Interfacial Evolution in Four Dimensions:
Growth and Coarsening in Highly Anisotropic Systems

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ABSTRACT

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Experimental studies into the morphological evolution of highly faceted systems have been performed in an effort to gain a more fundamental understanding of the role of anisotropy during growth and coarsening. The interfacial dynamics in solid-liquid mixtures were examined using four dimensional (i.e., space and time resolved), synchrotron-based X-ray tomography. The following three phenomena were investigated using this novel approach: (1) the coarsening of Si particles in Al-Si(-Cu) liquids; (2) the growth of Si particles in Al-Si-Cu; and (3) eutectic growth in Al-Ge.

Initially, the isothermal coarsening process of hyper-eutectic Al-Si samples was analyzed via ex situ X-ray tomography. The results show that the inverse surface area per unit volume increases with the cube root of time despite the lack of microstructural self-similarity and highly anisotropic particle morphology. More specifically, the Si particles evolve from mostly faceted domains to a more isotropic structure that is not given by the fully-faceted Wulff shape of the crystal [198]. These trends can be rationalized by
the presence of twin defects that intersect the particle edges and that may provide the kink sites necessary for interfacial propagation, thus leading to a more isotropic structure. Qualitatively, the same behavior was observed for Si particles in an Al-Si-Cu liquid, studied via in situ X-ray tomography [199]; this suggests that the thermal cycling in the ex situ experiment has negligible influence on the coarsening dynamics.

Twin-mediated crystal growth has long been a mystery due to the lack of four dimensional experiments. To shed light on the mechanism by which twin defects facilitate growth, we probe the real-time interfacial dynamics of polycrystalline Si particles growing from an Al-Si-Cu liquid. Our analysis of the time evolution of the interfacial normals allows us to quantify unambiguously the habit plane and grain boundary orientations during growth [197]. This, when combined with direct measurements of the interfacial morphology, provide the first three dimensional confirmation of twin-mediated growth, proposed over 50 years ago by Wagner, Hamilton and Seidensticker [85, 237].

Lastly, we track the solidification of an irregular eutectic via in situ X-ray tomography. One example of an irregular eutectic alloy is Al-Ge, in which the Ge phase is faceted, and the Al phase is non-faceted. The faceted phase does not change direction easily due to its atomic structure and defect-mediated growth mechanism; as a result, the microstructure is non-periodic with varying interphase spacing. Our results show that the eutectic morphology in Al-Ge is markedly different from previously employed model systems and theories based upon the ex situ analysis of microstructure [200]. In particular, defects play a critical role in the growth process, in which pockets of the non-faceted phase engulf the exposed facets and control the growth rate of the eutectic colonies.
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CHAPTER 1

Introduction

Solidification and coarsening continue to be phenomena of great interest to scientists and engineers, involving a complex interplay of many physical effects. Various interfacial morphologies with pronounced orientational order have been observed, e.g., dendritic and faceted, depending on the physical properties of the material. One prominent example of crystal growth dynamics involves the formation of ice crystals (or snowflakes) from a vapor phase. Snowflakes exhibit a broad range of morphologies (Fig. 1.1), that are functions of temperature, supersaturation, and other external parameters [132]. The inherent complexity of snowflakes, including their morphological evolution, remain unexplained by existing theories and simulations. Thus, there is ample potential to better understand the growth and coarsening dynamics of such morphologically complex systems.

Beyond the scientific merit of these problems, the burgeoning commercial interest in the processing of advanced materials has reinvigorated our desire to understand the fundamental processes underlying the formation of complex patterns from a featureless liquid. An ability to tune the solidification pathways of materials to technological demands has the potential to accelerate the design of new advanced alloys, thereby fulfilling the promise of the materials genome initiative [1]. Thus far, crystal growth studies in thin samples with transparent materials have proven to be central in understanding the growth of phases with nonfaceted solid-liquid interfaces. Unfortunately, the most important growth process from a technological standpoint involves a faceted phase: the silicon
(Si) phase in the aluminum-silicon (Al-Si) alloy. For instance, the Al-Si eutectic is present in nearly every Al casting alloy, from engine blocks to bicycles, and the anisotropy of the Si phase has profound impact on the chemical and mechanical properties of the material. Anisotropy refers to the directional-dependent free energy and mobility of the solid-liquid interfaces and can have important consequences on the microstructural dynamics.

The growth and coarsening behaviors of faceted materials (such as Si) have been debated for the past fifty years. Early investigators conducted *ex situ* “quench and look”-type experiments. However, the quenching operation may distort the solid-liquid interfaces present during growth. Several other studies were performed using thin samples with transparent materials, as mentioned above; in this case, the constraints imposed by the thin film geometry prohibit a three-dimensional (3D) visualization of the growth process. Thus, it is in our best interest to make time-resolved, 3D measurements of evolving microstructures. This would resolve any issues with the thin film, quasi-2D samples, in which the interfacial dynamics are influenced by the geometric constraints [67]. In addition, the 3D information is necessary to characterize the microstructure in terms of curvatures, velocities, and orientations. This detailed, quantitative analysis allows us to compare the experimental data against theories and simulations with high precision.

In this work, we provide the long-sought answers to this age-old conundrum. In particular, we use synchrotron-based, dynamic X-ray tomography to follow the evolution of microstructure in three dimensions. Hence, we obtain 4D datasets (3D space plus time) during the *in situ* growth and coarsening of highly faceted materials. Due to the sheer volume of data collected over the past four years – on the order of 40 TB – we propose a toolbox of algorithms for processing 4D datasets in an automated manner. The advent of
novel techniques in reconstruction, processing, visualization, and analysis now opens the doors to a class of problems that was previously unexplored due to the lack of real-time experiments. As such, and to the best of our knowledge, we have made the first ever 4D measurements of the interfacial dynamics in highly anisotropic materials. On the basis of our experimental results, we provide a unified picture of the mechanisms governing the growth and coarsening behaviors of these fully-faceted microstructures.

This thesis is organized in three parts. The first is distributed over two chapters and contains the background on the classical theories of crystal growth and coarsening. The second part introduces the experimental and computational methods used in this work. Finally, the third part consists of the results and discussion of the four experiments described in Refs. [82, 196, 197, 198, 199, 200] and conducted in 2012, 2014, and 2015.
Part 1

Background
CHAPTER 2

The Morphology of Crystals

The morphology of crystals results from an interplay between crystallographic anisotropy and growth kinetics. Anisotropy in the surface free energy $\gamma$ results in the equilibrium Wulff shape whereas anisotropy in the kinetic coefficient $M$ gives rise to the kinetic Wulff shape. These two shapes are not necessarily the same. In particular, the kinetic shape is possible when the long-range transport of solute is fast. Both $\gamma$ and $M$ have been determined experimentally and theoretically for a range of metallic and semi-metallic systems. Furthermore, crystal morphology is sensitive to temperature and driving force, giving rise to a so-called roughening transition, as explained in section 2.3.

2.1. Equilibrium and Kinetic Wulff Shapes

Under isothermal conditions, a crystal in equilibrium with its melt will take on an equilibrium shape in order to minimize its interfacial free energy,

$$\Omega = \int_A \gamma(\hat{n}) \, dA$$

subject to the constraint of constant volume. In Eq. 2.1, $\gamma(\hat{n})$ is the anisotropic interfacial free energy per unit area and $\hat{n}$ is the unit normal vector pointing from the crystal to the melt. In two dimensions, $\gamma$ depends only on angle $\theta$, measured relative to a crystallographic direction. According to the so-called Wulff construction [247], the equilibrium shape is the inner convex hull bounded by planes drawn perpendicular to each $\hat{n}$ at a
distance $\gamma(\hat{n})$ from the origin. In two dimensions, one draws lines instead of planes. It is possible that some lines are farther from the origin than lines corresponding to other orientations; therefore, certain orientations may be missing and the equilibrium Wulff shape may be composed of shape edges separating planar facets or smoothly curved surfaces.

The situation is more complicated in three dimensions, because $\gamma$ depends on the polar and azimuthal angles, $\theta$ and $\phi$, respectively. The problem is made more tractable by using the $\xi$-vector formalism proposed by Hoffmann and Cahn [29, 95], where

$$
\xi = \nabla [r \gamma(\theta, \phi)] = \gamma \hat{r} + \gamma_\theta \hat{\theta} + (\gamma_\phi / \sin \theta) \hat{\phi}
$$

and where $\nabla$ is the divergence operator and the subscripts indicate partial derivatives. It can be shown [193, 194] that the equilibrium shape in 3D is similar in shape to a polar plot of $\xi$ as a function of $\hat{n}$. In the isotropic case (i.e., $\gamma$ = constant), $\xi$ reduces to $\gamma \hat{r}$. Examples of the Wulff construction for 2D and 3D shapes are shown in Fig. 2.1.

In the alternate case in which growth is controlled by anisotropic interface kinetics (e.g., source- and sink-limited attachment), we adopt a growth law of the form

$$
U = M(\hat{n}) \Delta T
$$

where $U$ is the local normal growth speed, $\Delta T$ is the interface undercooling, and $M(\hat{n})$ is the anisotropic kinetic coefficient that depends on orientation $\hat{n}$. In spherical coordinates, the velocity $V$ along a trajectory of constant orientation is given by

$$
V = U \hat{r} + U_\theta \hat{\theta} + (U_\phi / \sin \theta) \hat{\phi}
$$
Figure 2.1. (a) The equilibrium shape of the crystal is obtained as an inner convex hull of the $\gamma(\hat{n})$ plot. (b) An example of a 3D $\gamma(\hat{n})$ plot for $\gamma = 1 + \sin^4 \theta (\cos^4 \phi + \sin^4 \phi) + \cos^4 \theta$. (c) The corresponding $\xi(\hat{n})$ plot. Note that the $\xi$ plot has six “ears” that must be truncated to give the equilibrium shape, which resembles an octahedron with curved faces.

Observe that Eq. 2.4 has the same functional form as Eq. 2.2. Thus, $U$ is analogous to $\gamma$ and $V$ is analogous to $\xi$. Then, in the kinetically controlled limit, a crystal grows along the trajectories of constant orientation until the kinetic Wulff shape is approached asymptotically. The kinetic Wulff shape refers to the Wulff shape of the kinetic coefficient $M$ (which is directly proportional to $U$). The faster growing orientations grow out and cease to exist, leaving the crystal bounded by its more slowly growing orientations [193, 194, 229]. An important consequence is that the growing crystal does not maintain a self-similar shape; in general, the shape of the growing crystal evolves with its size.

2.2. Determination of $\gamma(\hat{n})$ and $M(\hat{n})$

It is well known that the solid-liquid interfacial energy of group IV semiconductor crystals is highly anisotropic, where the $\{111\}$ planes have the lowest energy. In particular, Eaglesham and coworkers [52] in 1993 determined the equilibrium shape in Si by imaging
in TEM small voids formed via He ion implantation in Si. One such TEM image is shown in Fig. 2.2(a). Surface free energies $\gamma(\theta)$ can be extracted from the void at equilibrium by measuring the void radius $r_i$ at each of the orientations $i$. Then, the relative $\gamma_i$ can be found using the Gibbs-Wulff theorem [35], i.e., $\gamma_i/r_i = \text{constant}$ for a surface without sharp intersections. The resulting surface energy plot in Fig. 2.2(c) indicates local minima at \{111\} and \{100\} orientations, where $\gamma_{\{100\}}/\gamma_{\{111\}} = 1.10$. For this reason, the equilibrium shape of Si is dominated by large flat \{111\} facets and smaller \{100\} facets. In 3D, this corresponds to a 14-faced tetrakaidecahedron (Fig. 2.2(b)).

It should be noted that the solid-vapor and solid-liquid equilibrium shapes are not necessarily equivalent. However, Barinovs et al. [16] have demonstrated via molecular dynamics simulation with Stillinger-Weber potential that the calculated equilibrium shape of Si crystal in the melt is geometrically similar to the equilibrium shape of the Si solid-vapor interface, observed experimentally by Eaglesham and coworkers [52]. Both shapes are plotted in Fig. 2.2(c). Other molecular dynamics simulations with empirical potentials show that, in general, the global minimum in $\gamma$ for Si occurs at the \{111\} orientation, with the next lowest being the \{100\} orientation [10, 71].

In similar fashion, kinetic coefficients in Si have been measured computationally using a Monte Carlo scheme. Beatty and Jackson [17] found that that the growth rate $V$ increases linearly with undercooling $\Delta T$ for a rough Si \{100\} plane ($V = 0.12 \Delta T$) while $V$ varies exponentially with $\Delta T$ for a \{111\} facet in a 2D poly-nuclear growth mode [168]. Their results are conveyed in Fig. 2.3. For low undercooling, then, the growth velocity on a facet plane is much smaller than on a rough plane. Thus, the kinetic Wulff shape must also be dominated by the slow-moving \{111\} planes. In fact, qualitative observations from
Figure 2.2. (a) Small void in Si imaged via TEM down the ⟨110⟩ axis [52].
(b-c) All voids show the same broad features, i.e., large flat {111} facets and smaller {100} facets. To a good approximation, the equilibrium shape of Si is a (b) tetrakaidecahedron, or a polygon with 14 facets. (d) The equilibrium shape of Si in the liquid phase (denoted Γ_{sl}, dashed curve) is geometrically similar to that in the vapor phase (denoted Γ_{sv}, filled curve) [16].

Figure 2.3. (a) Velocity versus undercooling for Si{100} and Si{111}. V depends linearly on ΔT for Si{100} and exponentially on ΔT for Si{111}. (b) Number of layers added versus time for Si{111}. The growth is characterized by time intervals of no growth followed by a nucleation event that starts a new layer and results in a rapid addition of layer atoms [17].
in situ microscopy suggest that the kinetic Wulff shape of Si in the melt is octahedral in shape and bounded by \{111\} \cite{251}. However, experimental investigations are so far limited owing to the difficulty of in situ imaging of the growth kinetics in opaque materials.

