image collected from X-ray tomography at Argonne National Laboratory and then the binary image created using IDL. Similar filters, described
Figure 4.2. Two-dimensional images of Al-Cu during segmentation. (a, b) Al-14wt% Cu coarsened for 10 minutes. (a) is the image reconstructed from X-ray tomography and (b) is the image converted to binary with filters in IDL.

above, are used in this automated process; the filters just go by different names. The images are converted straight to binary by specifying a threshold value for the whole image. Then, the image is either eroded or dilated. The erode filter removes pixels, of a specified radius, touching areas already distinguished as background (either black or white). The dilate feature would do just the opposite. Interestingly, these filters extend or retract the interface without significantly changing the actual curvature.

4.1.2. Three-Dimensional Reconstructions

Once the images, collected from the serial sectioner, have been converted to binary, they are aligned and stacked in IDL. Fig. 4.3 shows a schematic of the process. A
Figure 4.3. Schematic representation of stacking and aligning pictures. Once the pictures are stacked, they are aligned by removing any unnecessary data along $y$, with information provided by the LVDT.

text file of the $y$-axis locations collected using the LVDT during the sectioning process specifies the location of each image with respect to every other image. The LVDT ensures that the translational misalignment is determined to an accuracy of less than 0.5 $\mu m$. This process is not necessary for the images collected using X-ray tomography because there is no $x-y$ plane misalignment. Once the images are stacked and aligned, the three-dimensional reconstructions can be completed.

4.2. Interface Shape Distributions (ISDs)

The principal curvatures, $\kappa_i$, are geometric properties of a curve or surface that define a change in the rotation angle of an object’s normal vector with respect to arc lengths along their respective surface coordinates. Consider a general surface that can be described locally by a patch, shown in Figure 4.4. The surface can be completely characterized by its two principal radii of curvature, $R_1$ and $R_2$. Each radius corresponds to an imaginary circle that is tangent to the surface patch. These circles are perpendicular to each other and represent the minimum and maximum radii of curvature on the patch. The minimum and maximum radii of curvature are related to the principal curvature by the following equation:

\[ \kappa_i = \frac{\partial \theta_i}{\partial S_i} = \frac{1}{R_i} \quad (i = 1, 2) \]
Figure 4.4. A monge patch with corresponding radii of curvature, $R_1$ and $R_2$. $n$ represents the unit normal vector, while $p$ is the point of interest.

where $\kappa_i$ represents the scalar principal curvatures, $\theta$ defines the angle made with each radius of curvature and the normal vector, and $S$ represents the arc length, shown in blue and red across the patch for $R_1$ and $R_2$ respectively. These principal curvatures define the diagonal elements in the $2 \times 2$ curvature tensor. The two important invariants of the curvature tensor, the mean and Gaussian curvatures, are significant to the geometric and thermodynamic properties of an interface. The mean curvature, $H_i$, is defined as half the trace of the curvature tensor:

$$(4.2) \quad H = \frac{1}{2} tr[\kappa_i] = \left( \frac{\kappa_1 + \kappa_2}{2} \right) = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

During melting or freezing, the mean curvature relates the local area and volume changes associated with the phase change; therefore, through geometric quantities, the
free energy change due to interfacial shape change can be determined. The Gaussian curvature, \( K \), is defined as the determinant of the curvature tensor:

\[
K = \det[\kappa_i] = \kappa_1 \kappa_2 = \frac{1}{R_1 R_2}
\]

A saddle-shaped region, like Figure 4.5 [25], illustrates the necessity for both mean and Gaussian curvatures for a full description of a surface. In this case, \( R_1 = -R_2 \), and \( H = 0 \). Thus, the interfacial solute concentration is the same as that of a planar surface, although the surface is clearly not planar. Studies have also shown both mean and Gaussian curvatures are essential during interface evolution [26].

Figure 4.5. A second representation of a patch of surface with representative principal curvatures.

The mean and Gaussian curvatures are extracted from the generated three-dimensional images by using the mixed Finite-Element/Finite-Volume method established by Guillaume et. al. [27].
After the mean and Gaussian curvatures have been measured, the principal curvatures, $\kappa_1$ and $\kappa_2$, are calculated by the following two equations:

\begin{align}
\kappa_1 &= H - \sqrt{H^2 - K} \\
\kappa_2 &= H + \sqrt{H^2 - K}
\end{align}

This curvature data can then be represented by a two-dimensional probability contour plot [16]. Suppose $P(\kappa_1, \kappa_2)$ is a probability density function, where $P(\kappa_1, \kappa_2)d\kappa_1d\kappa_2$ is the probability that any randomly chosen interface point will have principal curvatures, $\kappa_1$ and $\kappa_2$, between $\kappa_1 + d\kappa_1$ and $\kappa_2 + d\kappa_2$. The two-dimensional probability contour plot, or interface shape distribution (ISD), is a measure of the probability of finding a patch of surface in the microstructure with a given set of principal curvatures, $\kappa_1$ and $\kappa_2$. It is divided into four regions, as seen in Figure 4.6.

The significant features of an ISD are:

- Below the $\kappa_1 = \kappa_2$ line is a forbidden region since by our definition of curvatures, $\kappa_2 \geq \kappa_1$. Thus, all contours must lie to the left of this line.
- Region 1 represents patches where $H > 0, K > 0$.
- Region 2 represents patches where $H > 0, K < 0$.
- Region 3 represents patches where $H < 0, K < 0$.
- Region 4 represents patches where $H < 0, K > 0$.
- The interface is planar at $\kappa_1 = \kappa_2 = 0$. 
The interface shapes are concave toward the solid when $H$ is negative and convex toward the solid when $H$ is positive.

Interfacial shapes located on the $\kappa_1 = \kappa_2 > 0$ line correspond to solid spherical shapes, and along $\kappa_1 = \kappa_2 < 0$ correspond to liquid spherical shapes. Shapes where $\kappa_1$ and $\kappa_2$ have the same sign (regions 1 and 4) are also known as elliptic shapes.
• Cylindrical shapes correspond to one of the principal curvatures being zero. If \( \kappa_1 = 0 \), the cylinder is solid, and if \( \kappa_2 = 0 \), the cylinder is liquid. These shapes, where one principal curvature is zero, are also known as parabolic shapes.

• The interface shapes are saddle-shaped when \( \kappa_1 < 0 \) and \( \kappa_2 > 0 \). These shapes, where one principal curvature is positive and the other is negative (regions 2 and 3), are also known as hyperbolic shapes.

### 4.3. Interface Normal Distributions (INDs)

In order to characterize preferential directionality in the microstructure, the probability of finding an interfacial normal, \( \mathbf{n} \), in a given direction is determined \([9]\). This probability is determined by projecting a unit interface normal, originating at the center of a sphere and ending on the surface of the sphere, onto a plane tangent to the sphere and perpendicular to the axis along which the projection is made. The data is binned in three dimensions before it is projected onto the sphere, which removes potential artifacts from the projections; these artifacts are seen in two-dimensional polar plots when the data is binned after the projection is complete. Thus, each bin encompasses the same three-dimensional area of the unit sphere. We then create a contour plot of the probability distribution of the interface normal orientations. A similar approach for grains and interfaces in crystals has been used by Saylor et. al. \([28]\) and Rowenhorst et. al. \([29]\), respectively, where the direction of the normals are referenced to the axes of the crystal.

Two views are generated by this technique. The near-hemisphere view presents the normals along the positive axis of choice, while the far-hemisphere view shows the
normals along the negative axis with the center of the sphere at the origin for both views. The two plots should appear qualitatively similar, but will not be exactly the same due to asymmetry within the experimental data, and the peak will be found on one of the two views. We choose to display the projection that contains this peak, regardless of the direction of the projection.

There are also two types of projections used in interface normal distributions (INDs): equal-area and stereographic projections, see Fig. 4.7. Equal-area projections enhance features near the center of the plot, while stereographic projections enhance features along the edges of the plot. In order to clarify what one would expect from an equal-area or stereographic projections, consider the INDs for a single sphere...
and a hollow cylinder. The probability of finding any normal for a spherical interface would be independent of orientation. Thus, both types of INDs, in any direction, would have a uniform color, see Fig. 4.8 [30]. The equal-area IND projected in the $x$-direction of a hollow cylinder with its axis parallel to the $z$-direction, for example, would be an infinitesimally thin line spanning the length of the IND through the center of the plot, see Fig. 4.9(a) [30], representing the equal probability of finding a patch of surface with interface normals perpendicular to the $z$-direction or, equivalently, parallel to the $x$-$y$ plane. The stereographic IND projected in the $z$-direction of the same cylinder, see Fig. 4.9(b) [30], shows the infinitesimally thin line encompassing the perimeter of the IND. This is an example of how stereographic projections enhance features at the
edge of the plot, which makes this representation of the cylindrical SG projection more accurate.

![Figure 4.9. Interface normal distributions (INDs) for a cylinder for the two types of projections.](image)

(a) Near-hemisphere equal-area (EQA) projection for a cylinder.

(b) Near-hemisphere stereographic (SG) projection for a cylinder.

4.4. Topology

Topologically, two structures are equivalent if, and only if, one shape can be continuously deformed into the other shape without being severed from or joined to itself. For example, a cube and a sphere are topologically equivalent because either can be deformed into the other. Conversely, a sphere and a torus are topologically different because the sphere would have to be severed to become a torus, or the torus would have to join to itself to become a sphere. Topology is important in studying dendritic
mixtures because it gives an accurate measure of the complexity of the microstructure as coarsening time increases. If two structures are self-similar, they must exhibit equivalent scaled morphologies and topologies.

The topology of the mixture is determined by measuring the genus, $g$, which quantifies the complexity of the microstructure, see DeHoff et. al. [10]. The genus of an object is one less than the number of cuts necessary to sever the object from itself, and, equivalently, it is related to the integral of the Guassian curvature over the interface, $K_{total}$, by [31]:

\begin{equation}
    g = 1 - \frac{K_{total}}{4\pi}
\end{equation}

A closed surface, such as a sphere, has an integral Gaussian curvature equal to $4\pi$, and a genus of zero. When a handle or loop is added to the sphere, or a hole is cut through the sphere, as in a torus, the genus is increased by one, and the integral Gaussian curvature is decreased by $4\pi$. Thus, the genus measures the number of loops present in a specified phase of the structure if there are no independent bodies (i.e.-the structure is fully interconnected).

In these studies, the genus is not determined using the integral Gaussian curvature, but instead calculated using the Euler characteristic, $\chi$. This is because $K_{total}$ is sensitive to surface anomalies, which are very common in experimental data due to segmentation errors. The Euler characteristic is calculated from the triangulated surface mesh, which creates a genus insensitive to small morphological changes. It relates
the number of vertices, \( n \), to the number of edges, \( e \), and faces, \( f \), by [32]:

\[
\chi = n - e + f
\]

(4.7)

The genus is then given by:

\[
g = 1 - \frac{\chi}{2}
\]

(4.8)

To illustrate how this methodology works, take a simple cube, where \( n = 8 \), \( e = 12 \), and \( f = 6 \). This results in \( \chi = 2 \) and \( g = 0 \), see Fig. 4.10(a) [33]. When a hole penetrates through the cube, \( n = 16 \), \( e = 32 \), and \( f = 16 \), resulting in \( \chi = 0 \) and \( g = 1 \). Thus, Fig. 4.10(b) [33], represents a structure topologically equivalent to a torus.

Figure 4.10. Genus of zero for (a) simple cube and one for (b) a cube with a hole.

The genus also accounts for topological singularities due to such phenomena as Rayleigh instability, where cylinders break up into spheres, see Fig. 4.11. Before the instability occurs, the structure is topologically equivalent to a square torus. When the void is formed, the structure is topologically equivalent to a cube with a cuboidal void, where \( n = 16 \), \( e = 24 \), and \( f = 12 \), resulting in \( \chi = 4 \) and \( g = -1 \).
Figure 4.11. A tube undergoing Rayleigh instability. Before the instability occurs, the structure is topologically equivalent to a cube with a hole. After the instability, a void is formed, and the genus changes from 1 to $-1$.

The volume analyzed during topological measurements is extremely important. There are still uncertainties with how the solid volume is connected outside the sample volume. Therefore, the methodology of DeHoff et. al. [10] is employed. The minimum scaled genus is determined by assuming the solid structure is capped at the bounding box and the maximum genus per volume is determined by assuming all the solid pieces touching the bounding box meet at an arbitrary point outside the box; this, in essence, creates handles or loops out of each solid piece that touches the side of the box. The number of independent bodies per volume is also found, as each independent body decreases the scaled genus by one. The size of the reconstruction box increases proportionally with increasing $S_v$ in order to assure that size scale effects are adequately captured as coarsening time increases. This will be revisited in the next chapter.

4.5. Four-Dimensional Probability Plots

The collection of in-situ coarsening data opens the realm of possibilities for further analysis of these structures. Inspired by Drew’s analysis [26] of the way shapes change
with time, we have begun to examine if and how his equations affect the dynamics of coarsening.

In order to optimize the characterization of the in-situ data, the same portion of two experimental microstructures, at different coarsening times, are analyzed. The mean and Gaussian curvatures are calculated using the level-set method, see Osher and Fedkiw [34] for more information. The mean curvature, for example, is the divergence of the normal vector of the interface, $\phi$:

$$H = \nabla \cdot \nabla \phi$$  \hspace{1cm} (4.9)

$$H = \nabla \cdot \left( \frac{\nabla \phi}{|\nabla \phi|} \right)$$  \hspace{1cm} (4.10)

This methodology gives identical results to that of Guillaume et. al. [27], and because the normal vector is the first derivative of $\phi$, which makes $H$ the second derivative of $\phi$, it is very sensitive to noise in the initial data set. Thus, sufficient smoothing of the interface is absolutely necessary for this methodology. It is more robust and useful for future phase-field calculations, which is why it is used here.