2.3. Thermal and Kinetic Roughening

In the 1960s, Jackson \cite{102} introduced the concept of what is now termed the roughening transition of a crystal surface. In his one-layer mean field model, \(xN\) solid blocks are mixed with \((1 - x)N\) fluid blocks of the same size and shape. The total number of blocks is \(N\). Then, due to the mixing process, the Helmholtz free energy \(\Delta F_{\text{mix}}\) is related to the entropy of mixing \(\Delta S_{\text{mix}}\) and energy of formation \(\Delta U_{\text{mix}}\) as

\[
\Delta F_{\text{mix}} = \Delta U_{\text{mix}} - T \Delta S_{\text{mix}}
\]

(2.5)

\[
= NkT [\alpha x(1 - x) + x\ln x + (1 - x)\ln(1 - x)]
\]

where

\[
(2.6) \quad \alpha = \frac{\eta \phi}{kT}
\]

and where \(k\) is the Boltzmann constant, \(T\) is temperature, \(\eta\) is coordination number of blocks on the surface, and \(\phi\) is the formation energy of a solid-liquid bond. The first term on the second line of Eq. 2.5 reflects the energy of the mixing process, while the latter two terms are due to the entropy of mixing of an ideal mixture. The quantity in Eq. 2.6 is known as the Jackson \(\alpha\)-factor \cite{102}. In general, and for more complex 2D crystals, \(\alpha = \sum \phi_i/kT\) where \(i\) indicates the character of the bond between adjacent blocks \cite{20}.
In Fig. 2.4(a), the relative free energy $f = \Delta F/NkT$ is plotted for different values of $\alpha$. When $\alpha < 2$, the minimum in $f$ is at 0.5 occupancy, whereas when $\alpha > 2$, there are two energy minima at 0 and 1 occupancies. The former corresponds to a rough interface (i.e., mixed solid-liquid layer), and the latter to a smooth interface (i.e., flat domains separated by steps). This key insight implies the following three points:

- If the latent heat $\phi$ (or the entropy of fusion $\Delta S_m$) are known, the Jackson $\alpha$-factor can be determined at $T = T_m$. Note that $\Delta S_m = \phi/T_m$ where $T_m$ is the melting temperature of the solid. Both $\phi$ and $\Delta S_m$ are characteristic of the material: for example, metals have $\alpha < 2$, semiconductors have $2 < \alpha < 3$, and polymer crystals have $\alpha \gg 3$. That semiconductors (e.g., Si, Ge, Sb, and Ga) all have $\Delta S_m \approx 3$ suggest that their growth rates are highly anisotropic [103].
• The $\alpha$-factor depends also on the geometry of the crystal face, by virtue of the coordination number $\eta$ in Eq. 2.6. For this reason, Si\{111\} is atomically smooth ($\alpha_{111} = 2.7$) while Si\{100\} is atomically rough ($\alpha_{100} = 1.8$) [103].

• According to Eq. 2.6, $\alpha$ depends on temperature $T$. Above a roughening transition temperature $T_r$, proportional to $\phi/k$, steps are spontaneously created on the crystalline surface. This is analogous to the Ising temperature of a 2D lattice gas, see the work by Bennema [19]. For Si, $T_r \approx 757^\circ C$ [213] and $T_m = 1414^\circ C$.

In case the one-layer model is exposed to a driving force $\beta = \Delta \mu/kT$, where $\Delta \mu$ is the difference in chemical potential between the solid and liquid phases, Eq. 2.5 becomes [19]

$\Delta F_{mix} = NkT [\alpha x (1 - x) + x \ln x + (1 - x) \ln (1 - x) - x \beta]$

Eq. 2.7 is plotted versus $x$ for $\alpha = 3$ in Fig. 2.4(b). It can be seen that, for the lowest value of $\beta = 0.0$, there are two minima separated by a maxima (as before); however, for the highest value of $\beta$ plotted, only one minimum survives. Physically, this means that the initially faceted surface undergoes a kinetic roughening transition under a high driving force $\beta$. Following Temkin [215, 216], we can solve for this transition–from two minima to one–for all values of $\alpha$, see Fig. 2.4(c). Note that solids with $\alpha < 2$ are atomically rough for all driving forces. On the other hand, solids with $\alpha > 2$ may undergo a thermal roughening transition by increasing temperature (decreasing $\alpha$) or a kinetic roughening transition by increasing driving force (increasing $\beta$). The roughening transition has been investigated extensively by computer simulations and crystal growth experiments [212].
CHAPTER 3

Crystal Growth and Coarsening

The nature of the solid-liquid interface, and the mechanism of its movement, must be understood in order to better control microstructure during the semi-solid processing of materials. As such, I present the basic concepts that underlie the growth and coarsening of solids in the melt. In addition, I assess the critical role of defects (e.g., screw dislocations and twin boundaries) in the evolution of solid-liquid interfaces. Finally, I describe the state of theory and experiment concerning the growth of eutectic mixtures.

3.1. Kinetics of Melt Growth

The growth kinetics of a crystal in the melt are highly dependent on the the interfacial structure of the crystal. Fig. 3.1(a) shows two “extreme” cases in which the structure is either atomically disordered (rough) or atomically ordered (smooth). For an atomically rough interface, there is no energy barrier for atom attachment and hence growth is bulk diffusion limited. On the other hand, atom attachment on a flat surface results in an increase in the surface energy because more broken bonds are created on the surface [114]. For this reason, growth on a flat surface requires relatively large driving forces.

3.1.1. Diffusion-Limited Growth

Consider the growth of an isolated sphere of radius $a$ in a supersaturated matrix. This is shown schematically in Fig. 3.1(b). Typically, there will be many such particles and their
Figure 3.1. (a) Two limiting cases of the surface structure of a crystal: (top) a spherical grain with a rough surface and (bottom) an angular grain with a flat surface \([114]\). (b) Schematic of the spherical grain and the diffusion field around it. The concentrations far from the grain, at the interface, and at the interior of the grain are \(c_\infty\), \(c_I\), and \(c_p\), respectively \([103]\).

Associated diffusion fields. However, we ignore diffusional interactions between particles, and assume that the concentration far from the single particle is fixed at \(c_\infty\). In addition, we assume that atom attachment is easy owing to the rough surfaces of the spherical particle (Fig. 3.1(a)). Thus, the growth rate of the particle is limited by the flux of solute in the matrix phase. The diffusional flux must equal the rate of mass change in the crystal,

\[
\oint_S J \cdot dA = D \nabla C \bigg|_{r=a} = \frac{4\pi a^2}{C_p} \left(4\pi a^2 \frac{da}{dt}\right)
\]

where \(J = -D \nabla C\) is the number of atoms per unit area per unit time arriving at the particle interface, \(dA\) is the differential area, \(S\) is the surface around the crystal, \(D\) is the diffusivity of the solute in the matrix phase, \(\nabla C\bigg|_{r=a}\) is concentration gradient evaluated at the interface \((r = a)\), \(C_p\) is the concentration in the precipitate, and \(t\) is time.
For the steady-state growth of the particle (i.e., $dC/dt = 0$), we can solve Laplace’s equation $\nabla^2 C = 0$ in spherical coordinates to find the concentration field $C(r)$ subject to the boundary conditions $C(r = \infty) = C_\infty$ and $C(r = a) = C_I$. This gives [103, 233]

$$C = (C_I - C_\infty) \frac{a}{r} + C_\infty \tag{3.2}$$

Using Eq. 3.2, $\nabla C\bigg|_{r=a}$ can be determined. Then, $\nabla C\bigg|_{r=a}$ can be substituted into the mass balance condition in Eq. 3.1 to determine the particle growth rate $da/dt$ as

$$U = \frac{da}{dt} = \frac{D}{a} \left( \frac{C_\infty - C_I}{C_p} \right) \tag{3.3}$$

The term in parenthesis corresponds to the supersaturation in the matrix phase. If the supersaturation is constant during growth, then the growth rate $U$ decays over time as the particle grows larger. If we assume that the particle starts out at $t = 0$ with radius $a = 0$, then by integrating Eq. 3.3 we arrive at a parabolic rate law, i.e., $a^2 \propto t$. An important limitation of Eq. 3.3 is that we ignore the change in concentration in the diffusion field; however, as the particle grows, the diffusion field around it also changes [103]. This is especially important when the radius of the particle is comparable to the “radius” of the diffusion field. In this case, corrections to the diffusive flux are given by Ham [84].

### 3.1.2. Interface-Reaction-Limited Growth

Instead, growth may be limited by the atoms incorporating into the particle at the interface. In this case, a liquid molecule must overcome an energy barrier before it can become a part of the particle. The energy landscape is given in Fig. 3.2. At some temperature $T$, a liquid molecule acquires the energy fluctuation $E_d$ with a probability proportional
to the Boltzmann factor; thus, the crystallization rate is given as \( \nu \exp(-E_d/kT) \). The pre-factor \( \nu \) indicates the Debye frequency \([103, 191]\). One must also consider the melting of a crystal molecule into the liquid state: since the chemical potential is higher in the liquid phase than in the solid phase, the rate of melting is smaller than that of crystallization by a factor \( \exp(-\Delta \mu/kT) \). Then, the net rate of growth can be found as

\[
U = \nu \exp \left( -\frac{E_d}{kT} \right) \left[ 1 - \exp \left( -\frac{\Delta \mu}{kT} \right) \right]
\]

\[
\approx \nu \exp \left( -\frac{E_d}{kT} \right) \frac{\Delta \mu}{kT}
\]

(3.4)

where we approximate the square bracket for small driving forces \( \Delta \mu/kT \). This formalism contains no details about the physical process in the first order transformation; however, it does demonstrate that the net rate of crystallization \( V \) is linearly proportional to the free energy difference for the two phases, for small departures from equilibrium.

In 1900, Wilson \([245]\) provided the first analysis of the growth rate of a crystal from a melt. He related the rate at which atoms join a crystal surface to the diffusion coefficient of the liquid phase. In other words, the energy barrier \( E_d \) in Fig. 3.2 corresponds to the activation energy for diffusion. In addition, the “modern version” of his expression for
crystal growth [103] includes a prefactor $f$ that depends on the roughness of the interface (see section 2.3), as well as an entropy term $\exp(-\Delta S/k)$. Observe that the quantity in parenthesis here is the Jackson $\alpha$-factor (Eq. 2.6). Taken altogether, this gives

(3.5) \[ U \approx \frac{6 \ a \ D}{\Lambda^2} f \exp \left( \frac{\Delta S}{k} \right) \frac{\Delta \mu}{kT} \]

where $\Lambda$ is the diffusion jump distance, $a$ is atomic diameter, and $D$ is diffusion coefficient of solute in the liquid phase. If we make the association that $\Delta \mu = \phi \ \Delta T/T_m$, where $\phi$ is the latent heat of fusion, $\Delta T$ is the undercooling, and $T_m$ is the melting temperature, then by virtue of Eq. 2.3, the kinetic coefficient $M$ is given by

(3.6) \[ M = \frac{6 \ a \ D}{\Lambda^2} f \exp \left( \frac{\Delta S}{k} \right) \frac{\phi}{kT_m T} \]

Both Eqs. 3.4-3.5 suggest that the growth rate of the crystal does not depend on its radius, and hence the particle radius in the interface-controlled limit grows linearly in time [233]. This conclusion can be used to distinguish whether growth is limited by the bulk diffusion of solute (Eq. 3.3) or the mobility of atoms approaching the growing interface.

In practice, crystals rarely obey the Wilson growth law in Eq. 3.5. Burton, Cabrera, and Frank [27] observed instead a nonlinear relationship between $U$ and driving force $\Delta \mu$. Their essential assumption was that no crystal grows with a perfect crystalline lattice. From a microscopic point of view, molecules in the liquid phase can attach to terraces and diffuse to ledges. They may also diffuse along the surface to kinks, see Fig. 3.3. When the whole step progresses toward a crystal edge, then the crystal would have grown by one atomic diameter $a$ (normal to the interface). This is the “terrace-ledge-kink” model of crystal growth [27, 209]. However, where do the steps and vicinal surfaces along the
Figure 3.3. “Terrace-ledge-kink” model of crystal surface showing monatomic height steps, kinks, single adatoms, and terrace vacancies [24].

solid-melt interface come from? We assume that a crystal is growing below its thermal and kinetic roughening transition. Steps may be produced by the edges of disk-like nuclei (e.g., in mono-nuclear or poly-nuclear growth modes [168]); however, it can be shown that the driving force required for heterogeneous nucleation is much greater than that observed experimentally. Instead, defects may provide an inexhaustible source of steps.

3.2. Defect-Mediated Growth Mechanisms

The dominant mechanism for interfacial propagation depends upon the growth conditions (e.g., driving force) and the nature of the solid-liquid interface. As previously mentioned, the growth of a defect-free monocrystal requires the nucleation of 2D layers (Fig. 3.4(b)); on the other hand, screw dislocations promote the continuous spiral growth of atomic layers (Fig. 3.4(a)) [3]. The influence of twin defects on the growth process is considered in section 3.2.2. Fig. 3.4(c) shows a plot of growth rate versus driving force in relation to spiral growth, 2D nucleation, and “adhesive” growth (Eq. 3.5) mechanisms [210, 212]. At the critical driving forces marked by * and **, we see boundaries
Figure 3.4. Schematic drawings of (a) spiral growth emanating from a screw dislocation, and (b) 2D nucleation [3]. (c) Growth rate versus driving force in relation to three types of growth mechanisms: curve (a) corresponds to spiral growth, (b) to 2D nucleation, and (c) to “adhesive” growth (Eq. 3.5). At points indicated by *, and **, two curves intersect. For driving forces below *, spiral growth is dominant; between * and **, 2D nucleation is dominant; and above **, kinetic roughening is expected [210, 212].

where two of the three curves cross. In the region below *, spiral growth is operative, whereas in the region between * and **, 2D nucleation is dominant. Therefore, crystals filled with screw dislocations can grow rapidly with very little undercooling below the liquidus [154]. For driving forces above **, kinetic roughening (section 2.3) is expected. In this regime, the interface will be atomically rough. While Fig. 3.4(c) is qualitatively correct, the growth behavior varies from crystal to crystal; in particular, Sunigawa [211, 212] notes that the positions of * and ** are different depending on crystallographic direction, solid-liquid interaction energies, as well as the size of crystals. For instance, when a material with $\alpha < 2$ grows into the melt, the position of ** is much closer to the origin.
3.2.1. Growth on Screw Dislocations

Growth spirals emanating from screw dislocations have been observed on the surfaces of silicon carbide and iron (III) oxide crystals [212, 233]. We consider here the interfacial kinetics of such growth spirals, following Frank [27]. In general, the growth rate depends on the height of the spiral growth layers and the separation between adjacent steps. The step height is determined by the lattice spacing, while the step separation is related to the critical radius of 2D nucleation. It can be shown [103, 233] that the critical radius $r_c \propto \Delta \mu$. Since the defect density $f$ in Eq. 3.5 is given by $1/r_c$, the growth rate of the spiral should then be proportional to $\Delta \mu^2$. This is consistent with the general form for the growth of a spherical particle by a second-order reaction. This is why curve (a) in Fig. 3.4(c) corresponding to the spiral growth mechanism is quadratic with driving force.

3.2.2. Growth on Twin Plane Re-Entrant Grooves

Another class of defects includes crystal twinning. Twinning occurs in crystals with two or more grains such that each grain is a reflected (mirror) image of its neighbor or is rotated with respect to it. The twin boundary between two adjacent grains can be classified using coincident site lattice (CSL) theory. In CSL notation, $\Sigma m$ describes the “degree of fit” between two adjacent grains, where the positive integer $m$ is the reciprocal of the ratio of the coinciding sites to the total number of sites [180]. Fig. 3.5(a) shows a 2D example of $\Sigma 3 \{111\}$ twin boundaries [135]. The coherent $\Sigma 3$ boundary represents a 70.53° tilt about [110] which is structurally indistinguishable from a 60° twist around [111] [180, 181]. The concave basin where the $\Sigma 3 \{111\}$ twin planes intersect the surface measures 141.06° (angle $BAB$ or $CAC$ in Fig. 3.5(a)) and is termed the re-entrant groove.
Figure 3.5. (a) 2D drawing of a doubly-twinned interface, in which the thick blue lines represent $\Sigma 3 \{111\}$ twin boundaries. The concave basin where the twin boundary meets the surface is known as the re-entrant groove. The re-entrant angle $\angle BAB$ (or $\angle CAC$) measures $141.06^\circ$. (b) 3D schematic drawings of a multiply-twinned structure [135]. Examples of twinned structures: (c) eutectic Si flake in Al-Si alloy, in which the lines in the interior of the particle are twins [137]; (d) singly-twinned Ge nanowire [64]. The boxed region corresponds to a single grain oriented along $\{111\}$.

The central assumption of twin mediated crystal growth is that the nucleation of new layers occurs at the re-entrant grooves along the solid-liquid interfaces. According to simple bonding arguments, an atom adsorbed on the groove has four nearest neighbors, compared to three on a flat $\{111\}$ plane [155, 225, 226], and thus the groove may act
as a preferential site for solute adsorption. For this reason, the line energy, which reflects the number of broken bonds per unit length, is negative along the trijunction and thus the nucleation barrier is greatly reduced [64, 131]. A singly twinned crystal contains three such re-entrant grooves along the \(\langle 211\rangle\) directions. Since nucleation readily occurs at the re-entrant grooves compared to the \{111\} surfaces, the singly twinned crystal grows rapidly at the re-entrant grooves and a trigonal solid with 60° corners is obtained. Rapid growth is terminated at the time owing to the disappearance of the re-entrant groove, hence why a multiply twinned interface is needed for steady-state crystal growth. In other words, the solid is bounded by convex 218.94° ridge structures; since an adatom has only three nearest neighbors on either side of the ridge [155, 225, 226], the ridges are not capable of continuous propagation. Figs. 3.5(b-c) show a schematic illustration and a micrograph, respectively, of multiply twinned microstructures [135, 137].

The situation is markedly different in nanoscale systems, in which steady-state growth is possible at a single twin boundary. Recently, Gamalski et al. [64] investigated the growth process of an Au-catalyzed, singly-twinned Ge nanowire (NW), see Fig. 3.5(d). The twin boundary is located at the NW center. Unlike bulk systems, the liquid catalyst-NW interface is nonplanar, but truncated towards the triple phase boundary (TPB) where the liquid catalyst, solid NW, and gas atmosphere meet. This interface near the TPB is highly mobile and requires little supersaturation to move. Hence, the NW grows at a rate completely determined by the nucleation rate at the single twin [64].

Returning to bulk systems, the growth model of a doubly twinned, face-centered cubic (FCC) crystal was first proposed by Wagner [237] and by Hamilton and Seidensticker [85] in 1960. We here review this twin-mediated growth mechanism, hereafter referred to as
Figure 3.6. Growth mechanism of (a) doubly-twinned interface, according to Ref. [85]. (b) Nucleation occurs at the type I re-entrant corner (141.07°). The initiated layer propagates to the second twin and forms a type II corner (109.47°). Growth then occurs at the type II corner until the solid is back to its original shape. The crystal has increased in thickness along ⟨211⟩.

Figure 3.7. Growth mechanism of (a) doubly-twinned interface, according to Ref. [60]. (b) Nucleation occurs at the type I corner, similar to Fig. 3.6(b). (c) A triangular corner is formed due to the rapid growth at the type I groove. (d) When the triangular corner propagates across the second twin, two type I corners are formed at the second twin. (e-g) In similar fashion, growth of the triangular crystals occurs at the newly created type I corners. The faceted dendrite repeats the process from (a)-(g), involving the appearance and dissapearance of the triangular corners.
the WHS model. The growth mechanism according to WHS is given in Fig. 3.6. For a crystal with two parallel twin planes, rapid growth occurs at the 141.06° re-entrant corner (referred to as a type I corner [85]), similar to the crystal with one twin. When the nucleated layer propagates to the next twin, it forms a new re-entrant corner with an angle of 109.47° (referred to as a type II corner [85]). Like the type I corner site, the type II corner site is four-fold coordinated [225, 226]. The type II corner is absolutely essential for the continuous propagation of the crystal because it relieves the shortage of nucleation sites caused by the formation of ridge structures. Growth occurs at the type II corner until the solid is back to its original shape. The important feature of the WHS model is that the type I corner does not disappear during growth, since it is regenerated by activity at the type II corner [85, 237]. Note that the WHS model allows for accelerated growth in 2D. In 1996, van de Waal [226] extended the WHS mechanism to include two crossing twin lamellae, thereby explaining isotropic, 3D FCC crystal growth.

In general, while it is widely accepted that at least two twin planes are needed for steady-state growth in bulk systems, the growth behavior of the twinned interface remains poorly understood due to the lack of in situ experimental evidence. To solve this puzzle, Fujiwara and coworkers [59, 61, 249, 250] developed a 2D in situ observation system to watch the growth of faceted Si dendrites. Based on their data, they presented a growth mechanism of a doubly-twinned interface, hereby referred to as the F model. The F mechanism is given in Fig. 3.7. In their approach, triangular 60° corners (at the length-scale of the crystal) form at the growth tip, and the direction of the 60° corners changes during growth; this is made possible by the alternate formation and disappearance of type I corners at each of the two twin planes, in contrast to the WHS mechanism. Thus, according
to the F model, type II corners play no role during growth. [59, 61] While this model satisfactorily explains the observations of Fujiwara and coworkers, many open questions remain: namely, how do the experimental conditions (e.g., temperature, undercooling, composition, etc.) influence the morphology of the twinned interface? To what extent is the F model applicable to other materials systems and solidification pathways?

It should be noted that the WHS and F models are not the only twin-mediated growth mechanisms put forth by the crystal growth community. In fact, several authors [106, 131, 155] suggest alternative mechanisms of a twinned interface involving the atomically rough \{100\} habit plane, but they disagree on the precise role of the \{100\} surface during microstructural evolution. The \{100\} surface is formed by the edges of the accumulated layers at the type I groove; thus, the solid-liquid interface has the structure \{111\}-\{111\}-\{100\}-\{111\}, in contrast to \{111\}-\{111\}-\{111\} shown schematically in Figs. 3.6(a)-3.7(a). According to Jagannathan et al. [106], the \{100\} habit plane eventually covers the entire surface of the middle crystal; on the other hand, Lee et al. [131] suggest that the \{100\} habit plane competes with the type I groove such that it prevents the groove from disappearing. These models lack experimental verification.

### 3.3. Asymmetry Between Growth and Melting

For the past 50 years, there has been much debate on whether the interfacial dynamics in a faceted system should be symmetric about the melting temperature, $T_m$ [217]. Early crystal growers [223] employed the principle of microscopic reversibility, i.e., that the rates of growth and dissolution should be continuous (with the same slope) across $T_m$. However, Kluge and Ray [119] showed using molecular dynamics simulation with
Figure 3.8. (a) The growth rate of Salol crystals as a function of temperature, indicating the asymmetry in the crystallization rate and the melting rate at the melting point (MP) [103]. (b-c) Alternate freezing and melting, respectively, in a 2400 Å thick Bi film [74]. Freezing is associated with facet formation, while re-melting occurs with the smoothing of facets.

Stillinger-Weber potential that growth of the melt into the superheated solid Si is actually faster than growth of the Si crystal into the undercooled liquid. Tymczak and Ray [221] performed similar simulations and observed the same trends for Na crystals with BCC symmetry. An example of this asymmetry is shown in Fig. 3.8 for the growth rate of Salol crystals as a function of temperature [103]. Since the growth rate comes into the melting point horizontally (from the left), the growth process exhibits nucleation-limited behavior for small undercoolings. The growth rate decreases at lower temperatures because the diffusion mobility or the melt viscosity decreases as the temperature is dropped. Above the melting point, the dissolution rate is linear with temperature. How do we interpret this asymmetry in terms of the atomic processes occurring at the solid-melt interface?

Experimentally, Glicksman and Vold [74] found via in situ electron microscopy that thin films of Bi are faceted upon freezing, but smoothly curved during melting. Refs. [162, 220] noticed the same behavior in Si. In particular, Moorthy and Howe [162] suggested
that the removal of atoms from the Si surface is a continuous process as opposed to occurring in abrupt jumps. On melting, step trains are able to move in from the edges of the crystal. Thus, the melt rate is not limited by the nucleation of new layers.

3.4. Coupled Growth of Eutectics

Thus far, we have treated only the case of a pure solid growing into a melt. How do eutectic mixtures solidify? There has been in the past fifty years an increasing interest—both theoretically [116] and experimentally [192]—in the problem of pattern formation of a moving boundary, such as an eutectic solidification front. Eutectics may exhibit outstanding mechanical and electrical properties because their microstructures act as natural or in situ composite materials [6, 73]. In order to tune the eutectic microstructures to technological demands, we must understand the fundamental processes underlying their formation from a featureless liquid. Here, we review the state of theory and experiment concerning the structure and dynamics of eutectic systems.

Eutectics have been discovered in a vast array of organic [56, 101, 130], metallic [104, 105], and semi-metallic alloys [46, 91, 92, 96, 120, 137, 150, 202]. The eutectic morphologies that may arise during solidification can be classified as either regular or irregular. Examples of both classes of eutectics are given in Figs. 3.9(a-d). Regularity refers to the periodic arrangement of lamellae, and is typical of non-faceted, metallic systems (e.g., Al-Cu and Pb-Sn). The situation is more complex when irregular eutectics are considered, in which one of the phases is faceted (e.g., Si and Ge) and the other non-faceted (e.g., Al and Ag). The faceted phase does not easily change direction due to its atomic structure, covalent bonding, and defect-mediated growth mechanism [130, 165].
Figure 3.9. Classification of eutectics: (a) regular Al-Au eutectic and (b) irregular Al-Si eutectic. Their organic analogues: (c) regular CBr$_4$-C$_2$Cl$_6$ eutectic and (d) irregular boreol-succinonitrile eutectic, observed during growth [43]. The faceted borneol phase leads the growth of the succinonitrile in between. (e) Growth mechanism of an irregular eutectic: the diffuse $\alpha$ phase can grow easily while the faceted $\beta$ phase is more sluggish [56].

Due to this inherent “stiffness” of the faceted phase, the microstructure is non-periodic with varying interphase spacing. Irregular eutectics are discussed in section 3.4.2.

### 3.4.1. Regular Eutectic Solidification

The theoretical explanation of eutectic growth in regular systems can be attributed to the classical work by Jackson and Hunt [105]. They analyzed regular eutectic growth by assuming a planar interface and equal undercooling of both solid phases, growing in a coupled mode from a melt of eutectic composition. Coupled growth denotes the lateral
exchange of solute \textit{via} interdiffusion through the liquid, ahead of the eutectic interface. In particular, they found the following relationship between total undercooling of the eutectic front $\Delta T$, interphase spacing $\lambda$, and growth velocity $v^*$ of the eutectic interface,

$$\Delta T = \Delta T_C + \Delta T_\sigma$$

(3.7)

$$= A \, v^* \frac{\lambda}{\lambda} + B / \lambda$$

where $A$ and $B$ are constants determined from materials parameters. The first term in the bottom line of Eq. 3.7 represents the contribution of solutal undercooling $\Delta T_C$ while the latter term represents the contribution of curvature undercooling $\Delta T_\sigma$. Kinetic undercooling is negligible for metallic eutectics. Note also that in 1D, curvature $\kappa$ is directly proportional to $1/\lambda$. Assuming that eutectic growth occurs at the minimum undercooling, i.e., the so-called “extremum criterion” [192], then we arrive at the relationships

$$\lambda_{ext}^2 \, v^* = \frac{B}{A}, \quad \frac{\Delta T}{v^*^2} = 2 (A B)^{\frac{1}{2}}, \quad \Delta T \lambda_{ext} = 2B$$

(3.8)

where $\lambda_{ext}$ is the so-called extremum spacing. Eqs. 3.8 can be used when the interfacial velocity or the local undercooling is set, e.g., during equiaxed solidification.

### 3.4.2. Irregular Eutectic Solidification

In irregular eutectics, the mean spacing is much larger than its extremum spacing $\lambda_{ext}$ derived above. Large mean spacings can be explained by the difficulty with which the faceted lamellae adapts its scale to the local growth conditions \textit{via} branching [130]. Thus, the above analysis may not be appropriate, since a kinetic undercooling term would need to be included in the expression for total undercooling (Eq. 3.7).
In 1980, Fisher and Kurz provided the first model of irregular eutectic growth [56]. In particular, they considered the growth process of the organic succinonitrile borneol and camphor-napthalene irregular eutectic systems. From their experimental observations, they were able to deduce the following features of irregular eutectic growth:

- The duplex solid-liquid front is markedly non-isothermal. If two adjacent lamellae diverge, *i.e.*, $\lambda$ increases, a negative curvature develops at the interface of the nonfaceted phase in order to compensate for the increase in solutal undercooling (Eq. 3.7). The growth undercooling increases until the curvature can no longer compensate for this change; hence, the eutectic interface is non-isothermal.
- This suggests that the faceted phase leads the solidification event, *i.e.*, the faceted phase has lower undercooling and therefore extends deeper into the melt, see the idealized schematic of irregular eutectic growth in Fig. 3.9(e).
- The non-faceted phase lags behind but spreads up the sides of the faceted flakes to near their growth edges, as shown in the optical micrograph in Fig. 3.9(d).

Despite its popularity in the metallurgical community, the Fisher-Kurz model has never been experimentally verified in bulk metallic systems. For this reason, the growth of an irregular eutectic remains widely contested. For instance, the Fisher-Kurz model has been disputed by Hogan and coworkers [150], who suggest instead that the non-faceted phase may nucleate heterogeneously and repeatedly (like islands) on exposed surfaces of the faceted flakes. According to these authors, the “re-nucleation” of grains may account for the polycrystallinity of the non-faceted phase in irregular eutectics [96, 120, 202].
Figure 3.10. Coupled zones (cross-hatched) on eutectic phase diagrams: (a) symmetrical coupled zone in a regular eutectic and (b) skewed coupled zone in an irregular eutectic. In the latter case, the coupled zone is skewed towards the faceted phase $\beta$ [43, 129]. (c) Broadening of the coupled zone in an irregular Al-Si alloy due to increasing thermal gradient $G$.

3.4.3. Competitive Growth Principle

The phase diagram indicates the phases that will be present at equilibrium, given an alloy temperature and composition. However, metastable phases (i.e., those not predicted from equilibrium thermodynamics) may appear in alloy samples. For instance, Al dendrites may grow below the eutectic temperature in an Al-Si alloy of eutectic composition. This metastable phenomenon can be explained by the competitive growth principle [43, 129], which states that the growth form having the highest interfacial temperature (or lowest undercooling) will be the one preferred by the system. Competitive growth of dendrites and eutectics gives rise to a “coupled zone,” which represents the range of growth conditions (e.g., $v^*$, alloy composition, etc.) within which the microstructure is wholly eutectic. Outside of the coupled zone, primary dendrites can grow before or simultaneously with the eutectic constituents, since its undercooling is smaller ($\Delta T_{dend} < \Delta T_{eut}$).
Fig. 3.10 depicts the coupled zone on the eutectic phase diagrams [43, 129]. In regular eutectic systems, the coupled zone is symmetric about eutectic composition, whereas in irregular eutectic systems, the coupled zone is skewed towards the faceted phase. The latter behavior can be explained by the fact that the growth kinetics of the faceted phase are more sluggish than the non-faceted phase, such that they require an undercooling that increases faster with velocity [43]. In directionally solidified samples, the coupled zone is sensitive to temperature gradient $G$: when the temperature gradient is steep, constitutional undercooling is suppressed and hence dendrites are less likely to grow below the eutectic temperature. For this reason, the coupled zone broadens with increasing $G$.