Once $H$ and $K$ are calculated, the time rate of change of the interface as well as $H$ and $K$ (following a point on the interface) must be determined. First, the spatial derivative, with respect to the initial coarsening time, of the microstructure, in the $x$-, $y$-, and $z$-directions is calculated by a standard central differencing scheme, shown below for the $x$-direction. The gray levels of the interface as a function of position
define $\phi$.

\[
\frac{\partial \phi_1}{\partial x} = \frac{\phi_1[2 : NX - 1, *, *] - \phi_1[0 : NX - 3, *, *]}{2\delta x}
\]

Next, the time derivative and gradient of $\phi$ are calculated:

\[
\frac{\partial \phi}{\partial t} = \frac{\phi_2 - \phi_1}{\delta t}
\]

Then the velocity of each of the components of $\phi$, as well as the magnitude of the velocity are calculated:

\[
V = V \cdot \overrightarrow{N}
\]

\[
V_x = -\phi_t \left( \frac{\phi_x}{|\nabla \phi_1|^2} \right)
\]

\[
V = \frac{-\phi_t}{|\nabla \phi_1|}
\]

The time derivative of $H$ and $K$ following the interface, $\dot{H}$ and $\dot{K}$ respectively, are given by:

\[
\dot{H} = \frac{H_2 - H_1}{\delta t} + \mathbf{V} \cdot \nabla H
\]

\[
\dot{K} = \frac{K_2 - K_1}{\delta t} + \mathbf{V} \cdot \nabla K
\]
Once these calculations are completed, the mesh is triangulated and the triangle normals and areas are determined. Then, velocity, $H$, $K$, $\dot{H}$, $\dot{K}$ are interpolated onto the mesh of the initial microstructure. Finally, $\kappa_1$ and $\kappa_2$ are calculated for the interpolated mesh as described above in Eqs. 4.4 and 4.5.

We can also examine two factors of $\dot{H}$ and $\dot{K}$. The time derivative of $H$ and $K$ are given by Drew [26]:

\begin{align}
(4.18) \quad \dot{H} &= -V(2H^2 - K) - \frac{1}{2}(V_{,11} + V_{,22}) \\
(4.19) \quad \dot{K} &= -2HKV - H(V_{,11} + V_{,22}) + \sqrt{H^2 - K}(V_{,11} - V_{,22})
\end{align}

where the first part of the eq. 4.18 gives the change in $H$ due to the curvatures of the structure. The second part gives, for example, a change in the shape of a planar interface if the velocity changes with position along the interface, where $V_{,11}$ and $V_{,22}$ are the second derivatives of $V$ with respect to the principal directions. Eqs. 4.18 and 4.19 give the second derivatives of the velocity:

\begin{align}
(4.20) \quad V_{,11} &= -\dot{H} - (V(2H^2 - K)) + \left(\dot{K} + 2HKV + \left(\frac{H(-2\dot{H} - 2V(2H^2 - K))}{2\sqrt{H^2 - K}}\right)\right) \\
(4.21) \quad V_{,22} &= -\dot{H} - (V(2H^2 - K)) - \left(\dot{K} + 2HKV + \left(\frac{H(-2\dot{H} - 2V(2H^2 - K))}{2\sqrt{H^2 - K}}\right)\right)
\end{align}

Initially, in order to quantify the relationship between any two of these variables, $H$, $K$, $\dot{H}$, $\dot{K}$, velocity, $\kappa_i$, etc..., the probability density function, as described in Section 4.2, can be calculated. As an example, suppose $P(H,V)$ is a probability
density function, where \( P(H, V) dH dV \) is the probability that any randomly chosen interface point will have a mean curvature, \( H \), and a velocity, \( V \), between \( H + dH \) and \( V + dV \). The two-dimensional contour plot of \( H \) with respect to \( V \) is thus a measure of the probability of finding a patch of interface in the microstructure with a given mean curvature, \( H \), moving at a specific velocity, \( V \).

Further, as suggested by Prof. Katsuyo Thornton of the University of Michigan, it would be more useful to quantify the relationship between any three of these variables, \( H, K, \dot{H}, \dot{K}, \) velocity, \( \kappa_i \), etc... Thus, the probability contour plots are expanded to include three variables, with probability being a fourth dimension. As an example, let \( P(\kappa_1, \kappa_2, V) \) be a probability density function, where \( P(\kappa_1, \kappa_2, V) d\kappa_1 d\kappa_2 dV \) is the probability that any randomly chosen surface point will have principal curvatures, \( \kappa_1 \) and \( \kappa_2 \) moving at a velocity, \( V \), between \( \kappa_1 + d\kappa_1, \kappa_2 + d\kappa_2, \) and \( V + dV \). The four-dimensional contour plot of \( \kappa_1 \) with respect to \( \kappa_2 \) with respect to \( V \) is thus a measure of the probability of finding a patch of surface in the microstructure with a given set of principal curvatures, \( \kappa_1 \) and \( \kappa_2 \), moving at a specific velocity, \( V \). Different probabilities are displayed as constant (probability) value isosurfaces, and each isosurface is represented by a different color with a different level of transparency in order to see all the probabilities in the plot. Thus, three separate two-dimensional probability contour plots are captured: \( V \) with respect to \( \kappa_1 \), \( V \) with respect to \( \kappa_2 \), and \( \kappa_2 \) with respect to \( \kappa_1 \) (or the standard ISD), along with the surface relationship between the three.

The binning of the data is represented most accurately if it is on the same order of magnitude in the \( \kappa_1 \) (or \( x \))- and \( \kappa_2 \) (or \( y \))-directions, because this creates the least amount of distortion in the resulting plot. The binning in the \( V \) (or \( z \))-direction is
more flexible and dependent on the variable of choice. We can examine any combination of these variables, with more experimentation necessary to establish if interesting correlations exist that are not apparent in the two-dimensional contour plots.
CHAPTER 5

Results and Discussion

5.1. 46% solid volume fraction

Two-dimensional micrographs of the evolution of Al-20wt%Cu during coarsening are shown in Fig. 5.1. It is evident that the size scale increases dramatically during coarsening and that the dendritic structure appears to be largely gone after 1060 minutes of coarsening. The Al-rich dendrites also undergo significant morphological changes, from a dendritic morphology to a more spheroidal or globular microstructure, which is reminiscent of observations made by Marsh and Glicksman [8].

5.1.1. Effect of Smoothing

Because equiaxed dendritic microstructures are not studied frequently, and because there are not many previous studies of these structures in three dimensions, it is imperative to understand the effects of smoothing on the characterization techniques, specifically on the ISDs, in these microstructures.

Prior to this study, there was one way to smooth the experimental data; it was called boxcar, or volume, smoothing. In essence, this procedure examines each array point, or pixel, and according to the specified width of smoothing, it will determine the majority color (either black or white) of the pixels within half that width in all three dimensions, and change the pixel, if necessary, to the majority color. So, for example,
if a width of three is specified, one pixel on each side of the pixel in question, in all three dimensions, will be examined. If the majority is white, the pixel become white, and vice-versa. This is identical to the noise-reduction filters in two dimensions, just occurring three dimensions, and it can have the same detrimental effects on the interface as the 2D filters because it is technically changing the interface location; it could create holes where there are not any and/or join surfaces that should not be joined.
However, it is critical to the accurate analysis of the microstructure because the experimental techniques used to create the three dimensional reconstructions, specifically serial sectioning, produces what is termed a ‘wedding-cake’ effect, where the individual sections can be seen in the three-dimensional reconstructions. This is an artifact that must be removed, and thus, smoothing is essential.

At the time of analysis of these structures, another type of smoothing, called mesh-smoothing, was being explored. This smoothing is more user-controlled, and it is applied to the polygonal representation of the microstructure called the mesh. Thus, the number of iterations of smoothing is specified, and it is applied to the mesh as a whole instead of to individual array points. The compliance of the mesh can also be specified, meaning the more pliable the mesh is, the more the iterations of smoothing affect the microstructure. Ultimately, the compliance factor and the number of iterations have the opposite effect; specifying a strict compliance and a large number of iterations has the same effect as specifying a compliant structure with a small number of iterations. Thus, the compliance is left at the default value, and the iterations are changed. In the following figures, the effect of smoothing are shown, with the corresponding ISD of the structure. The two examples shown are of Al-20wt%Cu, coarsened for 10 minutes and 1060 minutes.

In order to further elucidate the effects of smoothing, Specific Microstructure Location (SML) figures can examine specific areas of the ISD to determine whether features are actual microstructure or an artifact of the data collection technique [30]. Fig. 5.4 shows the Al-20wt%Cu 1060 minute coarsened structure, with volume smooth of five and mesh-smooth of 250 iterations, with $\kappa_1 = \kappa_2 = 0$, or flat interfaces, highlighted
(a) 3D reconstruction with volume smooth of five.

(b) Corresponding ISD for volume smooth of five.

(c) 3D reconstruction with mesh-smooth of 150 iterations.

(d) Corresponding ISD for mesh-smooth of 150 iterations.

in red. If the structure still has a 'wedding-cake' present, these artifacts will be red. There are three green arrows pointing to examples of such artifacts that are present in
(e) 3D reconstruction with mesh-smooth of 250 iterations.

(f) Corresponding ISD for mesh-smooth of 250 iterations.

(g) 3D reconstruction with mesh-smooth of 350 iterations.

(h) Corresponding ISD for mesh-smooth of 350 iterations.

Figure 5.2. Three-dimensional reconstructions of the Al-rich dendrites in Al-20 wt%Cu after 10 minutes of coarsening with different smoothings applied, and the corresponding ISDs for the structures. Ultimately a mesh-smooth of 250 iterations was chosen for this structure.
(a) 3D reconstruction with volume smooth of five.

(b) Corresponding ISD for volume smooth of five.

(c) 3D reconstruction with mesh-smooth of 150 iterations.

(d) Corresponding ISD for mesh-smooth of 150 iterations.

the volume smooth five structure and not present in the mesh-smooth of 250 iterations
Figure 5.3. Three-dimensional reconstructions of the Al-rich dendrites in Al-20\textit{wt}\%Cu after 1060 minutes of coarsening with different smoothings applied, and the corresponding ISDs for the structures. Ultimately, a mesh-smooth of 250 iterations was chosen for this structure.
Figure 5.4. Specific Microstructural Location (SML) figures of Al-20wt%Cu coarsened for 1060 minutes with $\kappa_1 = \kappa_2 = 0$ illuminated in red. Three green arrows point to 'wedding-cake' artifacts present in the volume smooth five structure that are not present in the mesh-smooth of 250 iterations.

It is imperative to understand that this examination is completed for each structure, because the smoothing is dependent only on the structure in question. It is also important to apply the least amount of smoothing for each structure to maintain the integrity of the interface. If the ISDs are converging on a similar distribution of curvatures, see Fig. 5.2(f) in comparison to 5.2(h) and 5.3(f) in comparison to 5.3(h).
and visually, the microstructure looks accurate in both, see Fig. 5.2(e) with respect to 5.2(g) and 5.3(e) with respect to 5.3(g), the structure with less smoothing is chosen.

5.1.2. Effect of Binning

Another factor influencing the shape and maximum probability observed in the ISDs is the binning of the experimental data when creating the plot. Two factors, $\kappa_{\text{max}}$ (the maximum value of the principal curvatures) and $nbins$ (half the number of bins in either the $x$- or $y$-direction in the plot), determine the fluidity of the contours as well as the maximum probability observed in the plot. Fig. 5.5 shows several ISDs with various numbers of bins and $\kappa_{\text{max}}$ for the Al-20wt%Cu sample coarsened for 10 minutes. If the maximum value of $\kappa$ is too low and/or the data is divided into too many bins, the plot will be spotted, see Fig. 5.5(a) for the best representation of this. If the maximum value of $\kappa$ is too high and/or there are not enough bins specified, the boarders of the bins will be evident in resulting plot, and some details of the ISD will be lost, see Fig. 5.5(g).

For comparison across multiple coarsening times, if the plot is not scaled by its characteristic length, $\kappa_{\text{max}}$ and $nbins$ must be the same at each coarsening time. If the plot is scaled by $S_v$, then the value of $\Delta \kappa / S_v$ must be the same.

\begin{equation}
\Delta \kappa = \frac{\kappa_{\text{max}}}{nbins}
\end{equation}

\begin{equation}
\frac{\Delta \kappa}{S_v} = \text{constant}
\end{equation}
Thus, for each coarsening time, the value of $\kappa_{\text{max}}$ and the designated number of bins changes. In the example of the 46% solid volume fraction sample, the representative ISD for the 10 minute coarsened sample has $\kappa_{\text{max}} = 0.4$ and $\text{nbins} = 175$. The
Figure 5.5. Examples of the effects of binning on the ISDs of the Al-20wt%Cu sample coarsened for 10 minutes. Ultimately, Fig. 5.5(h) is chosen as the representative ISD for this microstructure.

(e) $\kappa_{max} = 0.2$, nbins = 150.

(f) $\kappa_{max} = 0.2$, nbins = 100.

(g) $\kappa_{max} = 0.4$, nbins = 75.