3.5. Coarsening in a Solution

During the early stages of transformation, nucleation and growth are the dominant processes. When the equilibrium volume fraction of the precipitate phase has been reached, coarsening occurs whereby large particles grow at the expense of small ones. By doing so, the total energy of the system is decreased by reducing the total interfacial area. Given that a two-phase mixture always possesses excess energy due to the presence of significant interfacial area, this coarsening behavior is observed in the late stages of nearly all phase transformation processes [233]. Here, the interfaces of interest are the boundaries between solid and liquid phases. For simplicity, we treat growth and coarsening as two separate processes; however, it should be noted that growth and coarsening do not necessarily occur in a strict chronological order but may overlap in time, see Ref. [233].

An important aspect of coarsening or Ostwald ripening is its self-similar nature. This means that the microstructure, after different periods of growth, appears unchanged (in
a geometrical sense) provided that the magnification of the viewing microscope is appropriately reduced to give the same particle size. An example of self-similarity is given in Fig. 3.11 for the coarsening evolution of solid Sb particles in a Pb-Sn eutectic [87]: when we change the magnification by the ratio of the average particle size (bottom row) at these times, the microstructures look identical. In practice, this means that the particle size distribution (PSD) is time-invariant for self-similar coarsening. In the sections below, I review the driving force for coarsening, and discuss the basic growth laws underlying the evolution of microstructure. In addition, I review the existing literature on coarsening.

3.5.1. Capillary Driving Force

Capillarity is the primary driving force for most microstructural evolution processes, including coarsening. Interfacial curvature gives rise to capillary forces. According to the Gibbs-Thomson equation [73, 233], for a system with isotropic interfacial energy, the chemical potential at the curved solid-liquid interface, \( \mu_I \), is given by

\[
\mu_I = \mu_\infty + 2 \gamma_{sl} V_s H
\]

where \( \mu_\infty \) is the chemical potential at a flat interface, \( \gamma_{sl} \) is the solid-liquid (sl) interfacial energy, \( V_s \) is the molar volume of the solid phase, and \( H \) is the mean curvature. The mean curvature is a signed quantity, so that positive curvature corresponds to an interface that is convex toward the melt. By contrast, when a concavity, such as a bowl-shaped depression, develops on a solid-liquid interface, the mean curvature of the interface becomes negative. In the latter case, the chemical potential of both phases falls relative to its value at a
Figure 3.11. Microstructures of solid Sb particles in a Pb-Sn eutectic. The top row shows constant magnification while the bottom shows variable magnification and illustrates the self-similar nature of coarsening [87].

planar interface [73]. In general, variations in $\mu_I$ at interfaces create solute concentration gradients, which cause solute flux from regions of high to low concentration.

If the interfacial energy is anisotropic, but with facets, the second term or excess chemical potential in Eq. 3.9 is replaced by either the surface divergence of the $\xi$-vector [29, 95] (introduced in section 2.1), $\nabla_{surf} \xi$, or the weighted mean curvature [8, 214] (denoted
Figure 3.12. Schematic drawing of facet $i$ and neighboring facets $i \pm 1$, where facet $i$ is oriented with some interface normal $n_i$ and moves at some velocity $V_i$. Likewise, facets $i \pm 1$ have normal and velocity given by $n_{i \pm 1}$ and $V_{i \pm 1}$, respectively. Note the indicated angles $\theta_{i, i \pm 1} = \cos^{-1}(n_i \cdot n_{i \pm 1})$.

$\kappa_\gamma$). The weighted mean curvature is defined as the local rate of interfacial energy change with a local addition of volume, i.e., $\kappa_\gamma = \partial W / \partial V_s$ where $W$ is the work to pass a small amount of material $\partial V_s$ through an interface [14]. In 2D, $\kappa_\gamma$ reduces to Herring’s definition [94], given by $\kappa_\gamma = (\gamma + \gamma_{\theta \theta}) \kappa$ where $\gamma_{\theta \theta}$ is the second partial derivative of $\gamma$ with respect to orientation $\theta$, and $\kappa$ is the curvature in the plane. In the fully-faceted limit, the expression for weighted mean curvature is further simplified: in this case, tractable expressions can be produced for morphological evolution, see for instance Refs. [33, 187]. An example is given below for the calculation of $\kappa_\gamma$ in the fully faceted limit.

Consider the 2D facet geometry shown in Fig. 3.12. Assume that facet $i$ has line energy $\sigma_i$, is oriented with some interface normal $\hat{n}_i$, and moves at speed $V_i$. Likewise, its neighboring facets $i \pm 1$ have energy, normal, and velocity given by $\sigma_{i \pm 1}$, $\hat{n}_{i \pm 1}$, and $V_{i \pm 1}$, respectively. When facet $i$ moves a distance $\Delta x$, what is the corresponding work $\Delta W_i$?
associated with the addition of new length at the two ends? We find \[185\]

\[
\Delta W_i = \Delta x_i \left( \frac{\sigma_{i+1} - \hat{n}_i \cdot \hat{n}_{i+1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i+1})^2}} + \frac{\sigma_{i-1} - \hat{n}_i \cdot \hat{n}_{i-1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i-1})^2}} \right)
\]

where we have made use of trigonometric identities and combined like terms. Note that the energy change, \(\Delta E_i\), for incorporating atoms into the facet \(i\) is given by

\[
\Delta E_i = \Delta x \int \mu_i(l) \, dl
\]

Equating Eqs. 3.10 and 3.11 and dividing through by the length of the facet \(L_i\) gives the average chemical potential of facet \(i\) along its length, denoted as \(\mu_I\), or

\[
\mu_I = \frac{1}{L_i} \int \mu_i(l) \, dl
\]

\[
= \mu_\infty + \frac{1}{L_i} \left( \frac{\sigma_{i+1} - \hat{n}_i \cdot \hat{n}_{i+1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i+1})^2}} + \frac{\sigma_{i-1} - \hat{n}_i \cdot \hat{n}_{i-1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i-1})^2}} \right)
\]

The integration constant is given by \(\mu_\infty\) and reflects the chemical potential at a crystal with infinitely large facets, while the excess chemical potential in Eq. 3.12 is the weighted mean curvature, \(\kappa_\gamma\). Observe that there is a facet length dependence to \(\kappa_\gamma\), such that the chemical potential at the interface decays as the facet becomes larger.

### 3.5.2. Theoretical Background

In order to form a theory for the rate of coarsening, it is necessary to develop a kinetic equation that describes the interfacial velocity as a function of the curvature. We make the following assumptions: the coarsening phase is composed of spherical particles that
are an infinite distance away from each other, i.e., the dispersion is very diluted; the diffusion rate is so slow during coarsening that a change in concentration as a function of time is assumed equal to zero, and hence Laplace’s equation is valid; the whole system is closed such that mass is only exchanged within the system. Similar to the analysis in section 3.1.1, the boundary conditions are \( c(r = \infty) = c_\infty \) and \( c(r = a) = c_I \), and the growth rate is given by Eq. 3.3. Since \( c_I \) depends on curvature, we can substitute the Gibbs-Thomson condition (Eq. 3.9) and \( H = 1/R \) into Eq. 3.3 to give \[233\]

\[
U = K_{\text{diff.}} \cdot \frac{1}{R} \left( \frac{1}{R_c} - \frac{1}{R} \right)
\]

where \( R_c \) is a critical radius at which the particle with neither grow nor shrink, and is often close to the average particle radius in the system \[233\]. In addition, \( K_{\text{diff.}} \) is the rate constant, which is a collection of materials parameters (e.g., \( D \) and \( \gamma_{sl} \)). Eq. 3.13 is the general form of diffusion-limited transport. The only source of the supersaturation is the excess solubility of the spheres due to the Gibbs-Thomson effect.

Ostwald ripening may also occur in a system governed by first-order kinetics, in which the growth rate has the general form \( U = M \Delta \mu \), see Eqs. 2.3, 3.4, 3.5. Using the same boundary conditions as above, the growth rate can be written as

\[
U = K_{\text{int.}} \left( \frac{1}{R_c} - \frac{1}{R} \right)
\]

where the rate constant is \( K_{\text{int.}} \) in the interface-controlled limit, and \( K_{\text{int.}} \neq K_{\text{diff.}} \).

The classical treatment of coarsening is due to Lifshitz, Slyozov, and Wagner (LSW) \[133, 236\]. They assumed infinitely separated spherical particles, as above. In this way, each particle is surrounded by a “mean field” concentration, \( c_\infty \), far away from
the particle. By solving the kinetic equation (Eqs. 3.13-3.14) with continuity and mass conservation conditions, they showed that the average particle radius $\bar{R}$ evolves as

\begin{equation}
\bar{R}^n(t) - \bar{R}^n(0) = K_{LSW} t \tag{3.15}
\end{equation}

where $\bar{R}^n(0)$ is the average radius at the onset of steady-state coarsening, $n = 2$ and $K_{LSW} = (4\sqrt{2}/9) K_{int}$ for interface-limited coarsening, and $n = 3$ and $K_{LSW} = (12/27) K_{diff}$ for diffusion-limited coarsening. Thus, the coarsening rate constant $K_{LSW}$ is related to either $K_{int.}$ or $K_{diff.}$ by a numerical pre-factor. Further analysis of the growth rate equation was done by LSW to determine the steady-state distribution of particle radii $[133, 236]$. These results are out of the scope of this work since they have little bearing on the dynamics of highly faceted, complex, and interconnected systems.

Importantly, the above LSW theory does not account for finite volume fractions of coarsening phase. In this case, each particle interacts not with its mean field, but with the local field between its neighboring particles. Diffusional interactions between neighboring particles lead to a coarsening rate constant $K$ that is a function of the volume fraction $V_v$, i.e., $K = f(V_v) K_{LSW}$. Note that volume fraction is sometimes also denoted $\phi$ in the literature. As $V_v$ increases, the interparticle separation decreases, leading to a value of $K$ that is higher than $K_{LSW}$ in the LSW approach $[231, 232]$. Recent simulations and theories (see Refs. $[231, 232]$) predict a modest increase in $K/K_{LSW}$ for small volume fractions of the coarsening phase. In general, $f(V_v) = V_v^{1/2}$, as shown in Fig. 3.13.

Another complication is that real particles are not perfectly spherical. This is certainly true for highly anisotropic materials such as Si and Ge. Thus, we seek another time-dependent length scale to characterize the system. One such possibility, suggested
Figure 3.13. (a) Coarsening rate constant $K$ as a function of the volume fraction $\phi$, relative to that at zero volume fraction. Theories and simulations predict an increase in $K$ with $\phi$ [231, 232]. (b) Simulations by Refs. [234, 235] show a dispersion in the interfacial source-sink rate ($B = R^2 \dot{R}$) as a function of particle size. Particles grow for $R > R_c$ and shrink for $R < R_c$. The spread in $B$ is due to diffusional interactions between particles.

by Marsh and Glicksman [145], is the inverse surface area per unit volume, $S_v^{-1}$, which has units of length. Thus, during coarsening, $S_v^{-1}$ varies with time $t$ as

$$S_v^{-n}(t) - S_v^{-n}(0) = K t$$

where for nonspherical particles, $K$ in Eq. 3.16 is related to $K_{LSW}$ by a geometrical pre-factor, i.e., $K = \zeta K_{LSW}$ [138]. Thus, the $\zeta$ factor connects the measured $S_v$ to an average particle radius $\bar{R}$. Taken altogether, the generalized coarsening rate $K$ in a system with a finite volume fraction of nonspherical particles is given by $K = \zeta f(V_v) K_{LSW}$, where the first two terms represent the corrections to LSW theory.
3.5.3. Experimental Findings

For a system of spherical particles undergoing diffusion-limited ripening, it has long been established experimentally that the relation $\bar{R}^3(t) \propto t$ is valid. However, the coarsening rate constant $K_{LSW}$ is more difficult to assess unless all of the assumptions of LSW theory are satisfied. To this end, Alkemper et al. [7] considered the coarsening process of Sn-rich particles in a Pb-Sn liquid. This system is ideal to study coarsening phenomena since the particles are spherical and the thermophysical parameters have been measured. In addition, to prevent the sedimentation of the particles and convection of the liquid phase, their experiments were conducted in microgravity. While the Pb-Sn sample never reached the steady-state coarsening regime, Alkemper et al. [7] found that the measured coarsening rate agreed well with predictions for transient Ostwald ripening.

Voorhees and Glicksman [234, 235] simulated the growth and dissolution rate $\dot{R}$ of finite volume fraction, spherical particles that interact diffusonally. This results in fluctuations of individual particle coarsening rates, as shown in Fig. 3.13(b). Here, $B = R^2\dot{R}$ is proportional to the change in particle volume. As expected, the fluctuations are smaller for small particles since these particles interact weakly with their neighbors. Alternately, larger particles experience “soft collisions” due to the overlapping diffusion fields. Growth occurs for $R > R_c$ while dissolution occurs for $R < R_c$ [234, 235].

Somewhat analogously, simulations of growth and coarsening in anisotropic systems were conducted by Roosen and Carter [186]. They presented a 2D model for microstructural development of $\text{Si}_3\text{N}_4$ particles growing from a seeded solution by mass diffusion. As shown in Fig. 3.14(a), these particles are faceted along the long sides and rough on
Figure 3.14. Simulations by Ref. [186] on the microstructural evolution of (a) Si$_3$N$_4$ particles which are partially faceted and partially rough. (b) Evolution of area and aspect ratio (inset) versus time for a single particle. While the particle is growing rapidly ($t < 1$), the high mobility ends move faster than the sides, elongating the particle. After the supersaturation has been absorbed ($t > 1$), the particle evolves towards its Wulff shape.

The short ends. Each facet moves according to a linear kinetic law (Eq. 2.3) with a chemical potential proportional to the weighted mean curvature (Eq. 3.12). By substituting Eq. 3.12 and $\Delta \mu = \mu_m - \mu_f$ into Eq. 2.3, the kinetic equation is expressed as [214]

$$U(\hat{n}_i) = M(\hat{n}_i) \left[ \mu_m - \mu_\infty - \frac{1}{L_i} \left( \frac{\sigma_{i+1} - \hat{n}_i \cdot \hat{n}_{i+1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i+1})^2}} + \frac{\sigma_{i-1} - \hat{n}_i \cdot \hat{n}_{i-1} \sigma_i}{\sqrt{1 - (\hat{n}_i \cdot \hat{n}_{i-1})^2}} \right) \right]$$

(3.17)
where $\mu_m$ is the chemical potential in the matrix. The evolution of a single particle growing from a small seed in a supersaturated field is shown in Fig. 3.14(b) [186]. Observed are two epochs of growth: up to time $t = 1$, the particle grows rapidly; since interfacial attachment is more rapid along the rough ends of the particle, the particle approaches a needle-like shape. Beyond $t = 1$, all the free solute has been absorbed by the particle and hence its area is constant. In this coarsening regime, the shorter facets have higher potentials, since $\kappa \gamma \propto 1/L_i$ (Eqs. 3.12 and 3.17), and thus they tend to recede faster. Eventually, the particle approaches its Wulff shape [186]. In addition, Roosen and Carter extended their simulations to investigate an ensemble of particles that grow and coarsen [186]. However, the complication here is that the particles may interlock at late times. In this case, more rigorous 3D calculations are needed to evaluate the growth dynamics.
Part 2

Methods
CHAPTER 4

Experimental Methods

Destructive, *post mortem* metallographic analysis can provide insight into what occurred at elevated temperatures, but *in situ* observations of a microstructure during processing provide direct evidence as to how the microstructure evolves. X-ray tomography is a nondestructive method to investigate the evolution of 3D microstructure in time. In this project, we are concerned with the interfacial dynamics of highly anisotropic systems. As such, this chapter will cover the highly faceted systems of interest as well as the experimental details for synchrotron-based X-ray tomography. In addition, we supplement our tomographic investigation with electron backscatter diffraction analysis in order to link the interfacial texture to the structure of the solid-liquid interfaces.