(h) $\kappa_{max} = 0.4$, nbins = 175.
representative ISD for the 1060 minute coarsened sample has $\kappa_{\text{max}} = 0.2$ and $n\text{bins} = 250$, and the representative ISD for the 6566 minute coarsened sample has $\kappa_{\text{max}} = 0.2$ and $n\text{bins} = 350$. This results in a $\Delta \kappa/S_v$ of $0.11 \pm 10\%$, which is sufficient for comparison.
5.1.3. Three-Dimensional Reconstructions

Figure 5.6. Three-dimensional reconstructions of the Al-rich dendrites in Al-20wt%Cu during coarsening: (a) after 10 minutes (b) 1060 minutes (c) 6566 minutes, where the reconstruction box used in (a)-(c) is 1800 x 1200 x 470 μm. The Al-Cu eutectic is transparent, and the solid volume fraction for the samples is 46%. (d) $S_v^{-1}$ as a function of the cube root of coarsening time, for the three coarsened samples. Note, the error bars for (d) are on the order of the size of the points at ±1.2μm.
The three-dimensional microstructures of Al-20wt%Cu (46% solid volume fraction) isothermally coarsened for 10, 1060, 6566 minutes are shown in Fig. 5.6, along with the corresponding plot of the inverse surface area per unit volume, Fig. 5.6(d). To illustrate the increase in size scale of the structure during coarsening, the dimensions of the reconstruction box shown in Fig. 5.6 are held fixed; thus, only a portion of a much larger data set are shown. The excellent linear fit of the $S_v$ data indicates that the characteristic length of the microstructure scales with the cube root of time, following Eq. 2.4. Moreover, $S_v^{-1}$ increases by a substantial factor of four from ten minutes to 6566 minutes. It is important to note the dendrite seen in the two-dimensional micrograph of the ten minute sample, Fig. 5.1(b), is not apparent in the three-dimensional reconstruction, Fig. 5.21(a). This is because the dendrite stem is positioned diagonally through the reconstruction box and is hidden by other microstructural features, see Fig. 5.7(d) for further proof of this. The presence of this dendrite stem affects both the ISD and the IND for this coarsening time, as will be discussed below.

There is no evidence of the initial dendritic microstructure after 10 minutes of coarsening, as the structure becomes highly interconnected and globular, encompassing a mix of cylindrical-like bodies with other hyperboloids, each of which have some spherically-capped ends. Examining the full structures for these coarsening times, Fig 5.7, and applying a 50% transparency to the reconstructions further proves the initial dendritic microstructure is gone after 10 minutes of coarsening.
5.1.4. Interfacial Shape Distributions (ISDs)

Figs. 5.8(a)–5.8(c) show the evolution of the interface shape distributions (ISDs) during coarsening. In order to assess changes in the ISDs with coarsening time, the minimum and maximum values on the color bar are time independent, and the principal curvatures are scaled by $S_v$. If the system is coarsening in a self-similar manner, scaling the curvatures by $S_v$ should render the ISDs time independent.
Figure 5.8. Interface shape distributions of samples coarsened for: (a) 10 minutes (b) 1060 minutes (c) 6566 minutes. The ISDs with time independent and time dependent color bars look very similar, so the time dependent ISDs are not shown.
There are general observations one can draw from these ISDs. First, the distribution, or general shape of the ISD, is broad, and the peak probability is not high, both of which indicate that the fraction of area encompassed by the peak is not a significant fraction of the total interfacial area in the structure. The location of the peak remains at, approximately, $\kappa_2/S_v = 1$, which indicates $S_v$ is a very accurate measure of the magnitude of the curvatures in the structure. In more detail, almost all the surface patches have at least one positive principal curvature. Further, almost all the surface patches have positive mean curvature, which encompasses regions 1 and 2, see Fig. 4.6. In region 1, the shapes are elliptic and convex toward the solid, while in region 2, the interfaces are hyperbolic toward the solid, where the absolute value of $\kappa_2$ is greater than the absolute value of $\kappa_1$. This is consistent with the fact that these are dendritic structures embedded in a liquid matrix, and the definition of the curvatures used to calculate the ISDs implies that most of the structure should have positive mean curvature. Since the volume fraction of the solid is nearly 50%, this would not be expected based on volume fraction alone. For example, results from Kwon et. al. [22] show that bicontinuous structures produced following spinodal decomposition at a 50% volume fraction have an average mean curvature of zero. However, not all patches have both positive $\kappa_1$ and $\kappa_2$. This is because there are many instances where the solid bodies have undergone coalescence, thus increasing the probability for interfaces with negative Gaussian curvature, which would be found in regions 2 and 3.

As coarsening time increases, the peak of each ISD remains centered along the solid cylinder line ($\kappa_1/S_v = 0$), where Gaussian curvature is zero. Interestingly, this occurs without solid cylinders being present in the microstructures. The microstructure is
highly interconnected at all coarsening times and dominated by more globular structures. To clarify, the microstructure is a combination of cylindrical-like bodies and hyperbolic-shaped bodies, each of which have spherically-capped ends. Thus, these bodies have regions of interface with zero Gaussian curvature without actually being cylindrical in shape, which accounts for the peak location on $\kappa_1/S_v = 0$. As discussed above, the distribution of interface shapes is broad and the value of the peak probability is not high, and thus, the location of the peak does not necessarily translate to the actual morphology observed in the microstructure.

The tear-drop-shaped peak region seen in the ten minute structure is caused by the remnants of the microstructure present prior to coarsening. As seen in Fig. 5.7(d), there is a large dendrite representing approximately one-eighth of the total volume analyzed. The interfacial areas associated with the secondary arms of this dendrite lead to an elongation of the peak toward $\kappa_1/S_v = \kappa_2/S_v = 0$ or flat interfaces. A cross-section view of these arms is elliptical, which leads to nearly flat interface patches up to the tips of the arms. The tips of the secondary arms, as well as shapes with similarly capped ends, are spherical and thus represented in region 1. So, as coarsening proceeds, the secondary dendrite arms disappear, and thus, the elongation disappears.

The scaled ISDs at all coarsening times are very similar. The location and magnitude of the peak, and the general shape do not change significantly with coarsening time. The largest change is observed going from ten minutes to 1060 minutes of coarsening, and this is due to the disappearance of a primary dendrite stem. The ISDs for the two longest coarsening times are very similar. The changes in the ISDs evident
in Fig. 5.8 are much smaller than those observed when the initial structure is produced using directional solidification \([9, 17–19]\) and analyzed below. It is clear that there is no evidence of the structure breaking up into quasi-spherical particles, as this would imply an increase in probability along the \(\kappa_1=\kappa_2\) line. In this case, the apparent spheroidization evident in the two-dimensional micrographs shown in Fig. 5.1 is misleading.

To quantify the small changes seen in the ISDs, the fractions of interfacial area with various curvatures are determined, as shown in Fig. 5.9. There is an approximate
10% increase in interfacial area with positive mean curvature as coarsening time increases. The fraction of interfacial area with hyperbolic and parabolic shapes, as well as the fraction of interfacial area with positive Gaussian curvature, remain constant at approximately 50%. The small increase in the fraction of interfacial area with positive mean curvature indicates that the solid is becoming more convex with respect to the liquid as coarsening time increases. This is consistent with the drive of the system toward the surface energy-minimizing shape of a sphere. However, this change in positive mean curvature is quite small given that the overall size scale of the system has increased by a factor of four during coarsening.

5.1.5. Interfacial Normal Distributions (INDs)

In order to quantify the anisotropy of the structures, we examine the interface normal distributions (INDs), see Fig. 5.10. The far-hemisphere (negative), z-axis projections of the INDs are provided because the location of the peak value appears strongest in these projections and because it best displays the two-fold symmetry of the interfacial structure found after ten minutes of coarsening. The color bars in the INDs have fixed minimum and maximum values based on the strongest directionality observed in the three samples, which occurs in the ten minute sample.

The IND of the ten minute sample has a strong peak implying that the microstructure has two-fold symmetry, which would typically be observed in a plate-like structure. The three-dimensional reconstruction of the ten minute microstructure was split into two sections, one including the dendrite located in the lower left portion of the microstructure and one not including the dendrite. This yielded one IND with only the
Figure 5.10. Interfacial normal distributions of the samples coarsened for: (a) 10 minutes (b) 1060 minutes (c) 6566 minutes. The far-hemisphere (negative) $z$-axis projections are shown.
Figure 5.11. INDs for the 10 minute coarsened sample volume: (a) encompassing the dendrite, (b) remaining volume surrounding the dendrite.

two-fold symmetry peak(s), see Fig. 5.11(a) and one IND with an isotropic distribution of normals, see Fig. 5.11(b) which is very similar to the INDs for the later
coarsening times. Thus, we conclude that the dendrite is responsible for the peak(s) seen in the ten minute IND. As discussed above, the secondary arms of the dendrite elongate the peak region in Fig. 5.8(a) toward $\kappa_1/S_v = \kappa_2/S_v = 0$, or flat interfaces, which would account for the peak representing planar interfaces seen in Fig. 5.11(a). Because this dendrite disappears as coarsening time increases, the INDs for the later times are approximately isotropic and quantitatively, very similar. We find that INDs provide a particularly sensitive measure of the heterogeneity of the structure. During coarsening, the heterogeneity decreases and the structure becomes isotropic.

The changes in the INDs can be seen clearly by determining the fraction of interface with normals nearly perpendicular to the $x$-, $y$-, and $z$-directions [9]. Nearly perpendicular to a given direction is defined as any angle, $\theta$, within $\pm 10^\circ$ of perpendicular to the axis in question. These values are then divided by the total corresponding interfacial area of the microstructure to give the fraction of interface in this interval.

The fraction of interface nearly perpendicular to each direction for each coarsening time, shown in Fig. 5.12, is between 16% and 19%. This shows that despite the presence of the peak in the ten minute IND, the structures are, on average, isotropic in nature. This is most likely due to the equiaxed microstructure present prior to coarsening.

Finally, to assess whether the structures are breaking up into solid particles, the interconnectivity of the solid phase of the microstructures at each coarsening time is evaluated. Interconnectivity of the solid phase increases from 87% to 95% to 96% after ten, 1060, and 6566 minutes respectively. It should be noted that the solid regions not interconnected for the two later coarsening times are located at the edges of the reconstruction box and are most likely interconnected elsewhere in the sample. As
Figure 5.12. The fraction of interface nearly perpendicular to each direction as a function of coarsening time for the three coarsened samples. Nearly perpendicular in each direction is defined as \( \pm10^\circ \).

Stated above, the volume of data used for this calculation increases proportionally to the increase in characteristic length with coarsening time; thus, we can be confident we are capturing any size scale effects that might be present as coarsening time increases. The increase in interconnectivity as coarsening time increases is on the same order as the increase in positive mean curvature seen in Fig. 5.9. This indicates that the microstructure is decreasing interfacial free energy not by breaking up into solid particles but by increasing the length scale of the microstructure and decreasing the fraction of interfacial area with negative mean curvature. What is important about
these results is that the assumptions made in traditional two-dimensional models of dendritic coarsening [4, 5, 8, 13, 35] do not apply to these equiaxed systems because the morphologies are so different than those assumed in the models. More experiments are necessary to elucidate the actual mechanisms for coarsening in these systems.

5.2. Solidification Comparison

5.2.1. Directionally Solidified 42% Solid Sample

We compare these results to an initially directionally solidified Al-26wt%Cu microstructure, which corresponds to 42% solid volume fraction. Comparing similar solid volume fractions allows us to directly examine the effects of the initial microstructure on coarsening. In the ISDs (Figs. 5.13(c) [19] and 5.13(d)), the principal curvatures are again scaled by $S_v$ to eliminate effects caused by an increase in the characteristic length scale with coarsening time. The color bars in both the ISDs and the INDs (Figs. 5.13(e) and 5.13(f)) also have fixed minimum and maximum values, corresponding to the highest probability and strongest directionality respectively.

The characteristic length scale of the initially directionally solidified microstructures increases in a similar fashion to the equiaxed dendritic samples. In both cases, the characteristic length increases with $t^{1/3}$, and the amplitudes of the temporal power law are within 20% of each other, see Fig. 5.14. This occurs, however, without any evidence of self-similarity in the samples that are directionally solidified prior to coarsening.

The three-dimensional reconstructions, Figs. 5.13(a) and 5.13(b) show the system evolving from a highly complex microstructure to one dominated by solid cylinders and solid cylindrical-like shapes. The change in the ISDs, Figs. 5.13(c) and 5.13(d) are
consistent with these observations. The peak moves from region 1 in the ten minute sample and aligns with $\kappa_1/S_v = 0$ in the 3600 minute sample. The peak probability also increases by over a factor of four between the two coarsening times. This increase, along with the change of dominant shapes in the microstructure from solid convex shapes, such as those present at the tips of dendrites, to solid cylindrical-like shapes verify the lack of self-similarity in the microstructure. As reported by Kammer et. al. [19], this volume fraction was ultimately coarsened for over three weeks, with solid cylinders
removing the dominant interfacial shape in the microstructure, and there was no evidence of break up into solid particles.

These results differ greatly from the initially equiaxed dendritic microstructures. By comparison, no significant change in the morphology of the interfaces, other than the size-scale increase, is observed in these equiaxed structures. For example, the peak probability in the ISD for the directionally solidified structures increases with comparable magnitude to characteristic length with coarsening time and is over two times greater than the peak probability observed in any of the initially equiaxed structures. The distribution, Fig. 5.13(d), is also very compact, which indicates that the peak region is representative of a significantly larger portion of the interfacial area in
Figure 5.14. $S_{w}^{-1}$ as a function of the cube root of coarsening time for both solidification techniques. Note, the error bars are on the order of the size of the points at $\pm 1.2 \mu m$.