4.1. Alloy Systems of Interest

The Al-Si alloy is one example from a large class of complex, heterogeneous alloys. Among the commercial aluminum alloy castings, the Al-Si alloy (*e.g.*, A390) is the most commonly used and constitutes 85-90% of the total aluminum cast parts produced [79]. They are widely used in the automobile and aerospace industries due to their low density, good strength, and excellent castability [86, 256]. The microstructure of the Al-Si alloy strongly influences its mechanical properties: for instance, in cast Al-Si alloys, the eutectic is flake-like. The Si platelets act as nuclei for internal cracks, thereby reducing the fatigue strength of the alloy [233]. Similarly, hyper-eutectic Al-Si alloys consist of primary Si
particles, which crystallize in anisotropic shapes, in a eutectic matrix. The morphologies of these primary Si particles have been identified as the main cause of fatigue and wear of engine parts [252]. The growth mechanism of the primary Si particles, as well as that of the Al-Si irregular eutectic, needs to be investigated in order to better control the microstructure during the semi-solid processing [42] of the alloy.

Besides its metallurgical applications, polycrystalline Si (poly-Si) is relevant to the energy sector. In particular, poly-Si is widely used as the substrate of thin-film photovoltaic (PV) cells. To be commercially viable, the efficiency of the poly-Si thin-film cells should reach the 40% efficiency offered by other PV technologies [166], including single-junction and multi-junction cells, see Fig. 4.1. However, the highest recorded efficiencies of the poly-Si thin-film cells are approx. 20% (as of 2010 [166]), due to the high defect densities in the poly-Si thin films. Recombination at dislocations and grain boundaries adversely impact the performance of these devices [66, 227]. For instance, the minority carrier lifetime depends on the character of the grain boundaries: coherent Σ3 (twin) boundaries are electrically inactive, while higher-order boundaries may be electrically active [36, 239]. Thus, a fundamental understanding of the structure of poly-Si during growth will provide the link between solidification microstructure and underlying materials behavior.

To shed light on the above, we study Al-Si alloys of hypereutectic compositions. The Al-Si equilibrium phase diagram is given in Fig. 4.2(a), and its metastable equivalent (below the eutectic temperature) is depicted in Fig. 3.10(c). One practical advantage of this system is its relatively shallow eutectic temperature (575 °C); this means that we can investigate the interfacial dynamics above the eutectic temperature using conventional furnaces capable of reaching such temperatures. In addition, Al is insoluble
Figure 4.1. The highest-confirmed conversion efficiencies of photovoltaic “research” cells, from 1976 to 2010. Results are provided for five classes of semiconductors: multijunction cells, single-junction GaAs cells, crystalline Si cells, thin-film technologies, and emerging photovoltaics [166].

Table 4.1. Crystal structures and entropies of fusion $\Delta S_m$ for some metals (left) and metalloids (right) [65]. “Hex.,” “rhomb.,” “orth.,” and “dia. cubic” stand for hexagonal, rhombohedral, orthorhombic, and diamond cubic, respectively. Metals have lower $\Delta S_m$ compared to metalloids.

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>$\Delta S_m$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Cubic</td>
<td>8.9</td>
</tr>
<tr>
<td>Al</td>
<td>Cubic</td>
<td>11.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Cubic</td>
<td>9.6</td>
</tr>
<tr>
<td>Fe</td>
<td>Cubic</td>
<td>7.5</td>
</tr>
<tr>
<td>Mg</td>
<td>Hex.</td>
<td>9.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>$\Delta S_m$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Rhomb.</td>
<td>20.0</td>
</tr>
<tr>
<td>Ga</td>
<td>Orth.</td>
<td>18.5</td>
</tr>
<tr>
<td>Ge</td>
<td>Dia. Cubic</td>
<td>28.3</td>
</tr>
<tr>
<td>Sb</td>
<td>Rhomb.</td>
<td>22.0</td>
</tr>
<tr>
<td>Si</td>
<td>Dia. Cubic</td>
<td>27.2</td>
</tr>
</tbody>
</table>
Figure 4.2. Equilibrium phase diagrams of Si and Ge with Al, shown in (a) and (b), respectively. Compositions in at% and temperatures in °C. The eutectic composition and eutectic temperature are 12.5 at% (13 wt%) and 575 °C in Al-Si, and 30 at% (53.6 wt%) and 425 °C in Al-Ge [146].

in Si (maximum solid solubility of 160 ppm [163]), and this gives rise to the formation of nearly pure Si particles. Because the atomic numbers Z of Al and Si are so similar ($Z_{Al} = 13$ and $Z_{Si} = 14$), we investigate the Al-Si system using phase contrast imaging, see section 4.2. However, a well-refined Al-Si eutectic is a very challenging contrast object to image in this way, even after phase retrieval and image processing. The interference of Fresnel fringes at the solid-liquid and solid-solid interfaces would require substantial mathematical reconstruction to arrive at the true form of the contrast object [148].

To circumvent these experimental challenges, we “dope” the Al-Si alloy with a heavy element, e.g., Cu ($Z_{Cu} = 29$), which serves as an agent to generate X-ray absorption contrast. The ternary Al-Si-Cu diagram is shown in Fig. 4.3 [90]. Consider alloys of hyper-eutectic composition, such as Al-32wt%Si-15wt%Cu. As can be seen in Fig. 4.3, this alloy consists of essentially pure Si particles in a Cu-enriched liquid at a temperature of 627 °C. The solid solubility of Cu in Si is less than 0.5 ppm [50, 83], and therefore
the Cu constituent is almost entirely dissolved in the liquid phase. In this fashion, we are able to resolve the solid-liquid interfaces by imaging this alloy system in the absorption mode. A similar “doping” strategy was employed by Ref. [148] to study irregular eutectic solidification in Al-Si-Cu and Al-Si-Cu-Sr alloys via realtime X-ray radiography.
Another option is to examine a binary system analogous to Al-Si. One option is the Al-Ge system, which is characterized by a simple eutectic phase diagram, see Fig. 4.2, and a shallow eutectic temperature (425 °C). The Al-Ge system is an ideal candidate for tomographic imaging for two reasons: firstly, the Ge constituent has a similar entropy of fusion $\Delta S_m$ as several faceted metalloids (Table 4.1) [65, 103], which means that we can generalize the results of our studies to a host of highly anisotropic systems. Such faceted materials have relatively high $\alpha$-factors indicating atomically smooth interfaces, as explained in section 2.3. Secondly, the Ge constituent provides good interphase contrast due to the large difference in atomic number between Al and Ge ($Z_{Al} = 13$ and $Z_{Ge} = 32$). For these reasons, we can image the Al-Ge system in the absorption mode. The alloy compositions investigated in this thesis are given in Table 4.2(a).

4.1.1. Sedimentation of Particles

In each of the above alloy samples, solid particles in a liquid experience viscous drag forces as well as gravitational forces. By balancing these two forces, we arrive at an expression for the terminal velocity, $V$, at which the particles have net zero acceleration [118]:

$$V = \frac{2}{9} \left( \frac{\rho_p - \rho_f}{\mu} \right) g R^2$$

where $\rho_p$ is the particle density, $\rho_f$ is the fluid density, $\mu$ is the dynamic viscosity, $g$ is the gravitational acceleration, and $R$ is the radius of the spherical particle. The sign of $V$ indicates the direction of the particle’s movement: if $\rho_p - \rho_f > 0$, then the particle flows downward, else it floats upward. Eq. 4.1 is known as Stokes’ sedimentation rate [118], and can be estimated using materials parameters. For instance, consider pure Si particles
in a liquid of composition Al-13wt%Si at 575 °C, and assume \( R = 50 \mu m \). Using values for the Al-Si system \([178]\) results in a terminal velocity \( V \) of \(-600 \mu m/s\). This is the correct order of magnitude for \( V \), as verified from the realtime experiments.

In particular, high-speed tomographic imaging allows us to investigate the interfacial dynamics during sedimentation. An example is given in Fig. 4.4 for Al dendrites growing in an Al-Cu liquid. Each image represents a 2D slice of the 3D reconstruction; the time between consecutive images is 1 s. The Al dendrite detaches from the oxide skin and floats to the top of the field-of-view. The motion of the dendrite is governed by its large size (\( R \) in Eq. 4.1) as well as the large density difference between the solid and liquid phases (\( \rho_p - \rho_f \ll 0 \)). The Si particles growing in an Al-Si liquid behave similarly. However, eutectics such as Al-Si and Al-Ge have extremely dense and highly interconnected (or web-like \([169]\)) morphologies, which prevent sedimentation from taking place.

Sedimentation may also occur due to the rotation of the sample during data acquisition. As such, we cannot neglect the influence of centripetal forces on the interfacial dynamics. If this centripetal acceleration is less than the gravitational acceleration, then the sedimentation due to rotation is negligible with respect to Stokes’ sedimentation \([67]\). We equate the force required to move the particle with its centripetal force to obtain \([67]\)

\[
(4.2) \quad a = \left( \frac{\rho_p - \rho_f}{\rho_p} \right) r \left( \frac{2\pi}{\Delta t} \right)^2
\]

where \( a \) is the centripetal acceleration, \( r \) is the radius of the rod-like sample, and \( \Delta t \) is the time taken to traverse \( 2\pi \) radians. The last term in parenthesis is the angular velocity of the particle, assuming the particle is located at the outer edge \( r \) of the rod sample.
Figure 4.4. Sedimentation process of a growing Al dendrite in an Al-Cu liquid, measured over eight time-steps (a-h). The time between consecutive X-ray reconstructions is 1 s. The Al dendrite detaches from the oxide skin and floats to the top of the field-of-view. Unpublished data.

Using the upper-limit values of $\Delta t = 1$ s and $r = 0.5$ mm, we find $a = 1 \mu$m/s$^2$ for Si particles in a liquid of eutectic composition at the eutectic temperature.

4.1.2. Sample Preparation

Al-Si, Al-Si-Cu, and Al-Ge rods were prepared by the Materials Preparation Center (MPC) at Ames Laboratory [147] via vacuum arc-melting. High purity powders (99.999% Al, 99.9999% Si, 99.99% Cu, and 99.99% Ge) were repeatedly melted in an atmosphere of high purity argon and flipped three times to ensure homogeneity. The
as-cast buttons were then machined into near-cylindrical samples of 1 mm diameter by 5.5 mm length using electrical discharge machining (EDM) at Northwestern University. To remove any impurity atoms that may be adsorbed on the surface of the sample, rod surfaces were etched with a 1:1 solution by volume of 70% HNO$_3$ and de-ionized water using a cotton swab for five minutes. Prior to the tomography experiment, sample compositions were confirmed via energy dispersive X-ray spectroscopy (EDX).

Despite etching the sample surfaces, the alloy sample is eventually covered by an oxide “skin” measuring a few nanometers deep. This is because Al has a relatively high standard oxidation potential [15], and thus loses electrons readily. Because Al$_2$O$_3$ has a high melting point (2072 °C) in comparison to the alloys of interest (Figs. 4.2-4.3), the oxide skin fully contains the molten alloy during the tomographic investigation.

4.2. Synchrotron-Based X-ray Tomography

X-ray tomography (XRT) was the first characterization technique to combine a computer with an imaging system, and the first to herald a new era of digital imaging [170]. The non-destructive nature of the method enables the study of the temporal evolution of microstructures in four dimensions [108]; for a review, see Ref. [189]. XRT experiments are often conducted at synchrotron facilities, as they provide high flux X-rays that are continuous over a wide energy range [63, 142, 242]. For example, Fig. 4.5 shows a plot of average spectral brilliance versus photon energy for typical synchrotron light sources, in comparison to conventional X-ray tubes; the latter emit X-rays of a characteristic energy. In contrast, in synchrotron-based XRT, we have the advantage of selecting either a monochromatic beam or an energy bandwidth (so-called “pink beam”). A third option is
Table 4.2. Details on the XRT experiments described in Refs. [82, 196, 197, 198, 199, 200], and conducted in 2012, 2014, and 2015.

<table>
<thead>
<tr>
<th>i.d.</th>
<th>Composition</th>
<th>Experiment</th>
<th>Beamline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al-29.9wt%Si</td>
<td><em>ex situ</em> coarsening of Si particles in a liquid</td>
<td>SLS TOMCAT</td>
</tr>
<tr>
<td>2</td>
<td>Al-32wt%Si-15wt%Cu</td>
<td><em>in situ</em> coarsening of Si particles in a liquid</td>
<td>Argonne APS 2-BM</td>
</tr>
<tr>
<td>3</td>
<td>Al-32wt%Si-15wt%Cu</td>
<td><em>in situ</em> growth of Si particles in a liquid</td>
<td>Argonne APS 2-BM</td>
</tr>
<tr>
<td>4</td>
<td>Al-54wt%Ge</td>
<td><em>in situ</em> growth of an irregular Al-Ge eutectic</td>
<td>Argonne APS 2-BM</td>
</tr>
</tbody>
</table>

(a) Overview of the experiments performed in this thesis.

<table>
<thead>
<tr>
<th>i.d.</th>
<th>Imaging Mode</th>
<th>Energy (keV)</th>
<th>OD Dist.</th>
<th>Scintillator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>phase contrast</td>
<td>28</td>
<td>110 mm</td>
<td>100 μm LuAg:Ce</td>
</tr>
<tr>
<td>2</td>
<td>atten. contrast</td>
<td>poly.</td>
<td>45 mm</td>
<td>20 μm LuAg:Ce</td>
</tr>
<tr>
<td>3</td>
<td>atten. contrast</td>
<td>poly.</td>
<td>45 mm</td>
<td>20 μm LuAg:Ce</td>
</tr>
<tr>
<td>4</td>
<td>atten. contrast</td>
<td>poly.</td>
<td>45 mm</td>
<td>20 μm LuAg:Ce</td>
</tr>
</tbody>
</table>

(b) Beamline setup parameters, where “OD dist.” is object-detector distance.

<table>
<thead>
<tr>
<th>i.d.</th>
<th>$f_s$ (Hz)</th>
<th>Exp. Time (ms)</th>
<th>$N_θ$</th>
<th>$K$</th>
<th>Rot. Rate (°/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>0.36</td>
</tr>
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<tr>
<td>3</td>
<td>50</td>
<td>14</td>
<td>1500</td>
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<td>4</td>
<td>34</td>
<td>27</td>
<td>2700</td>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

(c) Data sampling parameters, where “exp.” is exposure and “rot.” is rotation.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1</td>
<td>2560 × 2160</td>
<td>2560 × 2560 × 2160</td>
<td>0.74</td>
<td>approx. 600</td>
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<td>varies</td>
</tr>
<tr>
<td>3</td>
<td>2560 × 1100</td>
<td>2560 × 2560 × 1100</td>
<td>0.65</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>2560 × 600</td>
<td>2560 × 2560 × 600</td>
<td>0.65</td>
<td>20</td>
</tr>
</tbody>
</table>

(d) Projection and reconstruction dimensions, and spatial and temporal resolutions.
Figure 4.5. Average spectral brilliance (brightness) versus photon energy for typical synchrotron light sources compared with conventional X-ray laboratory sources. In contrast to characteristic tube sources, synchrotrons provide very high fluxes over a wide energy spectrum [63].