The structure, which is also not true of the ISDs for the initially equiaxed structures shown in Fig. 5.8. This is evident also in a visual inspection of the three-dimensional reconstructions, as solid cylinders dominate the 3600 minute directionally solidified structure. Because the evolution of morphology in the directionally solidified structure occurs in the $z$-direction, parallel to the initial solidification direction, it is evident that the initial morphology of the structure is the cause of these differences.

The far-hemisphere (negative), $x$-axis equal area projection INDs, Figs. 5.13(e) and 5.13(f) are provided because the location of the peak value appears strongest in these
projections and because it best displays the directionality that develops as coarsening time increases. It should be noted that in the ten minute microstructure, there is a strong four-fold symmetry, but due to the scale of the color bar chosen for the plot, this is not clear. During coarsening, a two-fold symmetry develops with a significant increase in the strength of the peak. This IND is significant because although there is a range of intensities, the locations of the probabilities span the length of the projection with the maximum probability located in the center. This indicates a strong preference for normals perpendicular to the $x$-direction, similar to the example of a hollow cylinder discussed previously. Thus, the IND is an illustration of a structure dominated by solid cylinders parallel to the directional solidification direction ($z$).

The interconnectivity of the Al-rich dendrites is also examined for the directionally solidified microstructure. The interconnectivity of the solid phase decreases from 84.7% to 13.5% to 12.1% after ten minutes, 3600 minutes, and three weeks of coarsening respectively. Although the lack of interconnectivity in the initially equiaxed dendritic microstructures could be attributed to sections of the structure intersecting the edges of the reconstruction box, and thus, they may be connected elsewhere in the structure, this is not the case in the initially directionally solidified microstructure. There are three or four independent solid bodies after ten minutes of coarsening for the directionally solidified structure, and as coarsening time increases, the number of independent solid bodies increases significantly, with at least 30 independent bodies in the three-week coarsened structure. This is attributed to the formation of independent solid cylinders, discussed above. Thus, in the directionally solidified structure, the decrease
in interfacial free energy is achieved by breaking up the structure into solid cylin-
ders, while in the initially equiaxed dendritic structure, this is attained by increasing
interconnectivity and decreasing the interfacial area with negative mean curvature.

5.3. 72% solid volume fraction

As described in Chapter 3, the Al-14wt%Cu sample was coarsened for 10, 1190, and
6960 minutes and then prepared for X-ray tomography. Because the images captures
through X-ray tomography require no alignment, many of the artifacts described above
are not present in these structures. Also, a much larger amount of z-direction data
can be analyzed with this technique. Thus, the structures can be characterized with
the same amount of data in all directions because the spatial resolution in the all
directions is the same (6 \( \mu m/px \)). The segmentation process is also simplified because
it is automated in IDL; therefore, the same procedure is applicable to every picture.

5.3.1. Three-Dimensional Reconstructions

Fig. 5.15 shows the three-dimensional reconstructions of the Al-14wt%Cu sample. This
corresponds to a solid volume fraction of 72%. There is no evidence of the initial den-
dritic microstructure after 10 minutes of coarsening. The solid is dominated by tubular-
like domains that are connected to other domains that have hourglass or hyperboloid-
type interfaces, some of which have spherically-capped ends. There is a significant
factor of four change in the length scale of the structures. The plot of \( S_v^{-1} \) versus \( t^{1/3} \)
can be seen below in Fig. 5.22 in Section 5.4. The increase in solid volume fraction in-
creases the amount of particle-particle interactions, so there are observably more solid
Figure 5.15. Three-dimensional reconstructions of the Al-rich dendrites in Al-14\textit{wt}\%Cu during coarsening: (a) after 10 minutes (b) 1190 minutes (c) 6960 minutes, where the full reconstruction for each coarsening time is shown. The Al-Cu eutectic is transparent, and the solid volume fraction for the samples is 72\%.
hyperboloid-type interfaces in this structure in comparison to the 46% solid structure in Section 5.1.

5.3.2. Interfacial Shape Distributions (ISDs)

Fig. 5.16 shows the ISDs for the 72% solid volume fraction. The ISDs are scaled by the characteristic length, but the color bar is time dependent, meaning it is not fixed by the highest probability found in the three samples. This shows that the 10 minute structure has a broad distribution of shapes with a lower probability than the longer coarsened samples. When the color bar is fixed by the highest probability, found in the 6960 minute structure, see Fig. 5.17, the distribution of shapes for the 10 minute coarsened sample contracts, and the most probable shapes are only half the maximum probability found during all stages of coarsening. The tear-drop-shaped peak region in the 10 minute structure can again be attributed to the dendrites, remnants of the microstructure present prior to coarsening. Because there is no evidence of dendrites remaining after 10 minutes of coarsening, the elongated peak region becomes a circular peak region.

In examining the interface patches that encompass the peak region, Specific Microstructure Location (SML) figures are created, see Fig. 5.18. The curvatures values of the peak region are colored red and displayed on the corresponding 3D reconstruction of the interfaces of the 1190 and 6960 minute microstructures. Because the peak value is large, there are many regions of the interface with these curvatures. The peak location in the ISD indicates solid cylinders should be present in the microstructure. However, this is not the case; instead, the peak represents cylindrical patches located on
Figure 5.16. ISDs for samples coarsened for: (a) 10 minutes (b) 1190 minutes (c) 6960 minutes. The ISDs are scaled by $S_v$, but the color bar is time dependent (not fixed).
Figure 5.17. Scaled and time independent ISDs for samples coarsened for: (a) 10 minutes (b) 1190 minutes (c) 6960 minutes.
Figure 5.18. SML figures for the two later coarsening times: (a) 1190 minutes (b) 6960 minutes. The peak region of the ISD is illuminated red on the microstructure. As is evident, the peak region does not represent specific interface shapes, but instead cylindrical patches on the interface.

To quantify the changes seen in the ISDs, the fractions of interfacial area with various curvatures are determined, as shown in Fig. 5.19. There is an approximate 10% increase in the positive mean and Gaussian curvatures as coarsening time increases. This corresponds to the increase in the amount of interfacial area that is convex toward the solid because the amount of interfacial area concave toward the solid (region 4 in the ISD), or with negative values of $\kappa_2$, remains constant. Also, the amount of interfacial area with hyperbolic shapes decreases by the same 10%. This is consistent with the drive of the system toward the surface energy-minimizing shape of a sphere.
Figure 5.19. The fraction of interface of specified curvatures as a function of coarsening time for the three coarsened samples.

Because this change is small with respect to the overall change in the length scale of the microstructure, it is evident that the interfacial free energy is decreasing by increasing the length scale of the system and decreasing the fraction of interfacial area with negative mean and Gaussian curvatures. This result is similar to what was found with the 46% solid samples, and it will be examined further in Section 5.4.

5.3.3. Interfacial Normal Distributions (INDs)

Fig. 5.20 shows the stereographic Interface Normal Distributions (INDs) of the 72% solid volume fraction. The far-hemisphere (negative) z-axis projection is shown for the
Figure 5.20. Stereographic INDs for samples coarsened for: (a) 10 minutes (b) 1190 minutes (c) 6960 minutes. The color bar is fixed for these INDs.
10 minute sample, while the near-hemisphere (positive) $z$-axis projections are shown for the 1190 and 6960 minute samples because the location of the peak value is strongest in these projections. For these samples, however, the peak is not important because the distribution is predominantly isotropic. Not only is the value of peak, found in the 6960 minute sample, very small, but the location of the peak(s) are not indicative of any specific anisotropy in the system. Thus, the samples are affected by the initial solidification technique used. Predominantly isotropic structures during coarsening were expected, and the INDs show that the structures are isotropic.

Although the dendrite seen in the 10 minute sample of the 46% solid structure caused two-fold peak(s) in the IND, this is not true with the 72% solid sample. This is because the amount of volume encompassing the dendrite for the 46% solid sample was significant (one-eighth the total volume of approximate 1 $mm^3$). This is not the case for the 72% solid sample. A significantly larger volume was analyzed ($> 8 \ mm^3$), which allows for the volume not encompassing the dendrite(s) to average out of the volume that does include the dendrite(s). Therefore, the effect of the dendrite(s) on the anisotropy, and the distribution of shapes for that matter, is not evident when scaling by the strongest directionality and highest probability respectively for all coarsening times analyzed.

5.4. Volume Fraction Comparison

The three-dimensional (3D) reconstructions of the Al-rich dendrites during isothermal coarsening for each solid volume fraction, 46% and 72% respectively, are shown in Fig. 5.21, and the corresponding plot of the inverse surface area per unit volume is
Figure 5.21. Three-dimensional reconstructions of the Al-rich dendrites in Al-20 wt%Cu after: (a) 10 minutes (b) 1060 minutes (c) 6566 minutes of coarsening, where the reconstruction box is $1800 \times 1200 \times 470 \, \mu m$, and Al-14 wt%Cu after: (d) 10 minutes (e) 1190 minutes (f) 6960 minutes of coarsening, where the reconstruction box is $1200 \times 1200 \times 1200 \, \mu m$. The Al-Cu eutectic is transparent, and the solid volume fraction for (a, b, c) is 46% and for (d, e, f) is 72%. The dimensions of the reconstruction boxes are held fixed for each volume fraction to illustrate the significant increase in size scale during coarsening; thus, only a portion of the full reconstruction is shown for the later coarsening times.

seen in Fig. 5.22. The excellent linear fit of the data for both solid volume fractions indicates that the characteristic length of the microstructure increases with the cube root of time, following Eq. 2.4. It is important to note that the different data collection techniques, i.e.-serial sectioning for the 46% solid samples and X-ray tomography for the 72% solid samples-have different advantages. Serial sectioning yields rectangular
3D reconstructions, with significantly more data in the $x$- and $y$-directions, while X-ray tomography yields cubic reconstructions, with equal amounts of data in all directions. Both data collection techniques are sufficient for the current analyses.

A general observation of the 3D reconstructions is that there is no evidence of dendrites remaining in the structures after ten minutes of coarsening. Fig. 5.21 shows that the Al-rich phase evolves into highly interconnected solid structure with a range of interfacial shapes. In particular, the solid is composed of tubular-like domains that are connected to other domains that have hourglass or hyperboloid-type interfaces, some of which have spherically-capped ends. Coarsening after ten minutes thus does

![Figure 5.22. $S^{-1}$ as a function of the cube root of coarsening time for the two solid volume fractions.](image-url)
not proceed by secondary arm disappearance described by the models in \([4, 5, 13, 35]\).

It is clear that a model that captures the details of the microstructure is necessary to predict the evolution of these complex structures. This volume fraction comparison will focus on the late stages of coarsening.

Fig. 5.23 shows the morphological evolution of the microstructures through the changes in interface shape distributions (ISDs). The curvatures are scaled by \(S_v\), and the minimum and maximum values of the color bar are fixed (for each solid volume fraction) for comparison purposes. If the microstructure is coarsening in a self-similar manner, scaling the curvatures by \(S_v\) should render the ISDs time-independent. The map detailing the locations of various interface shapes is given in Fig. 4.6.

A general observation is that the ISDs of a given solid volume fraction are very similar, despite the approximate factor of two change in the length scale of the system. Almost all the surface patches in the 46% solid structure have at least one positive principal curvature and have positive mean curvature because most of the nonzero probability is located in regions 1 and 2, see Fig. 4.6 [36]. This is commonly observed for dendritic structures surrounded by a liquid matrix. This is also the case for the 72% solid sample, although there is a shift of the distribution into region 3, hyperbolic surfaces with negative mean curvature. The distribution at this higher solid volume fraction is also more compact with a higher peak probability. These changes are consistent with an increase in solid volume fraction from 46% to 72%. As the solid volume fraction increases, there is more coalescence, resulting in an increased fraction of hyperbolic surfaces, regions 2 and 3.
Figure 5.23. ISDs of samples coarsened for: (a,b) 1060 and 1190 minutes, (c,d) 6566 and 6960 minutes. (a,c) represent the 46% solid structure and (b,d) represent the 72% solid structure.
Quantitatively, the fraction of hyperbolic shapes present in the microstructures has increased from $51\% \pm 2\%$ for the 46% solid samples to $57\% \pm 4\%$ for the 72% solid samples. This net increase of 6% can be added to a slight shift (3%) of shapes from region 2 to region 3 to result in a 9% total increase in the fraction of shapes in region 3 for the 72% solid samples. Thus, the increase in solid volume fraction results in a smaller amount of interfacial area with spherically-capped ends (region 1), or conversely, more negative mean and Gaussian curvature (region 3). The more compact distribution along with a higher peak probability in the 72% solid structure also indicates that there is a larger fraction of interfacial area in the structure represented by the peak region. Thus, a larger fraction of the interfacial area in the high volume fraction sample has cylindrical-like patches. However, since there is still considerable breadth to the ISD about the peak, it is clear that the interfacial morphologies in these structures are not cylinders. This was also proven through the SML figures seen in Fig. 5.18.