“white beam,” which includes most of the available energy bandwidth. The high flux of X-rays in synchrotron-based XRT allows managing “beam hardening,” a classic problem with conventional X-ray tubes, by filtering the incident X-rays as necessary [63].

Fig. 4.6 shows a schematic layout of a synchrotron-based XRT experiment. A high flux beam of X-rays is transmitted through a rotating cylindrical sample; then, the corresponding X-ray projections on the imaging detector plane are used to reconstruct the sample in 3D. The second step of reconstruction is necessary because the projected image represents a superposition of the materials structure along the path of the beam. Typically, we collect hundreds to thousands of projections as the sample is rotated from 0 to 180°. Then, we apply reconstruction methods on the collected projection data in order to decode the materials structure in 3D. The focus of this section is to shed light on how
these projections are collected, including the physics of X-ray imaging, while Chapter 5 discusses the reconstruction methods and data processing routines.

One of the key parameters of an XRT experiment is the sample-detector (propagation) distance. In absorption (attenuation) contrast tomography (ACT), the detector plane is located immediately behind the sample, see Fig. 4.6(a). On the other hand, in phase contrast tomography (PCT), the detector plane is found a greater distance downstream.
More specifically, the propagation distance in an in-line PCT experiment must satisfy the near-field condition, \( i.e., z \ll d^2/\lambda \), where \( z \) is the propagation distance, \( d \) the characteristic size of the smallest discernible features in the sample, and \( \lambda \) is the X-ray wavelength \([173, 241]\). Thus, the sample-detector distance determines the contrast mechanism in an XRT experiment. To see why, consider the free space propagation of an X-ray wavefront behind an aperture, as shown in Fig. 4.7. The wave profile is calculated as a function of distance using the Kirchoff-Fresnel diffraction integral \([219]\). The wavefront represents a step function at the contact plane due to X-ray absorption; however, at greater distances, Fresnel diffraction of the X-ray beam enhances the visibility of edges and boundaries \([149]\). PCT experiments take advantage of this edge enhancement. Both ACT and PCT are discussed below in terms of their contrast mechanism.

4.2.1. Contrast Mechanism

When an X-ray beam passes through an absorbing material, the interaction between the photons and the atoms changes the amplitude and the phase of the propagating wavefront. This behavior is described by the object’s complex refractive index \( n \) given by

\[
(4.3) \quad n = (1 - \delta) + i\beta
\]

where \( \delta \) is the refractive index decrement and \( \beta \) is the attenuation index \([37, 142]\). Note that in contrast to optical light, the real part of the refractive index is close to but less than unity \([9]\). In the hard X-ray regime, in which photon energies exceed 5-10 keV, and

\footnote{It should be noted that the meaning of phase contrast is different based on the method used. These include an interferometric method, holography-like method, and others \([149]\). Here, we restrict our discussion to inline PCT, in which a sample imposes a phase-shift to the incident X-ray beam.}
assuming a multicomponent material, $\delta$ and $\beta$ can be written as \([9, 39, 160]\)

\[ (4.4) \]

\[
\delta = \frac{r_e \lambda^2}{2\pi} \sum_k N_k (Z_k + f_r^k), \quad \beta = \frac{\lambda}{4\pi} \sum_k N_k \mu_{ak}
\]

where $r_e$ is the classical electron radius, and $N_k$, $Z_k$, $f_r^k$, and $\mu_{ak}$ are the atomic density, atomic number, atomic scattering factor (real part), and the atomic absorption coefficient (photoelectric absorption cross-section) of element $k$, respectively. Note that $\sum_k N_k f_r^k$ is the electron density; thus, the refractive index decrement $\delta$ is linearly proportional to electron density. In addition, the absorption cross-section $\mu_{ak}$ is directly proportional to $Z_k^4$ \([9, 39, 160]\). This latter variation gives rise to the conventional absorption contrast between different elements in a microstructure (e.g., Al and Ge in an Al-Ge eutectic).

As a result, ACT provides limited contrast for materials with low atomic number, or for systems consisting of elements with similar atomic numbers (e.g., Al and Si in an Al-Si
eutectic). PCT, on the other hand, provides better contrast in such systems since the real part of the refractive index $\delta$ in Eq. 4.3 dominates over the imaginary part $\beta$ [37, 244].

Suppose that photons impinge on a material of thickness $d\ell$ and that imaging takes place in the absorption mode. Assume a parallel beam geometry, as in Fig. 4.6, and a spatially uniform incident illumination $I_0$. Then, the intensity $I$ on the detector plane is

$$\ln[I(r_1, r_2; \theta)/I_0] = -\int_{\mathcal{L}(r_1, r_2; \theta)} \mu(x, y, z) \, d\ell$$

where $(x, y, z)$ refers to the object coordinate system, $(r_1, r_2)$ refers to the coordinate axes on the detector plane, $\theta$ is the projection angle (Fig. 4.6), and $\mathcal{L}(r_1, r_2; \theta)$ is the ray path of the X-ray beam. The linear attenuation coefficient $\mu$ is related to the imaginary part of the refractive index as $\mu = 4\pi \beta/\lambda$. Eq. 4.5 is known as the Beer-Lambert law [9]. It is also known in applied mathematics as the forward Radon transform $\mathcal{R}$ [111].

Alternatively, in PCT, regions of the material with different $\delta$-values produce by refraction different phase-shifts $\phi$ of the collimated beam [37, 244], according to

$$\phi(r_1, r_2; \theta) = \frac{2\pi}{\lambda} \int_{\mathcal{L}(r_1, r_2; \theta)} \delta(x, y, z) \, d\ell$$

For cases with not too high spatial resolution and moderate propagation distance, the PCT projection image satisfies the transport of intensity equation, described elsewhere [167,
Then, it can be shown [246] that the intensity on the detector plane is

\[
\ln \left( \frac{I(r_1, r_2; \theta)}{I_0} \right) = - \int_{L(r_1, r_2; \theta)} \mu(x, y, z) \, d\ell \\
+ R^2 \nabla^2 \int_{L(r_1, r_2; \theta)} \delta(x, y, z) \, d\ell \\
- R \left[ \nabla \int_{L(r_1, r_2; \theta)} \mu(x, y, z) \, d\ell \right] \cdot \left[ \nabla \int_{L(r_1, r_2; \theta)} \delta(x, y, z) \, d\ell \right]
\]  (4.7)

Eq. 4.7 is undoubtedly more complex than the analogous equation for absorption-based projections (Eq. 4.5). Here, the expression for \( \ln \left( \frac{I(r_1, r_2; \theta)}{I_0} \right) \) includes not only a ray-integral of the object’s linear attenuation coefficients, but also (second term) the Laplacian of the ray-integrals of the object’s refraction index decrements, and (third term) the mixed products of the gradients of ray-integrals of both the attenuation coefficients and refraction indices [246]. The dominant term in Eq. 4.7 is the Laplacian of the X-ray phase-shifts, \( \nabla^2 \phi(r_1, r_2; \theta) \), since the \( \beta(x, y, z) \) terms in Eq. 4.7 do not provide appreciable contrast for lightweight materials [196], as previously discussed. Consequently, the PCT projections and reconstructions feature dark-bright Fresnel fringes, see for example Fig. 4.8(a). Thus, \( \nabla^2 \phi(r_1, r_2; \theta) \) is responsible for edge enhancement in PCT images.

4.3. Experimental Details for XRT

Several parameters in the beamline setup influence the quality of the images collected. Selecting the optimal parameters is often a difficult task as there are competing objectives of spatial resolution versus temporal resolution between consecutive reconstructions [67]. For example, to produce high quality images (i.e., with high contrast-to-noise ratio), it may be necessary to increase the camera exposure time per projection. However, this
Figure 4.8. 2D slice of 3D reconstructed data of primary Si particles in an Al-Si eutectic. This sample is imaged using PCT. (a) First order Fresnel fringes are visible in the reconstructed data. Conventionally, X-ray projections acquired from PCT undergo a filtering process known as phase retrieval [28] prior to reconstruction. (b) The effect of phase retrieval on the collected data is to “fill in” the particles with uniform intensity [196].

comes at a cost of a reduced speed of acquisition, since more time would be required to traverse 360°. This may be an issue if the material is evolving rapidly, as in eutectic growth, such that the dynamic imaging may not be able to keep pace with the evolution of the interfaces. For these reasons, we must consider the interplay between several parameters in order to tune the beamline setup to our experimental demands.

Fig. 4.9(a) shows a photo of the experimental setup at APS sector 2-BM at Argonne National Laboratory. In our experiments at APS, we focus a high flux “pink” X-ray beam (see section 4.2) on the samples and a LuAg:Ce scintillator is used to convert the transmitted X-rays to visible light. The scintillator and the camera comprise the
Figure 4.9. (a) Photo of the full setup at APS sector 2-BM at Argonne National Laboratory. (b-e) Components of the tomography experiment, including the furnace, thermocouples, and alumina rod sample holder. The BN crucible (containing the sample) sits atop the Al₂O₃ rod.

“detector” indicated in Fig. 4.9(a). We analyze in greater detail below the components of this setup, including the detector, furnace, and sample holder.

4.3.1. Detector Considerations

With respect to the scintillator, one of the key parameters is its thickness, which can range from 20 to 200 µm. In general, X-rays scatter through the scintillator material [44], which causes some blurring (also known as “blooming”) artifacts on the detector plane. In fact, the blooming length scale is directly proportional to the thickness of the scintillator screen. Therefore, one might suppose that a thinner scintillator is beneficial for
imaging fine features, *e.g.*, individual lamellae in an eutectic matrix. However, lowering
the screen thickness lowers the amount of absorbing converter material that the X-rays
travel through, and therefore the X-ray detection efficiency is proportionally reduced. The
scintillator material and thickness are given in Table 4.2(b) for our experiments.

Following scintillation, the visible light is magnified using a 10× fixed objective and
saved as an image using a PCO.Edge 5.5 CMOS camera. The camera field-of-view mea-
sures 2560 pixels wide by 2160 pixels tall (at maximum), with a pixel size of $0.65^2 \mu m^2$.
Ultimately, the camera frame rate, denoted $f_s$, and the exposure time determine the tem-
poral resolution of the tomographic scan. Note that the exposure time has an upper
bound of $f_s^{-1}$. While longer exposure times undoubtedly increase the signal-to-noise ratio
of the projections collected, in some cases it may be advantageous to expose well below
the $f_s^{-1}$ limit. Since the sample is rotating during the exposure time of each projection,
there may be some blurring artifact due to the sample rotation. This is especially pro-
nounced for relatively fast rotation rates. For instance, consider a sample rotation speed
of 720 °/s and an exposure time of 4 ms; then, the corresponding angular blue is 2.88°.
Frames rates $f_s$ and exposure times for our experiments are provided in Table 4.2(c). The
other two scan parameters, $N_\theta$ and $K$, are discussed in section 5.

4.3.2. Furnace Considerations

To exploit the tomography capabilities of the APS, and to study transformations *in situ*,
we make use of a specially designed furnace. This furnace is water cooled, copper-clad,
and contains resistive heating elements. A schematic is shown in Fig. 4.9(b). As can
be seen, the furnace contains a window for the incident X-ray beam to pass. There is
also an opening located at the top of the furnace, such that a thermocouple (Fig. 4.9(c)) can be conveniently inserted. The thermocouple reads two temperatures along its length, denoted $T_1$ and $T_2$, where $T_1$ is measured 0.5 in below $T_2$. For the isothermal coarsening experiments, the furnace must be capable of holding a stable temperature for long periods, on the order of a few hours. In addition, the axial temperature gradients (i.e., along the long axis of the sample) must be small. Note that the radial temperature distribution is assumed to be uniform given the 1 mm diameter of each sample. However, any axial temperature gradients lead to compositional gradients in the liquid phase via the liquidus curve in the equilibrium phase diagram (Fig. 4.2). This in turn leads to the flux of solute and an interfacial motion that is not due to capillary driving forces [67].

Fig. 4.10 shows temperature measurements for $T_1$ and $T_2$ during heating and cooling experiments [81]. The axial temperature gradient is calculated as approx. 1.5 °C/mm. This temperature gradient does not pose an issue for the eutectic growth experiments, given that these tomographic scans are relatively short (i.e., an hour or less). However, for the coarsening experiments, we use instead a double zone furnace (not pictured) that allows for the independent control of two heating elements located on opposite ends of the furnace. With the double zone furnace, there is no temperature-induced migration, and thus the axial temperature gradients are assumed to be negligibly small.

4.3.3. Sample Holder Considerations

During the experiment, the samples are placed in a 3 mm diameter BN crucible, which is then inserted on top of a 100 mm Al$_2$O$_3$ rod, see Figs. 4.9(d-e). The Al$_2$O$_3$ rod sits on a rotation stage, as shown in Fig. 4.9(a), which can be raised into and lowered out of the
Figure 4.10. The furnace used at APS at Argonne National Laboratory allows for controlled (a) heating and (b) cooling rates. Shown are two temperature readings from the thermocouple: temperature $T_1$ (black curve) is measured 0.5 in below temperature $T_2$ (red curve), see Fig. 4.9(c). The axial temperature gradient is approx. 1.5 °C/mm. [81].

The BN holder is used because it is transparent to the incident X-rays; in addition, for the temperatures and alloy samples of interest, BN exhibits outstanding thermal stability and chemical inertness. Occasionally, however, the BN crucible undergoes brittle fracture, especially during rapid thermal cycling. Presumably, this is due to the mismatch in the coefficient of thermal expansion between the BN crucible and the Al$_2$O$_3$ skin of the sample, which touches the walls of the crucible. Therefore, it is imperative to adjust temperatures very gradually to avoid the formation of cracks in the BN crucible.

### 4.4. Electron Backscatter Diffraction

Through XRT, we can peer into the dynamics of the *external*, solid-liquid interfaces during growth and coarsening. However, we cannot access the *internal* structure of the solid particles, including the 3D network of grain boundaries. Therefore, to fully characterize the grain misorientation within the particles, we make use of the conventional
electron backscatter diffraction (EBSD) technique, as illustrated in Fig. 4.11(a). When an electron beam enters a crystalline solid, it is diffusely scattered in all directions. Thus, there must always be some electrons arriving at exactly the Bragg angle $\theta_B$ according to

$$\lambda = 2d \sin \theta_B$$

where we consider only first order diffraction, $\lambda$ is the wavelength of the monochromatic radiation, and $d$ is the interplanar spacing. The locus of diffracted radiation forms the surface of a Kossel cone with a half-apex angle of $90 - \theta_B^\circ \ [180, 206]$. There are two such Kossel cones for each family of planes $\{hkl\}$. The phosphor recording medium is positioned so as to intercept the diffraction cones. The pair of lines on the detector plane corresponding to these Kossel cones are known as Kikuchi lines $[180, 206]$. The spacing between the Kikuchi lines is $2\theta_B$, and thus the width of the Kikuchi “bands” relates to a particular crystallographic plane. The resulting Kikuchi diffraction pattern can be indexed by comparing it to a dictionary of such patterns. If the electron beam is raster-scanned across the sample surface, we can evaluate the interfacial texture over large regions, an example of which is shown in Fig. 4.11(b). Here, interfacial texture refers to the distribution of crystallographic orientations of a given material $[180]$. 