It is important to note that the small changes seen between the ISDs of the same volume fraction are due solely to sample-to-sample variations in the microstructure. X-ray tomography, performed on the 72% solid volume fraction, allows us to analyze a significantly larger volume than the serial sectioning technique. We are able break the structures into three smaller volumes and determine the variation in the resulting ISD with position in the sample. These tests reveal that the ISDs do in fact converge to the ones seen here, and that the variations observed in the scaled ISDs shown in Fig. 5.23 at different times are due to the variations in the microstructure from sample to sample.
Figure 5.24. Scaled genus calculations for both solid (s) and liquid (l) phases for: (a) 46% solid volume fraction, (b) 72% solid volume fraction. The error bars are ± one standard deviation. There are no error bars on the 46% solid structure for the liquid genus per volume since the data at this volume fraction was collected using the serial sectioning technique.

The scaled genus, $g_v S_v^{-3}$, for each coarsened sample is shown in Fig. 5.24. If the structures are self-similar, the genus per volume, $g_v$, scaled by $S_v^{-3}$ should be time-independent. Scaling by $S_v^{-3}$ also removes the effects caused by the increasing length scale with coarsening time. Both the solid and liquid phases are analyzed separately, yielding a scaled genus for each phase at each coarsening time. The solid phase can have both a maximum and minimum scaled genus due to the inability to determine how the solid is connected outside the sample volume, see DeHoff et. al. [10]. We thus determine the minimum scaled genus by assuming the solid structure is capped at the bounding box and the maximum genus per volume by assuming all the solid pieces touching the bounding box meet at an arbitrary point outside the box; this, in essence, creates handles or loops out of each solid piece that touches the side of the box. Thus,
we report the average of the minimum and maximum scaled genus, with the error bars encompassing the variation between the two numbers.

However, the error bars for the liquid phase are not calculated this way, since it is the matrix phase. Therefore, to provide an estimate of the effects of a finite sample size, we use the standard deviation from the average of the scaled genus taken from three different sections of a given microstructure, specifically for the 72% solid samples. We also determine the number of independent bodies per volume, as each independent body decreases the scaled genus by one. The size of the reconstruction box increases proportionally with increasing $S_v$ in order to assure that size scale effects are adequately captured as coarsening time increases.

The 72% solid volume microstructure exhibits a self-similar topology for both the liquid and solid phases, see Fig. 5.24b, as the average value of the scaled genus for each phase is independent of coarsening time. Since the scaled genus for the 46% solid samples show variations that are just outside one standard deviation, we cannot be certain that the topology of the solid-liquid mixture at this volume fraction is self-similar. This is because of the limited sample size associated with the serial-sectioning technique used to collect the data. However, the uncertainty displayed by the liquid scaled genii measured in the 72% solid samples (almost double) indicates that the differences observed in the 46% solid samples could well be due to sample variations, which would render the samples self-similar as well.

Because the solid phase is fully interconnected, not including the pieces touching the edges of the box, for both volume fractions, the scaled genus measures the number of handles per scaled volume. For example, the 46% sample has a solid scaled genus of
0.12, which implies that a cube of volume \((8.3S_v^{-1})^3\) would contain one tunnel or loop, making this region topologically equivalent to a torus. The 46% solid structures have almost a factor of five more handles per scaled volume than the 72% structures. The openness of the 46% solid structure permits handles to remain during coarsening. As the solid volume fraction increases, these handles disappear due to coalescence, thus decreasing the complexity of the interfacial topology, and scaled genus of the structure. The scaled genus of the liquid phase provides a measure of the number of tunnels or handles in the liquid. This is related to the ease with which fluid will flow through these structures and hence the permeability of the mush. Thus, we expect the 46% solid volume fraction samples to have a higher permeability than the 72% solid volume fraction samples.

5.5. In-Situ Measurements

5.5.1. Initial Three-Dimensional Reconstructions and ISDs

As described in Chapter 3, initially directionally solidified Al-26wt%Cu and Al-15wt%Cu, and initially equiaxed dendritic Al-14wt%Cu were prepared for in-situ X-ray tomography. The samples were held, at temperature, for up to 15 hours, while scans were collected at specific time intervals ranging from 2.5 - 7 minutes. This amounted to over 2 TB of data collected for analysis. Because we are looking to create movies of coarsening, real-time, it is very difficult to publish all the characterization completed. The images captured through X-ray tomography require no alignment, and the segmentation process is automated in IDL. The spatial resolution is the same for all experiments,
1.4 \( \mu m^3/\text{voxel} \). Examples will be given of the capabilities we have developed to examine these structures, as well as detailed interface dynamics calculations that we have completed.

Fig. 5.25 shows the evolution of the Al-rich dendrites for the directionally solidified Al-26wt\%Cu sample. The initial solidification direction is along the \( z \)-axis, which, in these images, is into the page. This structure corresponds to a 42% solid volume fraction. Each reconstruction is approximately \( 450 \times 450 \times 550 \mu m \). This represents approximately the largest square section in the \( x \)- and \( y \) directions because the sample is approximately 1 \( mm \) in diameter. It also represents approximately 50% of the data collected in the \( z \)-direction.

As discussed previously in Section 5.2.1, this solid volume fraction evolves into solid cylinders parallel to the initial solidification direction, which is evident by the long pillar-like structures forming through the length of the \( z \)-direction. Since this sample yields an approximate 50% solid volume fraction, it provides a comparison to the higher solid volume fraction sample also examined.

The time evolution of each subfigure in Fig. 5.25 shows the coarsening of dendrites by three of the four mechanisms described in Chapter 2, Fig. 2.2. Each colored arrow represents a different mechanism. The red arrows show examples of radial remelting, where the secondary or tertiary arms remelt, or shrink back, into the primary stalk or secondary arms of the dendrite. The blue arrows show arm detachment, and in this specific example, the arm disappears. This disappearance could be a sampling effect because it is occurring on the front face of the reconstruction volume. Thus, the arm may not actually disappear. The yellow arrows show coalescence, or joining, of the solid...
dendrites. The green arrows show hole formation and the subsequent disappearance of the hole. In essence, this is another form of coalescence, but it is distinct from the coalescence of the dendrite arms.

Fig. 5.26 shows the evolution of the liquid in initially directionally solidified Al-15wt%Cu. This corresponds to a solid volume fraction of 74%. Each reconstruction is approximately $550 \times 550 \times 550 \, \mu m$. This represents approximately 50% of the data collected in the $z$-direction. The liquid is displayed because the formation of a dominant liquid wall, spanning the length of the sample, and the persistence of the liquid droplets, as first reported by Mendoza et. al. [16], are very evident. It also contrasts Fig. 5.25 significantly.

The colored arrows each show a different mechanism occurring in the coarsening process. The red arrows denote topological singularities, or pinch-off events, that result in a liquid droplet. The blue arrows show pinch-off events not resulting in liquid droplets; they are breaks in the liquid channels that occur to decrease the energy of the system. The green arrows indicate holes that are disappearing. The yellow arrows show the formation of a liquid droplet and its subsequent shrinkage into the liquid wall. The pink arrows point to arms of the liquid wall shrinking into itself. The orange arrows, occurring only in the very late stages of coarsening, show a liquid droplet formation. It is evident that the increase in solid volume fraction has a dramatic effect on the mechanisms with which the system coarsens.

The corresponding ISDs for the microstructures shown in Fig. 5.26 are displayed in Fig. 5.27. The ISDs detail the transition of dominant shapes from solid convex or elliptic shapes (region 1 in the ISDs) to saddle- or hyperbolic shapes both convex and
(a) $t_{\text{elapsed}} = 3.83$ min
(b) $t_{\text{elapsed}} = 7.67$ min
(c) $t_{\text{elapsed}} = 11.50$ min
(d) $t_{\text{elapsed}} = 15.33$ min
(e) $t_{\text{elapsed}} = 19.17$ min
(f) $t_{\text{elapsed}} = 26.83$ min
(g) $t_{\text{elapsed}} = 30.66$ min
(h) $t_{\text{elapsed}} = 42.16$ min
(i) $t_{\text{elapsed}} = 53.66$ min
Figure 5.25. Three-dimensional reconstructions of the Al-rich dendrites in Al-26 wt% Cu. The change in each image is dependent on $S_v$. $S_v^{-1}$ increases by 2.5 $\mu$m per reconstruction. $t_{\text{elapsed}}$ represents the amount of time the microstructure has been coarsening. The change in length scale between the earliest (29.3 $\mu$m at 3.83 minutes) and latest (76.3 $\mu$m at 372 minutes) coarsening times is three-fold. This is a classic and beautiful example of solid dendrites coarsening.

concave toward the solid (regions 2 and 3 in the ISDs). The formation of secondary peaks, one representing liquid cylinders (from Fig. 5.27(g) on), identified with a white
(a) $t_{\text{elapsed}} = 2.57 \text{ min}$  
(b) $t_{\text{elapsed}} = 5.20 \text{ min}$  
(c) $t_{\text{elapsed}} = 9.20 \text{ min}$  
(d) $t_{\text{elapsed}} = 15.0 \text{ min}$  
(e) $t_{\text{elapsed}} = 22.50 \text{ min}$  
(f) $t_{\text{elapsed}} = 32.30 \text{ min}$  
(g) $t_{\text{elapsed}} = 45.0 \text{ min}$  
(h) $t_{\text{elapsed}} = 60.0 \text{ min}$  
(i) $t_{\text{elapsed}} = 78.10 \text{ min}$
(j) \( t_{\text{elapsed}} = 99.75 \text{ min} \)

(k) \( t_{\text{elapsed}} = 125.0 \text{ min} \)

(l) \( t_{\text{elapsed}} = 154.30 \text{ min} \)

(m) \( t_{\text{elapsed}} = 187.80 \text{ min} \)

(n) \( t_{\text{elapsed}} = 226.0 \text{ min} \)

(o) \( t_{\text{elapsed}} = 268.75 \text{ min} \)

(p) \( t_{\text{elapsed}} = 317.0 \text{ min} \)

(q) \( t_{\text{elapsed}} = 370.0 \text{ min} \)

(r) \( t_{\text{elapsed}} = 429.0 \text{ min} \)
(s) $t_{elapsed} = 494.10$ min  
(t) $t_{elapsed} = 565.50$ min  
(u) $t_{elapsed} = 643.20$ min

Figure 5.26. Three-dimensional reconstructions of the Al-Cu eutectic in Al-15wt%Cu. The change in each image is dependent on $S_v$. $S_v^{-1}$ increases by 2.5 µm per reconstruction. $t_{elapsed}$ represents the amount of time the microstructure has been coarsening. The change in length scale between the earliest (38.5 µm at 2.6 minutes) and latest (86 µm at 643 minutes) coarsening times is approximately two-fold. This is an example of the formation of liquid walls and liquid droplets at high solid volume fractions in these Al-Cu systems.

arrow, and one representing elliptic shapes that are convex (i.e.-liquid droplets: from Fig. 5.27(q) on), identified with a green arrow, are also evident.

Fig. 5.28 shows the evolution of interfacial velocity, in µm/sec, for initially equiaxed dendritic Al-14wt%Cu. This corresponds to a 72% solid volume fraction. Each color bar is specific to the microstructure; thus, it is not fixed for the duration of coarsening. The velocity is calculated as described in Chapter 4, Section 4.5, and then displayed on the interpolated mesh of the initial microstructure. Each velocity-colored interface represents an increase of 2 µm in the characteristic length ($S_v^{-1}$). As an example, in Fig. 5.28(a) the velocity was calculated as the difference in the microstructure between
2.5 and 5.0 minutes of coarsening because $S^{-1}$ increased by 2 $\mu m$ in that length of time.
What is perhaps most interesting for this structure is that liquid droplets form not by one topological singularity, as seen with the directionally solidified Al-15wt%Cu
Figure 5.27. Corresponding ISDs for the coarsening of Al-15wt%Cu. This is an example of how an ISD changes from being dominated by solid convex shapes to being dominated by solid and liquid hyperbolic shapes with secondary peaks forming to show the existence of liquid cylinders and liquid droplets.

structure. Instead, they form by two topologically singularities. Two bridges in the liquid phase join together, and then each side pinches off within a few time steps of each other, see Figs. 5.28(e) through 5.28(g) for the joining of the liquid bridges and Figs. 5.28(j) through 5.28(m) for two different liquid droplet formations by two separate pinch-off events. What is also interesting about this structure is the absence of the liquid wall dominating the reconstruction volume. This is most likely due to the solidification procedure prior to coarsening. There is not a significant change in the distribution of shapes in the samples (72% solid volume fraction) produced with equiaxed techniques prior to coarsening, see Section 5.3. This is in stark contrast to the samples produced through directional solidification (74% solid volume fraction), where the dominant shapes change from convex solid shapes to hyperbolic shapes both convex and concave toward the solid, which represents the liquid wall, and secondary peaks.
(a) $t_{elapsed} = 2.5 \text{ min}$  
(b) $t_{elapsed} = 7.5 \text{ min}$  
(c) $t_{elapsed} = 12.5 \text{ min}$  
(d) $t_{elapsed} = 15 \text{ min}$  
(e) $t_{elapsed} = 22.5 \text{ min}$  
(f) $t_{elapsed} = 27.5 \text{ min}$  
(g) $t_{elapsed} = 37.5 \text{ min}$  
(h) $t_{elapsed} = 45 \text{ min}$  
(i) $t_{elapsed} = 57.5 \text{ min}$
Figure 5.28. 3D reconstructions showing the interface colored by velocity ($\mu m/sec$) of Al-14wt%Cu (74% solid volume fraction). $t_{\text{elapsed}}$ represents the amount of time the microstructure has been coarsening. The increase in $S_v^{-1}$ from the earliest (33 $\mu m$ at 2.5 minutes) to the latest (75 $\mu m$ at 253 minutes) coarsening times is over two-fold. Note: The latest time is not shown.

representing liquid cylinders and liquid droplets, see Fig. 5.27 for this transition. This is further proof that the initial solidification technique and the microstructure present prior to coarsening have a significant impact on the evolution of the microstructure during coarsening.
There are many other sets of data, showing everything from mean- and Gaussian-colored interfaces to different views of the same microstructure, to 3D reconstructions of every time step for these three microstructures as well as an equiaxed dendritic Al-20wt%Cu structure.