Our samples are prepared for EBSD by first grinding the surface with 14.5, 12.2, and 6.5 $\mu$m sandpaper, then subsequently polishing with a diamond suspension and etching with Keller’s reagent. For each measurement, the sample is tilted to about 70° with respect to the electron beam. The electron microscope is operated at 30 keV with a working distance of 6 mm; the step size and spot size during EBSD data collection are 1.3 $\mu$m and 4.5 nm, respectively $[198]$. Indexing of electron backscatter patterns is performed on-site
Figure 4.11. (a) The principle of EBSD: diffraction occurs from the interaction of the “backscattered” electrons with the lattice planes. The resulting Kikuchi pattern can be indexed by comparing to a dictionary of such patterns. (b) The electron beam can be raster-scanned across the sample surface, as shown for primary Si particles in an Al-Si eutectic (black). The particles are colored according to the standard triangle (see inset). 

*via* the integrated Oxford AZtec software. Indices are accepted when the misfit between the simulated and detected Kikuchi bands has a mean angular deviation of less than 1°. Then, the texture data is analyzed *via* the MATLAB toolbox MTEX [12], in order to generate the orientation maps and misorientation distributions [198].
CHAPTER 5

Tomographic Reconstruction Methods

The collection of the X-ray projections at a synchrotron facility (chapter 4) represents only the first step of the experimental workflow. Extracting quantitative information from the X-ray images, following the X-ray tomography experiment, requires a significant amount of computational work. For instance, it is necessary to reconstruct the raw projection into usable, real-space images of the evolving microstructure. The reconstructions are then segmented (binarized) in order to determine accurately the location of the interfaces (chapter 6); then, we calculate the local curvatures, orientations, and velocities on the basis of the segmented data (chapter 7). The flowchart in Fig. 5.1 depicts the typical data processing pipeline following the X-ray tomography experiment.

The process of reconstruction is the focus of this chapter.\footnote{The subject matter of this chapter is adapted in part from Ref. \textsuperscript{196} by A. J. Shahani and coworkers.} Reconstruction falls within the class of inverse problems, in which we calculate from a set of observations (\textit{i.e.}, the X-ray projections) the causal factors that produced them (\textit{i.e.}, the 3D microstructure); it is called an inverse problem because we start with the “results” and calculate the “causes” \textsuperscript{[156]}. In particular, the inverse problem of tomographic reconstruction is sketched out in Fig. 5.2. The chapter will be comprised of the computational methods needed to reconstruct the X-ray projections collected \textit{via} attenuation and phase-contrast XRT experiments. Furthermore, we propose \textsuperscript{[196]} a multimodal technique for reconstructing weakly absorbing samples (in which $\beta \approx 0$, see Eq. 4.3) in the near-field regime.
Figure 5.1. Flowchart depicting typical data processing pipeline following (1) XRT experiment: (2) data are reconstructed using conventional FBP or higher level TIMBIR algorithm; then, (3) reconstructions are segmented to determine accurately the location of interfaces; these interfaces are meshed, or represented as a sequence of triangle faces and vertices for (4) quantitative microstructural analyses, which include the determination of interfacial curvatures, orientations, and velocities. See chapters 5, 6, and 7.

5.1. Attenuation-Based Reconstruction

5.1.1. Filtered Backprojection

The filtered backprojection (FBP) algorithm is the conventional approach of reconstructing projections collected from an X-ray tomography experiment. We use FBP to reconstruct datasets #2 and #3 in Table 4.2. It is commonly employed for attenuation-based
Figure 5.2. Schematic of the difference between (a) projections, (b) sinograms, and (c) reconstructions. Projections have the three dimensions $(x, z, \theta)$, while sinograms are $(x, \theta)$ slices of the dataset. To achieve the real space representation of the data, i.e., in moving from (b) to (c), one must solve the “inverse problem” of tomographic reconstruction $[156]$.

projections, but as will be demonstrated in section 5.2, it can also be used to reconstruct phase-based datasets. As its name implies, there are two steps in the FBP algorithm: (1) the filtering part, which can be understood as a simple “weighting” of each projection in the frequency domain, and (2) the backprojection part, which is equivalent to finding the “elemental reconstruction” corresponding to each weighted projection $[111]$. The filtering step is performed in the Fourier domain, while the backprojection step is done in the space domain. Filtering of the projections is necessary because the “unfiltered” backprojection yields a blurred version of the original object. For instance, consider the Dirac impulse centered at $(x_0, y_0)$ and given by $f(x, y) = \delta(x - x_0, y - y_0)$. It can be shown $[78]$ that unfiltered backprojection of $f(x, y)$ gives the $(x^2 + y^2)^{-1/2}$ or $1/r$ function (in polar coordinates), which has heavy tails. Details of the FBP algorithm are given below.
First, denote the 1D projection $P_\theta(t)$ and its Fourier transform $S_\theta(w)$ as

\begin{align}
P_\theta(t) &= \int_{-\infty}^{\infty} f(t,s) \, ds \\
S_\theta(w) &= \int_{-\infty}^{\infty} P_\theta(t) \, e^{-i 2\pi w t} \, dt
\end{align}

(5.1)

where each projection is collected at some angle $\theta$ (Fig. 4.6) along lines of constant $t$, $f(t,s)$ is the 2D function to be reconstructed and $w$ is the transform variable. Note the projection of a planar object is a line. Following from Eq. 4.5, $P_\theta(t) = -\ln[I(t;\theta)/I_0]$ and hence $f(x,y) = \mu(x,y)$ for a 2D attenuation-contrast experiment. We multiply the projection data transform $S_\theta(w)$ by a filter $\mathcal{P}(w)$ (i.e., the weighting function) and take the inverse Fourier transform of the result, giving the filtered projection $Q_\theta(t)$ \[111\],

\begin{equation}
Q_\theta(t) = \int_{-\infty}^{\infty} S_\theta(w) \, \mathcal{P}(w) \, e^{i 2\pi w t} \, dw
\end{equation}

(5.2)

Note that by the convolution theorem, the Fourier transform of a convolution is the pointwise product of Fourier transforms (in this case, $S_\theta(w)$ and $\mathcal{P}(w)$). In practice, we use for weighting function $\mathcal{P}(w)$ the following piecewise expression:

\begin{equation}
\mathcal{P}(w) = \begin{cases} 
  w^2 - 6 \frac{w}{w_m} \left( \frac{w}{w_m} \right)^2 \left( 1 - \frac{|w|}{w_m} \right), & \text{if } |w| < \frac{w_m}{2}, \\
  2 w^2 \left( 1 - \frac{|w|}{w_m} \right)^3, & \text{if } \frac{w_m}{2} < |w| < w_m, \\
  0, & \text{otherwise},
\end{cases}
\end{equation}

(5.3)

where $w_m$ is some user-selected cut-off frequency. Note that $\mathcal{P}(w)$ is the product of the Parzen filter \[88\] and the ramp filter $|w|$, see Fig. 5.3. Here, $w_m$ is 250 px\(^{-1}\). The combined
Figure 5.3. Types of filters $\mathcal{R}(w)$ in the FBP reconstruction algorithm, which are applied in Fourier space [111]. “Combined” refers to the product between “Ramp” (high-pass) and ”Parzen” (low-pass) filters.

filter (Eq. 5.3) optimally offers both edge-enhancement ($i.e.$, high pass characteristics below $w_m$) and smoothing ($i.e.$, low pass characteristics) of the projection data.

Then, we must sum over the image plane the filtered projections $Q_\theta(t)$ according to

$$f(x, y) = \int_{0}^{\pi} Q_\theta (x \cos \theta + y \sin \theta) \, d\theta$$

Eq. 5.4 represents the backprojection step of the FBP algorithm, where we have used the substitution $t = x \cos \theta + y \sin \theta$ [111]. The backprojection procedure is simulated in Fig. 5.4 by changing the upper limit of the integral in Eq. 5.4 from $0^\circ$ to $180^\circ$. During the backprojection operation, the projections are iteratively “smeared” onto the image plane along the path that they were originally acquired. Finally, the last image (Fig. 5.4(f)) represents a 2D map of the attenuation indices, $\mu(x, y)$. Taken altogether, the FBP algorithm represents the inverse Radon transform $\mathcal{R}^{-1}$ of the projection data [111].

A key parameter when conducting XRT experiments is the number of projections $N_\theta$ to collect per sample rotation, evenly spaced between $0^\circ$ and $180^\circ$. According to the Nyquist sampling criterion [98], $N_\theta$ should be the same as the number of pixels along the length of
Figure 5.4. Simulation of the backprojection procedure, wherein projections are “smeared” [111] onto the image plane along the path that they were originally acquired. Each image (a-f) adds more consecutive projections that help improve the quality of the reconstruction: (a) 120, (b) 240, (c) 360, (d) 480, (e) 600, and (f) 720 projections (per 180° rotation).

the reconstruction. For “fast” tomography experiments, fewer projections than this are used in order to save time during data acquisition. The influence of $N_\theta$ on the quality of the FBP reconstruction is shown in Fig. 5.5. With an increasing number of projections, the microstructure becomes clearer and the streak artifacts are reduced. Thus, there is a delicate balance between speed of acquisition and spatial resolution requirements.
Figure 5.5. The effect of increasing the number of projections used in the reconstruction of a $512 \times 512$ domain: (a) 4, (b) 8, (c) 16, (d) 32, (e) 64, and (f) 90 projections. The microstructure becomes clearer and the streak artifacts are reduced with increasing number of projections.

5.1.2. Time-Interlaced, Model-Based Iterative Reconstruction

State-of-the-art reconstruction methods (e.g., the Gridrec algorithm [144]) are able to achieve micrometer-scale spatial resolution or sub-second temporal resolution independently but not concurrently [67]. Recent efforts led by Purdue University electrical engineers have led to a new framework for collecting XRT data that offers vast improvements in the temporal resolution with no degradation in the spatial resolution. This method is known as time-interlaced, model-based, iterative reconstruction (TIMBIR) [158], and is
described in detail below. Note that experiment #4 (table 4.2) in this thesis makes use of the TIMBIR approach for imaging eutectic growth in realtime [200]. We found that the eutectic lamellae are approx. 3 μm thick, and grow at a rate of 10 μm/s (order of magnitude). In comparison, a temporal resolution of approx. 20 s is now achievable in the traditional approach to sampling and reconstruction [248]. However, within 20 s, eutectic lamellae may have moved 200 μm! Therefore, the TIMBIR framework is needed to achieve a temporal resolution similar to the timescale at which the lamellae are growing.

TIMBIR is the synergistic combination of two innovations: time interlaced sampling (TI) and model-based iterative reconstruction (MBIR) [68, 158]. In the conventional, progressive sampling approach, \( N_{\theta} \) projections per reconstruction are collected such that the rotation angle is proportional to time, see Fig. 5.6(a). Alternatively, in TI sampling, each frame of data consisting of \( N_{\theta} \) projections is acquired over \( K \) interlaced sub-frames; each sub-frame of data then collects \( N_{\theta}/K \) equally spaced projections, but together the full frame of data contains all \( N_{\theta} \) distinct projections of the object. Examples of TI sampling are shown in Figs. 5.6(b-c) for \( N_{\theta} = 16 \) where \( K = 2 \) and \( K = 4 \), respectively [158]. In other words, a total of \( N_{\theta} \) views are split into \( K \) sets [158]. For progressive sampling, \( K = 1 \). Note that the progressive and TI sampling approaches measure projections at the same angles, although not in the same order. Thus if \( N_{\theta} \) meets the Nyquist criterion in the progressive sampling scheme, it meets it using the TI method as well [67].

The second novelty in the TIMBIR framework is the MBIR reconstruction, a schematic model for which is shown in Fig. 5.7. In MBIR, the reconstruction is typically formulated as the maximum a posteriori (MAP) estimate of the unknowns given the measurable data. If \( y \) represents the data, \( x \) the unknown voxels, and \( \phi \) the unknown calibration parameters
associated with the measurement, then the reconstruction is given by

\[
(\hat{x}, \hat{\phi}) = \text{argmin} \left[ -\log p(y|x, \phi) - \log p(x) \right]
\]

where the bracketed term represent the MAP cost function, \( p(y|x, \phi) \) is the conditional distribution of \( y \) given \( x \) and \( \phi \), and \( p(x) \) is the prior distribution of \( x \) \([157, 158, 228]\). The "forward model" \( p(y|x, \phi) \) incorporates the physics of X-ray transmission as well as measurement variations and the presence of "zinger" artifacts or high-energy photons \([157]\); the "prior model" \( p(x) \) accounts for nearest-neighbor interactions between voxels in space and time. MBIR computes the 4D reconstruction by searching for the result \((\hat{x}, \hat{\phi})\) that best fits these forward and prior models until convergence is reached. Convergence refers to the smallest possible difference between the collected and reconstructed data. In practice, Eq. 5.5 is minimized using non-homogeneous iterative coordinate descent, which works by more frequently updating those voxels with a greater need for updates. Furthermore, we use a multi-resolution initialization to speed convergence, which performs reconstructions at coarser resolutions first, in order to initialize the reconstruction at finer resolution. For mathematical details, see Refs. \([157, 158, 228]\).

The MBIR reconstruction interfaces with the TI sampling as follows: for each \( N_\theta/K \) views, an MBIR reconstruction is calculated. This allows each reconstruction to be focused on a narrow slice in time; simultaneously, the temporal regularization across different datasets (in the prior model \( p(x) \) in MBIR) allows for the Nyquist sampling criterion to be satisfied \([67, 68]\). These advances allow TIMBIR to achieve a temporal resolution of approx. 1 s, a factor of 20 better than conventional approaches. A comparison of Gridrec \([144]\) and TIMBIR reconstructions of eutectic growth is given in Fig. 5.8. Because
TIMBIR offers clear gains in the reconstruction quality, we use the TIMBIR framework to reconstruct sample #4 (table 4.2) at all slices and time-steps.

5.1.2.1. Parameter Selection. In practice, we use a q-generalized Gaussian Markov random field (qGGMRF) as the prior model \( p(x) \) (Eq. 5.5) for all voxels [158]. The prior is used to model the sample in space and in time. Two of the most important parameters in the qGGMRF model that require sample-specific tuning are the spatial and temporal regularizations, denoted \( \sigma_s \) and \( \sigma_t \), respectively [158]. Reducing \( \sigma_t \) will increase the temporal “smoothness” which can improve the reconstruction quality. However, excessive smoothing in time may introduce artifacts. Similarly, reducing \( \sigma_s \) will make the reconstruction smoother, and increasing it will make the reconstruction sharper (and perhaps also noisier). Picking the optimal values of \( \sigma_s \) and \( \sigma_t \) often requires trial and error.