From these initial studies, we decide to focus on two specific coarsening times for each solid volume fraction. The time between the two steps is calculated as the necessary spatial and temporal resolution to adequately represent the velocity of the features in the microstructure. For example, if the velocity observed is 0.01 $\mu m/sec$, and the time elapsed between steps is 900 sec, then $(velocity) \times (time \ elapsed) = 9 \mu m$. With a spatial resolution of 1.4 $\mu m^3/voxel$, this amounts to 5-7 voxels representing the velocity of the features, which is an excellent representation of these features. It is important though to recognize that velocities moving much slower than this example (i.e. those very close to zero) would not be determined accurately.
5.5.2. Four-Dimensional Data Analysis

As discussed in Chapter 4, there are several quantities that could help elucidate the interface dynamics during coarsening. Previously, the principal curvatures, $\kappa_1$ and $\kappa_2$, were used to characterize the interface, ex-situ, during coarsening. Thus, we will focus on them as well, and initially examine their relationship to the velocity of the interface. We will attempt to answer whether specific shapes move in certain, predictable ways, as well as attempt to elucidate the effect of mean and Gaussian curvature on the dynamics of the interface.

For each of the following calculations, the time elapsed between coarsened microstructures, $\phi_i$ and $\phi_f$ respectively, is approximately 900 sec. Also, the same point in time for the coarsening process is observed for each microstructure. Therefore, the initial $S_i^{-1} = 50-60 \mu m$, and the change in $S_f^{-1}$ is $< 2 \mu m$. This allows for comparison across microstructures because, on average, coarsening is happening at similar rates.

5.5.2.1. Preparation for Analysis. Fig. 5.29 shows the specific portion of the microstructure ($350 \mu m^3$) for the 42% solid volume fraction used for this analysis. These figures qualitatively show the relationship between $\kappa_1$, $\kappa_2$, and $V$. The microstructure is colored by different curvatures and the velocity to ensure that the transition between different values of curvature is smooth, making the calculations of the derivatives less noisy, as well as to illustrate the changes between the two microstructures during this time.

Figs. 5.29(a) and 5.29(b) show the interface locations of the two microstructures. The red arrows point out the creation or destruction of hyperbolic-type interfaces. In other words, two of the three arrows show coalescence of the solid. The third shows
a hyperbolic region becoming a near-planar interface. The green arrows point out the loss of high positive curvature regions. In this specific example, the interfaces are encompassing the solid. The interfaces colored by $\kappa_1$ and $\kappa_2$, Figs. 5.29(c) and 5.29(d), as well as the mean- and Gaussian-colored interfaces, Figs. 5.29(e) and 5.29(f), show...
how the curvatures are distributed in the initial microstructure. Thus, the initial microstructure is dominated by positive mean curvature and (both positive and negative) Gaussian curvature near zero. This translates to positive, near zero and predominantly
negative regions of $\kappa_1$ and almost all positive regions of $\kappa_2$. The velocity-colored interfaces, Fig. 5.29(g), show how the interface locations, and therefore the curvatures, are changing with time. Velocity is defined with its normal pointing into the solid; thus, positive velocity indicates that the solid region is shrinking into itself and negative velocity represents regions pushing out of the solid (or into the liquid). High curvature
regions are moving faster, as expected. This is pointed out, for example, by the black arrows showing that the highest positive mean and Gaussian curvatures correspond to some of the largest positive velocity regions, and the white arrow shows a region where large negative mean and Gaussian curvature correspond to a large negative velocity region.

Fig. 5.30 shows the specific portion of the microstructure (300µm³) of the 74% solid volume fraction microstructure used to create the 4D probability plots. The initial and final microstructures, Figs. 5.30(a) and 5.30(b), display the change in the interface locations. In this case, the interfaces encompass the liquid phase. The red arrows show high curvature regions that are shrinking into themselves, while the green arrows point out topological singularities. The initial microstructure is then colored by mean and Gaussian curvatures, Figs. 5.30(c) and 5.30(d), and velocity, Fig. 5.30(e). The white arrows in these figures point out the same high curvature regions previously pointed out
with the red arrows. Because the interface encompasses the liquid, the mean curvature is negative (instead of positive) and the Gaussian curvature is (still) positive, with negative velocity because, as defined, it is traveling into the liquid. Although not pointed out with an arrow, the topological singularities (indicated with green arrows in Figs. 5.30(a) and 5.30(b)) have both negative mean and Gaussian curvature and negative velocity. The red arrows point out regions of equal and opposite velocity, which will become important below.

5.5.2.2. Four-Dimensional Contour Plots. Fig. 5.31 shows 2D contour plots of $V$ with respect to $H$ for both solid volume fractions, along with the corresponding 4D semi-transparent probability plots. The distributions are not identical because the binning is not the same in the $\kappa_1$ and $\kappa_2$ directions. In general, we observe a similar peak distribution and location in both. For both samples, the surface average of $H$, $< H >$, is located in the peak region (or average of the two peak regions for the case of the 74% solid sample). In addition, the peak crosses $V = 0$ axis at approximately this value of $< H >$ (0.01 $\mu m$ for the 42% solid sample, and $-0.01 \mu m$ for the 74% solid sample). The highest probability of the peak is approximately half an order of magnitude higher for the 42% solid sample than for the 74% solid sample. This would seem to indicate that the amount of interaction between interfaces with similar $H$ is higher in the 42% solid sample because the probability of finding specific velocities associated with them is higher. The distribution of velocity has an almost linear correlation, which indicates that the interaction between $V$ and $H$ is moderately coupled. Although there is also an almost linear relation between $V$ and $H$ for the 74% solid sample, see for example the peak region, the slope is approximately
Figure 5.31. 2D contour plots for 42% solid and 74% solid representing (a,b) $V$ vs $H$. (c,d) are the corresponding 4D semi-transparent probability plots. The plots are only qualitatively similar because the binning of data in the $\kappa_1$ and $\kappa_2$ directions are different.
two times greater. This indicates that for a specific value of mean curvature, there is a large range of interfacial velocities, and very small changes in $H$ cause large changes in velocity. Thus, the dispersion of velocity in this sample is higher and the coupling is not as strong. Further, predicting how specific curvatures move with time appears to be much more straightforward for the 42% solid volume fraction.

Because mean curvature is only part of what characterizes an interface in three dimensions, it is difficult to understand how the distribution of probable velocities relates to $H$. This is why we proceed to three dimensions to examine principal curvatures with respect to velocity.

Fig. 5.32 shows the 4D semi-transparent probability contour plot for the 42% solid volume fraction. There are five isosurfaces created at increasing probabilities as indicated by the different colors in the color bar. The highest probability, the red peak region, is $\frac{1}{3}$ of the maximum probability for this structure. Fig. 5.32(d) shows the representative ISD for this sample, which is exactly what was observed using the standard 2D techniques described in Section 4.2.

In examining this plot further, the high probability (red) region of the distribution is predominantly located in the $\kappa_1 > 0, \kappa_2 > 0, V > 0$ quadrant of the plot, see Fig. 5.32(b). This indicates that the velocities of convex solid shapes are positive, which is expected because the curvature of these regions is decreasing in magnitude to decrease the energy of the system. When the velocity goes negative in this peak region, it is due to $\kappa_1$, which changes sign or is near zero, while $\kappa_2$ is still positive, but closer to zero. This is representative of all parts of the dendrites except the tips. The dendrites are growing into the liquid, which makes the velocity of these regions
Figure 5.32. 4D semi-transparent probability contour plot of the Al-26wt%Cu sample comparing $\kappa_1$ (along $x$), $\kappa_2$ (along $y$), and $V$ (along $z$).
negative. In examining where $\kappa_1 = 0$ ($K = 0$), or solid cylindrical-like interface patches, there is a large dispersion of velocities, see Fig. 5.32(c). In other words, higher values of $\kappa_2$ correspond to large, positive $H$, and have positive velocities, while values of $\kappa_2$ closer to zero correspond to small, positive $H$ regions, and have negative velocities. The dispersion closer to zero is moderate in these regions because as the curvature gets closer to zero, the velocity is sometimes positive and sometimes negative. This indicates that the diffusional interactions between these shapes will determine whether or not they will grow or shrink.

Fig. 5.33 shows the 4D semi-transparent probability contour plot for the 74% solid volume fraction. Five isosurfaces are created at increasing probabilities as indicated by the color bar. The highest probability, the red peak region, is $\frac{1}{2}$ the maximum probability observed in this structure. Note that the probabilities in this structure are much smaller than what was observed for the 42% solid sample. This indicates that the correlation between these three features is not as significant as it is for the 42% solid volume fraction. Fig. 5.33(d) shows the ISD for this structure.

In observing the distribution, the general shape of the highest probability (red) region is similar to what was observed for the 42% solid sample. Fig. 5.34 shows a solid, instead of semi-transparent, 3D representation of the peak region through the three highest or most probable isosurfaces, which is why it is a blue-green color. The general shape, elliptic-like with an approximate circular cross-section, of the peaks is very similar. There are two main differences between the peaks, however. First, the 42% solid volume fraction peak clearly has more positive velocity than negative. The 74% solid volume fraction peak is very close to symmetric about zero velocity.
Figure 5.33. 4D semi-transparent probability contour plot of the Al-15wt%Cu sample comparing $\kappa_1$ (along $x$), $\kappa_2$ (along $y$), and $V$ (along $z$).

Figs. 5.34(b) and 5.34(d) show this most clearly. Thus, there is a general drive for the 42% solid sample to decrease higher positive curvature regions because there is, on average, a positive velocity for the structure. There is no such drive, only as indicated
Figure 5.34. Solid representation of the peak (first three isosurfaces) of the probability distribution for both volume fractions.
by the peak region, for the 74% solid sample because the velocity of peak region is, on average, zero. Second, the slope of the peak, specifically referring to $V$ with respect to $\kappa_1$ is very close to one for the 42% solid sample (see Fig. 5.34(a)). The slope of the peak for the 74% solid volume fraction is approximately two (see Fig. 5.34(c)). This indicates that for a specific value of $\kappa_1$, there is almost double the range of possible velocities for that curved interface in the 74% solid volume fraction than in the 42% solid volume fraction. Thus, the dispersion of velocity for a specific curvature increases as solid volume fraction increases.

As mentioned above, the highest probability region in the 74% solid samples is almost centered about zero velocity. This would seem to indicate that there should be equal and opposite velocities in a significant part of the microstructure. In examining the velocity-colored interfaces, we see that several shapes located close to each other in the microstructure have equal and opposite velocities, specifically the liquid wall spanning the sample volume, and then regions of interface that border what would be convex and cylindrical-like solid shapes (see the red arrows in Fig. 5.30(e)). Thus, we can say that only regions in close proximity to each other are actually communicating with each other. Further, this would imply that the diffusional distance has decreased with increasing solid volume fraction. The secondary peak formation, not only evident in the ISD but also in this 4D semi-transparent probability plot, would also indicate that the interfacial shapes encompassing these regions, i.e.,-liquid cylindrical shapes and planar-like shapes, are not communicating because they have their own distribution of shapes and velocities. Thus, when the solid volume fraction increases, the diffusional
distance gets shorter, the coupling gets weaker, and therefore the communication and interaction between shapes gets smaller.

5.5.2.3. Preliminary 2D Contour Plots. Preliminary 2D contour plots of the relationship between any two of the following, $H, K, V, \dot{H}, \dot{K}, V_{11}, V_{22}$, have also been completed. When the peak probability is extremely high, the log of the probability is taken. An example of these plots is shown below. They are included for completeness, but will not be discussed because further analysis using 4D semi-transparent probability plots is still necessary.
(a) 74% solid

(b) 42% solid

(c) 74% solid

(d) 42% solid
Figure 5.35. Various 2D log probability plots for both coarsening times.
CHAPTER 6

Collaborations

6.1. Morphological Analysis of Pores in Directionally Freeze-Cast Titanium Foams

This collaboration was conducted with fellow Northwestern Master’s student, Jessica C. Li, who worked for Prof. David C. Dunand.

Metallic foams have an interesting combination of properties, such as high specific strength and stiffness when incorporated into sandwiches, and high gas permeability with high thermal conductivity. This makes them useful in low-weight structural applications, filtration, battery electrodes, and acoustic damping [37]. Titanium-based foams, in particular, also combine the advantages of outstanding mechanical strength with low density, high corrosion resistance, and surface oxide biocompatibility, which make them especially promising for use in medical implants as a bone replacement material [38–41]. Thus, it is of great interest to create titanium foams which exhibit the same aligned, elongated pore architecture as bone, which gives it both its structural and mechanical anisotropy.

Directional freeze-casting is a method which relies on directional solidification to create aligned pores in ceramics [42–46] and, recently, in titanium [47]. First, a liquid, usually water, is mixed with solid powders to make a slurry. The slurry is then subjected to directional solidification so that the porous structure is determined
by the growth of the solid ice crystals, rejecting the powders to the interdendritic space. After solidification, the structure is freeze-dried, sublimating the ice out of the sample, leaving large aligned, elongated pores separated by walls of lightly bound solid powders, corresponding respectively to the dendritic and interdendritic regions. These powders are finally sintered to create dense walls separating the pores.

X-ray tomography has been used previously to visualize ice crystals in the fields of food science and glaciology [48–52]. For instance, directional solidification of ice into meat was studied using tomography, but the information was not used to create 3D reconstructions [52]. A more comprehensive study analyzed the microstructural evolution of snow in three dimensions, over time, while holding temperature constant, [51] calculating porosity, specific surface area, anisotropy, and curvature distribution of the snow crystals. Optical and x-ray tomography have also been used to create reconstructions of soap foams and to study the individual cell shapes of the foam [53,54]. In the field of metallic foams, tomography has been used to study deformation and yield mechanisms during tensile and compressive testing and for cell size and shape characterization [55–58].

The present study quantitatively characterizes the structure of porous titanium foams created by directional freeze-casting and sintering of titanium powders of two different sizes. The calculations are performed on three-dimensional foams reconstructed from two-dimensional tomography data to determine pore interconnectivity, inverse surface area per unit volume, pore volume fraction, interface shape distributions, as well as interface normal distributions. This analysis is useful both for understanding the structure of the metallic foam and how it compares to bone, and for investigating
the dendritic solidification of water slurries. To our knowledge, it is the first time these techniques have been used to study metallic foams produced using this technique.

6.1.1. Experimental Procedure

Unalloyed titanium powder with an average particle size of $< 20 \mu m$ was procured from Atlantic Equipment Engineers (Bergenfield, NJ) and will be referred to as the coarse powder. Unalloyed titanium powder with average particle size of $10 \mu m$ was purchased from Phelly Materials Inc. (Bergenfield, NJ) and will be referred to as the fine powder. A titanium foam is created from each of these powders using the directional freeze-casting process.

A 22$vol\%$ Ti slurry is made by mixing 3.9 g of titanium powder with 3 mL of vacuum degassed water containing 0.2$wt\%$ agar (Eden Foods, Inc., Clinton, MI). Agar is used as a binder preventing powder collapse after ice removal. The slurry is then poured into a cylindrical glass vessel with an inner diameter of 13 mm, a height of 38 mm, and a thickness of approximately 1 mm. The vessel is placed in a freezer, with its flat bottom surface in direct contact with a copper block, which has been cooled to 268 K. All other surfaces of the vessel are insulated with polystyrene foam to induce directional solidification of the slurry. The vessel is kept in the freezer for at least three hours to ensure complete solidification of the ice. Experimental measurement of the average solid-liquid interface growth velocity is $3.0 \pm 0.2 \mu m/s$ ($n = 3$).

The ice in the solidified ice/titanium billet is then sublimated under a 7.4 Pa vacuum at 233 K for 24 hours. This results in a porous titanium powder preform which is sintered under vacuum ($< 5.6 x 10^{-6}$ torr) at 1273 K for 2 hours and then at 1423 K for
7.75 hours. From the two resulting foams, one from each powder size, approximately-rectangular specimen, 4 x 4 x 8 mm, are cut in preparation for tomography. The specimen is taken from the center of the billet, approximately 1 cm from the top and bottom surfaces. Multiple specimens are cut from this area, such that the tomography specimen does not contain any of the billets original outside surfaces and far from the cylindrical billet surfaces. A total of 5 x 9 = 45 contiguous 300x magnification optical micrographs are used to determine pore size in material adjacent to the tomography sample.

The x-ray tomography is performed at the Advanced Photon Source (APS), at the DND-CAT 5-BM-C beamline at Argonne National Laboratory. A bending magnet is used to deliver the synchrotron x-ray beam at an energy of 45 keV. The x-ray image is created on a cryo-cooled CCD camera through a 4x objective. A resolution of 6µm/pixel is used, which creates a 7 mm objective. The tomography reconstructions are then carried out on a 16 node Linux cluster using filtered back projection techniques. These two-dimensional images are then segmented to create binary images, and three-dimensional reconstructions are generated and used for the quantitative measurements.

After tomography, the specimen closed porosity is determined by helium pycnometry. The total porosity is determined using the Archimedes method, which is performed in deionized water after coating the sample in a thin layer of grease to prevent water infiltration. From these two porosity values, the open porosity is calculated.
6.1.2. Analysis

The procedure for analyzing this system is specified in Chapter 4. As a note, in this analysis, stereographic INDs are used.

6.1.3. Results and Discussion

Fig. 6.1 shows optical micrographs of polished cross-sections of the two samples. Surfaces parallel to the freezing direction clearly show aligned, elongated pores, resulting from the growth of ice dendrites during the directional freeze-casting process. These will be referred to as macropores. Surfaces perpendicular to the freezing direction indicate that the ice dendrites grow as plates, not as needles, as expected from literature [44, 59, 60]. The plates show various orientations in the plane, though there are small groups of parallel plates corresponding to grains, indicating there is no preferred growth orientation for the ice crystals in the plane perpendicular to the main ice growth direction that is visible in two dimensions. Since the pores are planar, there is one dimension in which the pores are much smaller, and this dimension is used for the pore width measurements.

Visual comparison of the micrographs for the two foams with two different powder sizes shows that while there is variation within each image, the foam made from the fine powders seems to have narrower macropores. Measurements on cross-sections reveal that the fine- and coarse-powder foams have pore widths of approximately 50 and 61 µms, respectively. In addition to the macropores caused by the ice dendrites, micropores are visible in the titanium walls in all four images. These micropores are due to incomplete sintering between the individual titanium powders. In addition to
causing micropores, incomplete sintering leads to surface roughness on the titanium walls, as illustrated in Fig. 6.2, where individual titanium powders are clearly visible. The inset of Fig. 6.2 shows necks between two adjacent titanium powders, a clear indication of incomplete sintering.

Helium pycnometry measurements reveal both samples have zero closed porosity to within the large experimental error due to the small sample size: 3.2 ± 5.5% and 1.6 ± 6.0%, for the fine- and coarse-powder billets, respectively. The total porosities, measured by the Archimedes method, for the fine- and coarse-powder billets are 41.4 ± 0.8% and 44.6 ± 0.6%, respectively, and are assumed to be fully open.

Fig. 6.3 shows the three-dimensional reconstructions of the two foams. It is apparent that the reconstructed cross-sections visible in Fig. 6.3 are generally similar to the experimental two-dimensional optical micrographs of cross-sections shown in Fig. 6.1. However, while the dendritic macropores are well-captured by the reconstruction, the micropores are poorly represented, as expected given the resolution of the tomography images is 6 μm/pixel. Ideally, any feature should be represented by no less than five pixels; thus, features such as the micropores that are less than 30 μm are poorly or not at all resolved. From Figs. 6.1 and 6.2, it is clear that the micropores in each foam are on the order of the initial titanium powder sizes, and thus either too small to be reconstructed, or on the same order of the resolution, so that they are represented in the reconstruction, but likely not accurately. Nevertheless, these reconstructions are, to our knowledge, the first rendering of directionally freeze-cast foam structures in three dimensions, and provide new insights into the structure of the highly anisotropic macropores produced by the ice dendrites.
Figure 6.1. Optical micrographs of titanium foams: (a and b) for fine powders (c and d) for coarse powders. Cross-sections are parallel (a and c) and perpendicular (b and d) to the main temperature gradient direction.
Figure 6.2. Scanning electron microscopy (SEM) image of the parallel cross-section of a macro-pore in titanium foam created by directional freeze-casting of coarse powders. Roughness and variation in curvature of the titanium walls are clearly visible at the scale of individual powders, and reflect the partially sintered state of the powders. Insert higher magnification SEM image showing partially-sintered powder with ridges.

From these reconstructions, the inverse surface area per unit volume is calculated as $S_v^{-1} = 48 \, \mu m$ for the foams created with the fine powder, and $S_v^{-1} = 42 \, \mu m$ for the coarse-powder foam. For comparison, image analysis of transverse cross-sections resulted in pore widths of 50 $\mu m$ and 61 $\mu m$, respectively, for the two foams. While both measurement methods are relevant to the size of the dendritic macropores, they should be interpreted differently. The image analysis technique is a two-dimensional measure, so it is an accurate measure of pore widths perpendicular to the section plane. Because $S_v^{-1}$ is a three-dimensional measure, it better represents the average size scale of all the features present in the foams. Also, the image analyses are performed on a section of the billet adjacent to the volume used for tomography at a shared surface, not on the tomography samples themselves. It has been previously shown that in these
Figure 6.3. Three-dimensional reconstructions of titanium foams: (a) for the fine powder (b) for the coarse powder. To highlight the pore volumes, the titanium is transparent and the pores are shown. The pore volume fraction for the samples are 52% and 63% for (a) and (b) respectively. The main ice growth direction is along the z-axis.
directionally freeze-cast titanium structures, pore width varies with distance from the heat sink [47]. Finally, Fig. 6.1 shows that pore width can also vary at the same distance from the heat sink.

The pore volume fractions differ significantly between the Archimedes and reconstruction measurements: 41.4 and 52% for the fine-powder foams and 44.6 and 63% for the coarse-powder foams. It is likely that this discrepancy is due to the resolution problem discussed earlier. It might also be due to varying pore volume fractions within the samples. Archimedes data is taken on a larger portion of the billet, so this value is a more accurate measure because it averages local variations. The three-dimensional reconstructions are confined to a smaller volume, a volume of approximately $8mm^3$ is reconstructed here, compared to the billet’s $62mm^3$ volume; therefore, it cannot provide the same averaging of data. Further, the long dimensions of the macropores are likely greater than the size of the tomography section leading to further inaccuracies.

The interconnectivity for the pore structures is also calculated and found to be 99.93% for both foams. This indicates that nearly all of the porosity within the reconstructed volumes is open porosity, in agreement with the pycnometric results.

Figs. 6.4(a)-6.4(b) show the interfacial shape distributions (ISDs) for the two foams in this study. Two important features of the ISDs are the color bar and the axes of the plot. First, the minimum and maximum values of the color bar are fixed so that any differences in peak probability are clearly visible. Second, the principal curvatures shown on the axes are scaled by the characteristic length scale, $S_v$, to eliminate effects caused by a difference in the length scale due to varying powder sizes and pore volume fractions.
Figure 6.4. Interface shape distributions of titanium foam samples created from: (a) a fine powder, (b) a coarse powder.
Two general observations can be drawn from these ISDs. First, the distributions, in both cases, are broad relative to $S_v$, which indicates a significant variation in the sizes of the pores in the structure. This can be explained by the fact that there are two different length scales in the foams: one corresponds to the dendritic, plate-like macropores and the other corresponding to the equiaxed, closed micropores. Because the size scale of these micropores is on the same order as the resolution of the images, it most likely corresponds to the regions of small probability (purple) in both ISDs. Simply because of the small size scale of the micropores, and lack of spacial resolution used in the x-ray tomography technique, curvatures of $|\kappa/S_v| > 2$ are probably not adequately reconstructed and therefore an estimate at best. Second, both ISDs reside predominantly in Regions 2 and 3, which encompass saddle-shaped or hyperbolic interfaces. This corresponds directly with the roughness of the titanium walls caused from partially sintered individual powders. Almost all the surface patches have at least one negative principal curvature, $\kappa_1$, which is a result of the fact that over 75% of the surface patches have negative Gaussian curvature. This measure is comparable to what has been previously observed by Jinnai et. al. [61, 62] for trabecular bone microarchitecture, indicating that the processing technique used here could provide porous metallic implants that mimic bone with respect to distributions and percentages of curvatures in the microstructure.

Comparing both ISDs, several observations can be made. The fine-powder foam has a very well-defined peak whose center is located close to $\kappa_1/S_v = \kappa_2/S_v = 0$, indicating a higher probability of near-planar or flat interfaces in the microstructure. This corresponds to the plate-like, titanium walls separating the pores produced by the
directional solidification. The distribution is also symmetrically located about the line $H = 0$ which is also a defining feature of the trabecular bone mentioned above [62] and other bicontinuous structures [22]. The coarse-powder foam, on the other hand, does not exhibit as strong a peak as the fine-powder foam, and the center of its peak is located in Region 3. The reason for the weaker peak is likely related to the degree of sintering. Assuming the ice dendrites grow identically with fine and coarse powders, the titanium walls between the ice dendrites should initially be the same width for each foam. However, because this width is not much larger than the powder size, the powder size can significantly effect how well it packs into the interdendritic space during solidification, with the packing of the fine powders expected to be tighter. The improved initial packing and the increased driving force for sintering associated with the smaller powders then reduces the microporosity and the wall roughness in the sintered foam. This is supported by Fig. [6.1] which shows the fine-powder foam displaying fewer micropores and smoother, more well-defined titanium walls. By contrast, the coarse powders did not sinter as well, because of looser initial packing and lower driving force for sintering, resulting in titanium walls with more roughness and higher microporosity. Because ISDs are local measurements, the roughness in the walls may hide the overall planar structure present in the foam, resulting in a peak that is both weaker and shifted away from the line $H = 0$ and from the origin ($\kappa_1/S_v = \kappa_2/S_v = 0$).

To quantify preferential directionality in the titanium foams, we examine interface normal distributions (INDs), see Fig. [6.5]. The near-hemisphere projection is provided for the fine-powder foam and the far-hemisphere projection is provided for the coarse-powder foam because the location of the individual peak values appears strongest in
Figure 6.5. Interface normal distributions of titanium foams formed with:
(a) a fine powder, (b) a coarse powder.

these projections. Because the results are qualitatively the same whether viewing the
near- or far-hemisphere projections, it is important to use the hemisphere that contains
the peak probability when comparing different structures. The $z$-axis is chosen as the
projection axis because it best displays the planar interfaces located in both structures.
The minimum and maximum values of the color bars in the INDs are fixed based on
the strongest directionality that is observed in the fine-powder foam.

As a general observation, there is a significant distribution of normals surrounding
the circumference of both INDs. In an ideal case, this would be representative of a
perfect cylinder parallel to the projection axis, where the IND would reveal a thin stripe
of equal probability encircling the outside of the projection. In the present case, it is
representative of the plate-like macropores parallel to the projection axis. The normals
to the interfaces of these macropores are oriented randomly in the $x - y$ plane but are still perpendicular to the solidification direction, $z$. Thus, the spread of probabilities is related to the imperfect alignment of the plates themselves, but the location of the probabilities on the circumferences of the INDs indicate interfaces parallel to, or, equivalently, normals perpendicular to the growth direction, which results from the directional solidification process used to produce the samples. The two peaks located 180 degrees apart in the IND for the fine-powder foam correspond to the more distinct plate-like macropores in the microstructure that are apparent from general observations of the 2D micrographs and 3D reconstructions. The IND for the coarse-powder foam appears more isotropic in comparison to the IND for the fine-powder foam. This again can be explained by the degree of sintering in the structure. We would expect that the same directional-solidification technique would produce a similar degree of anisotropy in the structure, but the wall roughness caused by incomplete sintering is most likely masking this anisotropy.

6.1.4. Conclusions

Two titanium foams, created by directional freeze-casting of two different sizes of titanium powders, were subjected to synchrotron x-ray tomography to create three-dimensional reconstructions. A quantitative morphological analysis was performed on these reconstructions, with the main results as follows:

- Aligned, elongated, plate-like macropores, resulting from the removal of the directionally-solidified ice dendrites, are easily resolved and reconstructed in three dimensions. Equiaxed micropores within the titanium walls separating
macropores, which are due to incomplete sintering of the original powders, are close to the resolution of the present technique.

- The morphological differences of the pores in the two foams can be quantified by interfacial shape distributions (describing interfacial curvatures) and interface normal distributions (describing preferential directionality). These are useful tools in assessing variations in pore shape or orientation within a foam due to differences in processing conditions, e.g., powder size. In particular, it is apparent that the foams produced with the smaller powder size show more complete sintering, resulting in reduction of the undesirable microporosity without affecting the desirable dendritic macroporosity.

- Directional freeze-casting is a first step towards creating aligned, elongated pores mimicking the anisotropic pore structure of bone. Despite differences between this porous macrostructure and that of trabecular bone macroarchitecture, the morphology of the titanium foams shows similarities with bone on a local level.

6.2. International Collaborations

We have been involved with Michel Rappaz’s Computational Materials Laboratory at Ecole Polytechnique Federale de Lausanne (EPFL) in Lausanne, Switzerland for over four years now. I have worked with several of his students and visited twice. The collaboration detailed below, with Dr. Frederic Gonzales, is one that he came to the US for, and I went to Switzerland to continue with. The background information is
acquired from the unpublished version of our paper together; therefore, it is modified from the original work of Dr. Gonzales.

6.2.1. Introduction and Motivation

Aluminum-zinc alloys constitute the 7000 series of wrought alloys, an important class of materials widely used as anti-corrosion coatings for steel sheets. They are also interesting from a more fundamental point of view because zinc has an hcp crystal structure, and it can be alloyed with aluminum up to 94 wt% while keeping aluminum an fcc crystal structure. Gonzales et. al. [63] report that the growth direction of fcc dendrites is a continuous transition from ⟨100⟩ to ⟨110⟩ as the concentration of Zn, $c_{Zn}$, increases from 5 wt% to 90 wt%. This is contrary to previous studies by Kurz et. al. [64] where ⟨100⟩ dendrites are normally expected to grow in cubic metals. This evolution, called Dendrite Orientation Transition (DOT), occurs between 25 and 60 wt% [63]. Textured seaweed structures were observed at the beginning and end of this DOT.

The change of dendrite orientation in fcc Al-Zn is interpreted as a modification of the solid-liquid interfacial energy of Al, $\gamma_{st}(c_{Zn})$, as $c_{Zn}$ increases [63, 65]. Dendrite growth directions are normally dictated by the anisotropy of $\gamma_{sl}$, and further, they are given by the minima of the so-called interface stiffness, $S_{st}$. The stiffness, $S_{st}$, is given in two dimensions by $(\gamma_{st} + \gamma''_{st})$, where $\gamma''_{st}$ is the second angular derivative of $\gamma_{st}(\phi)$ [66]. The stiffness in three dimensions is similarly given by $\gamma_{st} + \nabla^2 \gamma_{st}$, where the Laplacian is applied to $\gamma_{st}(\theta, \phi)$. In both 2D and 3D, the minima of the stiffness correspond to the most convex parts of the equilibrium crystal shape, from which dendrites will naturally initiate growth. For example, the anisotropy of $\gamma_{st}$ has been measured in Al-Cu with a
low copper composition [67] and is very low, approximately 1%. However, \( \gamma_{st} \) is much higher in hcp Zn (about 30% between the c-direction and the basal plane) [68], which makes dendrites grow primarily along the \( \langle 10\bar{1}0 \rangle \) direction.

In this study, two Al-Zn samples are analyzed, an Al-55wt%Zn obtained by directional solidification (DS) and an Al-90wt%Zn obtained by Bridgman solidification (BS), see [63] for more details about set up and methodology. Two-dimensional sections reveal that the Al-55wt%Zn has a seaweed structure. In other words, the dendritic structure is not well-defined with primary trunks and secondary/tertiary arms. Using electron backscatter diffraction (EBSD), the structure shows significant texture and grows along the preferred direction of \( \langle 110 \rangle \) [63]. The overall grain structure appears to be composed of narrow columnar grains of fairly constant cross-section orienting perpendicular to the thermal gradient. Thus, seaweed structures appear to be growing in planes, which are quite often parallel to the grain boundaries as a consequence of the growth mechanism. Theses layers were clearly identified to be (001) planes. These 2D observations indicate that seaweeds are growing mostly in the form of (001) layers. 3D observations by serial sectioning will allow the investigation and characterization of such structures. The Al-90wt%Zn grow similarly to conventional dendrites, in the \( \langle 110 \rangle \) direction. This indicates that the primary trunks and secondary arms are along this direction. 2D sections parallel to the trunk should reveal the primary stalk and secondary arms clearly at 60°. This will be examined below.
6.2.2. Experimental Procedure

The 2D images for these Al-Zn samples were collected using serial sectioning, as described in Chapter 3. Spacing of 5 $\mu$m in the $z$-direction with a 20x objective (0.254 $\mu$m/px) used in the $x$- and $y$-directions for the seaweed samples and a 10x objective (0.507 $\mu$m/px) used in the $x$- and $y$-directions for the Al-90wt%Zn samples. Once the images are reduced, this results in a resolution of 1.27 $\mu$m in the $x$- and $y$-directions for the seaweed structure and a resolution of 4.563 $\mu$m in the $x$- and $y$-directions for the Al-90wt%Zn samples. The 2D images are segmented, aligned, and stacked as described in Chapter 4, and 3D reconstructions are created along with the ISDs for the structures.

6.2.3. Results and Discussion

Table 6.1 shows a summary of the results of this study. It displays solid volume fraction, $f_s$, along with the amount of positive and negative mean curvature in the structures, and the characteristic length, $S_v^{-1}$.

Fig. 6.6 shows the 3D reconstruction of the Al-90wt%Zn sample. The region encompassed by the black box is blown up in Fig. 6.6(b) to illustrate that the growth direction of the dendrite is $(110)$. 

<table>
<thead>
<tr>
<th>Composition wt%</th>
<th>$f_s$ [%]</th>
<th>$H &gt; 0$ [%]</th>
<th>$H &lt; 0$ [%]</th>
<th>$1/S_v [\mu m]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-90</td>
<td>69.1</td>
<td>30.9</td>
<td>22.43</td>
<td></td>
</tr>
<tr>
<td>Al-55</td>
<td>59</td>
<td>69.1</td>
<td>30.9</td>
<td>22.43</td>
</tr>
</tbody>
</table>

Table 6.1. Summary table of the two Al-Zn samples examined.
Figure 6.6. 3D reconstructions of Al-90wt%Zn. Fig. 6.6(b) shows the dendrite along the $\langle 110 \rangle$ direction.

Fig. 6.7 shows the 3D reconstruction of the Al-55wt%Zn sample. This so-called seaweed structure is evident as it appears there is no specific orientation to the growth of the dendrites. Fig. 6.7(b) shows the interface colored by mean curvature, $H$, to illustrate the significant curvature distribution in the structure.

Fig. 6.8 show the ISDs for the two samples. What is most interesting about these two samples is the difference in the curvature distribution. The Al-90wt%Zn shows a classic dendritic distribution, where the structure is dominated by solid convex shapes and solid hyperbolic shapes, regions 1 and 2 in the ISD. The seaweed structure shows a distribution similar to what has previously been observed in bicontinuous structures [22] and titanium foams [69]. This type of distribution is centered on $H = 0,$
Figure 6.7. 3D reconstruction of Al-55wt%Zn showing the seaweed structure. Fig. 6.7(b) shows the interface of the seaweed structure colored by mean curvature, \( H \).

and therefore dominated by solid and liquid hyperbolic interfaces which normally are interconnected throughout the structure. The fraction of interfacial area having positive and negative \( H \) is very close to 50\%, which corroborates this finding. Thus, because the distribution of shapes is significantly different, the mechanisms behind the formation of each structure must also be very different.
Figure 6.8. ISDs of (a) Al-90 wt% Zn and (b) Al-55 wt% Zn
CHAPTER 7

Conclusions

Three initially equiaxed dendritic Al-20wt%Cu microstructures are isothermally coarsened for 10, 1060 and 6566 minutes. Three initially equiaxed dendritic Al-14wt%Cu samples are isothermally coarsened for 10, 1190, and 6960 minutes. The microstructures are analyzed in three dimensions by observing changes in characteristic length scale, $S_v^{-1}$, interface shape distributions (ISDs), and interface normal distributions (INDs).

It is found that $S_v^{-1}$ scales linearly with the cube root of time for both microstructures. All evidence of the initially-solidified dendritic microstructure disappears after ten minutes of isothermal coarsening, and the structures evolve into highly interconnected, complex globular-like structures with a combination of tubular-like domains that are connected to other domains that have hourglass or hyperboloid-type interfaces, some of which have spherically-capped ends. There is no evidence of break up into spherical solid particles. As coarsening time increases, the scaled interface shape distributions show microstructures dominated by convex and hyperbolic solid shapes (regions 1 and 2 in the ISDs) with only very small changes. There is also no preferential directionality within the microstructures because the interface normal distributions are approximately isotropic.

In the late stages of coarsening, the microstructures are evolving, morphologically and topologically, in a self-similar manner as characterized by time-independent ISDs.
and scaled genii. The differences observed in scaled morphologies and topologies can thus be attributed solely to the different solid volume fractions. We find that the higher volume fraction samples exhibit more interfacial area with negative mean and Gaussian curvatures and a topologically less complex structure due to coalescence in the solid phase.

Comparing the evolution of the initially equiaxed dendritic Al-20wt%Cu structure with its initially directionally solidified counterpart (Al-26wt%Cu) of a similar solid volume fraction provides further evidence that the initial solidification procedures and the microstructure present prior to coarsening have a significant impact on the evolution of the microstructure during coarsening.

Finally, the interface dynamics of the Al-Cu system is studied using in-situ X-ray tomography and a new four-dimensional characterization technique. Expanding on the idea of an ISD, we add a third dimension to these probability contour plots. Thus, the resulting probability of finding any three characteristics in relation to one another is represented as isosurfaces of constant probability. The plot is semi-transparent such that each of the isosurfaces can be seen. The first test of these plots has been completed using the principal curvatures, $\kappa_1$ and $\kappa_2$, and velocity, $V$ in an effort to connect the velocity of an interface to its morphology. Thus, the most probable interface shapes in the microstructure and how they move with coarsening time are found.

In examining the Al-26wt%Cu (42% solid volume fraction) structure and the Al-15wt%Cu (74% solid volume fraction) structure, we find that as solid volume fraction increases, the diffusional distance, or distance with which shapes interact, decreases. Thus, as volume fraction increases, most shapes are interacting only within a small
distance of themselves, or conversely, not interacting with their environment. The clearest evidence of this is provided by the 74% solid samples because the two sides that make up the liquid wall have equal and opposite velocities. This indicates that the wall is interacting diffusionally with itself but not with a significant amount of interface surrounding it. The liquid cylinders are also interacting with each other. When we examine the 42% solid sample, there is no distinct evidence of equal and opposite velocities for specific shapes. This indicates that the diffusional distance is longer, which makes the coupling in the microstructure stronger, and the interaction between shapes increases. We also find that as the diffusional distance increases, the dispersion of velocities for a given pair of principal curvatures decreases significantly. Thus, predicting how specific interface shapes evolve in these microstructures will be much more straightforward.

This new four-dimensional characterization technique will prove extremely important in elucidating the interface dynamics of coarsening. We are in the process of exploring its robustness and future work will highlight this technique as a novel way to characterize microstructural evolution.
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