Examples of the resulting reconstructions of a fully-solidified Al-12.7wt%Si alloy using different \( \sigma_s \) and \( \sigma_t \) combinations are given in Fig. 5.9. It can be seen that the Al-Si eutectic microstructure is highly sensitive to the regularization parameters. Upon manual inspection, we find that the highlighted reconstruction is the one that offers the best balance between noise removal and detail preservation, both spatially and temporally.

5.2. Phase-Based Reconstruction

Thus far, we have addressed reconstruction approaches for attenuation-contrast tomography datasets, including the FBP algorithm and the higher-level TIMBIR framework. Here, we provide details on the reconstruction of PCT datasets. Conventionally, phase-based reconstruction (section 4.2.1) involves two steps: first, a phase map is obtained by applying phase-retrieval algorithms to the projections collected by a similar
Figure 5.6. Illustration of (a) conventional, progressive views, and (b-c) interlaced data collection scheme. (b) 16 views have been interlaced over two sub-frames, such that each sub-frame contains eight equally spaced views. (c) Four sub-frames with four views each. The arrows point to the relative angular difference between two sub-frames [158].

Figure 5.7. Workflow for MBIR, where $y$ represents the data, $x$ the unknown voxels, and $\phi$ the unknown calibration parameters. The reconstruction is subject to a prior model, $p(x)$, and a forward model, $h(x, \phi)$; the resulting data can then be compared to the collected data until convergence is reached, i.e., until the difference is below some threshold [157, 158, 228].
Figure 5.8. Comparison of (a) Gridrec [144] and (b) TIMBIR reconstructions of an Al-Ge eutectic during the growth process. With a limited number of projections per 180° rotation, noise is more severe in the Gridrec reconstruction (see arrows and also Fig. 5.5). For this reason, we use TIMBIR to reconstruct the evolving dataset at all slices and time-steps.

setup to Fig. 4.6(b) [173, 246]. Then, FBP is applied to these phase maps in order to recover the refractive index decrement [111]. This two-step approach of phase-retrieval followed by backprojection will hereafter be referred to as PAG. On the other hand, it is possible to reconstruct the 3D tomograms directly from the projection images, collected at the same object-detector distance, using the FBP algorithm; this one-step approach will be referred to as PFBP to distinguish it from attenuation-based FBP.

There are a multitude of phase retrieval methods suitable for PAG, and the application of each depends on the refractive properties of the material being imaged. Table 5.1 includes some commonly-encountered phase-retrieval algorithms. Even though the assumptions for each method are different, they all involve a smoothing operation. In other words,
Figure 5.9. Different $\sigma_s$ and $\sigma_t$ regularization parameter combinations applied to a fully-solidified Al-12.7wt%Si dataset. Reducing $\sigma_s$ and $\sigma_t$ smooths the data in space and time, respectively. We pick those values of $\sigma_s$ and $\sigma_t$ in the prior model that give rise to the highlighted reconstruction.

The single-image phase-retrieval algorithms that are conventionally used show inherently low-pass characteristics. Note that the phase maps are obtained by direct integration in the image domain, which is equivalent to dividing by spatial frequency $|w|$ in the Fourier domain; this, in turn, acts as a low-pass filter [100, 174]. In our study, the smoothing operation leads to diffuse interfaces in the PAG reconstructions (Fig. 4.8(b)), since the high frequency edges are damped during phase-retrieval. Unfortunately, smoothing of the interface makes it difficult to determine accurately the interfacial morphology.

On the other hand, the PFBP images are characterized by dark-bright fringes at the interfaces (Fig. 4.8(a)), giving rise to the so-called “halo effect” [171]. In the near-field regime, only the first-order Fresnel fringes are visible in the reconstructions [142, 37]. Recall that the unfiltered intensity on the detector plane is proportional to the Laplacian...
Table 5.1. Methods of phase retrieval for in-line PCT, where \( g(I) \) represents the input function on which the filter \( H_p(|w|) \) is applied. The filtering operation is done in Fourier space, where \( w \) is the spatial frequency. Note \( r_e \) is the classical electron radius, \( \sigma_{KN} \) is the total cross-section for X-ray Compton scattering from a single free electron, and \( A(r) \) is the total projected thickness of the object on the detector plane \( r = (r_1, r_2) \) (Fig. 4.6). [28].

| Method                 | \( g(I) \)          | \( H_p(|w|) \)                  | Assumptions               |
|------------------------|----------------------|---------------------------------|---------------------------|
| Bronnikov              | \( \frac{I}{I_0} - 1 \) | \( [2\pi \lambda z |w|^2]^{-1} \) | \( \mu = 0 \)             |
| Modified Bronnikov     | \( \frac{I}{I_0} - 1 \) | \( [2\pi \lambda z |w|^2 + \alpha]^{-1} \) | \( \mu \approx 0 \)        |
| Phase-Atten. Duality   | \( \frac{I}{I_0} \)   | \( [2\pi \frac{r_e \lambda^2 z}{\sigma_{KN}} |w|^2 + 1]^{-1} \) | \( \mu \propto \delta \)  |
| Single Material        | \( \frac{I}{I_0} \)   | \( [4\pi^2 z^2 |w|^2 + 1]^{-1} \) | Known \( \delta, \mu; \mu \propto \delta \) |
| Two Materials          | \( \frac{I}{I_0} \exp[\mu_2 A(r)] \) | \( [4\pi^2 z^2 \frac{\delta_1 - \delta_2}{\mu_1 - \mu_2} |w|^2 + 1]^{-1} \) | Known \( \delta_1, \delta_2, \mu_1, \mu_2 \) |

of the X-ray phase-shifts, \( \nabla^2 \phi(r_1, r_2; \theta) \), see Eq. 4.7. These images are very challenging to segment, because the “halo effect” leads to spurious edges in the binary images. Current efforts in the development of TIMBIR (section 5.1.2) are focused on modifying the forward model to account for these Fresnel dark-bright fringes typical of PCT experiments.

5.3. Multimodal Reconstruction Technique

We propose an integrated image processing methodology [196] that utilizes both phase and absorption contrast, derived from applying PAG and PFBP algorithms separately to the raw PCT data, along with a suite of data processing methods (section 6) to allow the automated segmentation of large datasets acquired through 4D XRT. Our multimodal reconstruction technique is illustrated schematically in Fig. 5.10. Unlike the work of Ref. [136], the PAG and PFBP images are combined in real space, and due to the complexity of the microstructure and the sensitivity of our measurements, a more robust...
Figure 5.10. Summary of multimodal reconstruction technique on projections collected via PCT (red outline). The top branch represents the FBP algorithm, whereas the bottom branch represents the conventional PAG approach of (1) phase-retrieval followed by (2) backprojection. The purple reconstruction is the linear combination of the two [196].

The phase map, $\phi(r_1, r_2; \theta)$, of each projection is calculated during the phase-retrieval step of the PAG technique [173, 241]. Taking the inverse radon transform $R^{-1}$ [111] of $\phi(r_1, r_2; \theta)$ in Eq. 4.6 gives the backprojected image, $\mu_{PAG}(x, y, z)$,

\begin{equation}
\mu_{PAG}(x, y, z) \propto \delta(x, y, z)
\end{equation}

While Ref. [173] derived the expression for phase map $\phi(r_1, r_2; \theta)$ by assuming a homogeneous material, it was shown that the method can still be used to reconstruct a multicomponent material with different $\delta$-values [18]. Thus, Eq. 5.6 represents a 3D map of $\delta$-values. While it is easy to qualitatively differentiate between components in this $\delta$-map, it is challenging to quantitatively characterize the system due to its low pass characteristics. When the projections are backprojected without the intermediate phase-retrieval image processing procedure is necessary (section 6). The hybrid images feature improved contrast-to-noise ratio and sharpness over their constituent images [196].
step the reconstructed image intensity, $\mu_{PFBP}(x, y, z)$, is such that [246]

\begin{equation}
\mu_{PFBP}(x, y, z) \propto \nabla^2 \delta(x, y, z) + \mu_{atten}(x, y, z) + \mu_{mixed}(x, y, z)
\end{equation}

where $\mu_{atten}(x, y, z)$ is the linear attenuation coefficient and $\mu_{mixed}(x, y, z)$ is a function of $\mu_{atten}(x, y, z)$ and $\delta(x, y, z)$ [246]. Eq. 5.7 comes about by taking the inverse radon transform $R^{-1}$ of Eq. 4.7; since $R^{-1}$ is a linear operator, the reconstructed image comprises three sub-images [246]. The dominant term is the Laplacian of refractive index decrements, $\nabla^2 \delta(x, y, z)$, as before. While the PFBP image offers sharper interfaces due to $\nabla^2 \delta(x, y, z)$, the grayscale intensity levels of the components are very similar [196].

A hybrid PCT reconstruction, $\mu_+(x, y, z)$, is given by the expression [196]

\begin{equation}
\mu_+(x, y, z) = c_1 \mu_{PAG}(x, y, z) + (1 - c_1) \mu_{PFBP}(x, y, z)
\end{equation}

which represents a linear combination of the PAG and PFBP images. Here $0 \leq c_1 \leq 1$, thereby combining the strong contrast present within the PAG image and the sharp interfaces found in the PFBP image. In other words, the PFBP image is a natural source of image sharpening. Thus, it is possible to extract two sets of data, PAG and PFBP, from a single PCT experiment, and the linear combination of the two provides a hybrid reconstruction crucial for quantitative analysis. It is anticipated that this multimodal approach could be generally applicable to weakly absorbing samples (in which $\beta \approx 0$) imaged in the near-field regime; these conditions would then give rise to the edge-enhancement of $\mu_{PFBP}$ and low-pass characteristics of $\mu_{PAG}$. However, the parameter $c_1$, reflecting the contribution of the PAG image in the hybrid reconstruction, may require sample-specific
tuning for other datasets [196]. Below, we show how this multimodal approach can be adapted to reconstruct an Al-Si alloy imaged via ex situ PCT (dataset #1 in Table 4.2).

### 5.4. Image Quality Metrics

The scalar $c_1$ in Eq. 5.8 is determined by optimizing $\mu_+(x, y)$ with respect to two image quality metrics: contrast-to-noise ratio (CNR) and sharpness (SH). The notation $(x, y)$ indicates a 2D slice of the 3D $(x, y, z)$ volume. In other words, whereas Ref. [136] tuned the propagation distance for optimal image quality, we optimize the relative contributions of PAG and PFBP images in $\mu_+(x, y)$, at a single object-detector distance [196]. In this way, varying this scalar allows for robust segmentation of our PCT images. Once the optimal scalar $c_1$ is determined by the above mentioned metrics, the resultant multimodal image, $\mu_+$, is segmented according to the procedure described in chapter 6.

#### 5.4.1. Contrast-to-Noise

One way to define contrast-to-noise ratio or CNR is using the following expression,

$$\text{CNR} = 2 \left( \frac{|S_f - S_b|}{\sigma_f + \sigma_b} \right)$$

where $S$ and $\sigma$ are the mean and standard deviation, respectively, of the pixel values in the manually-defined foreground, $f$, and background, $b$, regions. For our images of hypereutectic Al-Si alloys (dataset #1 in Table 4.2), the foreground refers to the Si particles and the background refers to the eutectic matrix. This PCT experiment is ex situ in that a quenched sample was imaged tomographically after annealing isothermally at 600 °C.
5.4.2. Image Sharpness

Although technically SH lacks a precise definition, intuitively, sharpness is related to the fineness of the resolvable details [196]. We use the global single parameter sharpness model, implemented by Shaked and Tastl [201] as the ratio between the output energy of an ideal high pass filter and an ideal band pass filter [201]:

\[
SH = \frac{\int_{\xi \in H} |\mu_+ (\xi)|^2 d\xi}{\int_{\xi \in B} |\mu_+ (\xi)|^2 d\xi}
\]

where \(\xi = (\xi_x, \xi_y)\) are the Cartesian frequency coordinates, and \(H\) and \(B\) are the high and low band pass frequency ranges, respectively. Additionally, the resolution of the multimodal images is crosschecked using the method described by Ref. [161]. First, the power spectral density (PSD) of an arbitrary line profile in the image is computed. This PSD converges to a value defined as the noise baseline. Resolution is computed by taking twice the value of the PSD at the noise baseline, and matching it to a spatial frequency, \(w_{res}\) [161]. Then, the spatial resolution, \(x_{res}\), is calculated as [161]

\[
x_{res} = \frac{2\pi}{w_{res}}
\]

Practical implementation of this resolution criterion is met if the maximum spatial frequency of the image is less than one-half of the sampling frequency of the line profile [161].

5.4.3. Assessment of Hybrid Images

Fig. 5.11(a-e) show multimodal images of primary Si particles in an eutectic matrix with varying contributions of \(\mu_{PAG}\) and \(\mu_{PFBP}\). In the extreme limits, Fig. 5.11(a) depicts
\( \mu_{PFBP} \), where \( c_1 = 0 \) in Eq. 5.8, and Fig. 5.11(e) shows \( \mu_{PAG} \), where \( c_1 = 1 \). The dark gray structures represent the primary Si particles and the light gray background along with the fine elongated darker features represent the eutectic. While there is sufficient contrast between Si particles and the eutectic in the PAG image in Fig. 5.11(e), the interfaces are quite diffuse, due to the low-pass characteristics of the phase-retrieval algorithm (Table 5.1). On the other hand, the PFBP reconstruction in Fig. 5.11(a) features prominent Fresnel fringes at the interfaces of the Si particles, due to \( \nabla^2 \delta \) in Eq. 5.7.

To assess the quality of the multimodal images, we measured CNR and SH for each image [196]. Since we are interested only in relative values of CNR and SH for comparison purposes, normalized values, denoted by \( \hat{CNR} \) and \( \hat{SH} \), respectively, will be used whenever possible. Specifically, \( \hat{CNR} \) in Fig. 5.11(f) is normalized with respect to the minimum and maximum values of CNR, at \( c_1 = 0 \) and \( c_1 = 1 \), respectively. It is also important to note that \( \hat{SH} \) is sensitive to the filter cut-off frequencies in Eq. 5.10. Thus, we investigate three high-pass frequency cutoffs, denoted \( w_1 > w_2 > w_3 \) in Fig. 5.11(f), where \( w_1, w_2, \) and \( w_3 \) are 0.32, 0.28, and 0.24 pixels\(^{-1} \), respectively; all \( \hat{SH} \) values are normalized with respect to the minimum and maximum values of SH at cutoff \( k_1 \). In all cases, the band pass frequency range is defined as [0.02, 0.2] pixels\(^{-1} \). As expected, \( \hat{SH} \) increases with decreasing high-pass cut-off frequency, for a given value of \( c_1 \), since the output energy of the high-pass filter increases. Regardless of the cut-off frequency selected, the results indicate that PFBP images are sharper than PAG images, while PAG images offer greater contrast-to-noise ratio. The optimal reconstruction is a trade-off between these two image quality metrics. In practice, we use \( c_1 = 0.5 \) to reconstruct dataset #1.
Figure 5.11. Multimodal images with varying contributions of $\mu_{PAG}$ and $\mu_{PFBP}$: (a) $c_1 = 0$, (b) $c_1 = 0.25$, (c) $c_1 = 0.5$, (d) $c_1 = 0.75$, and (e) $c_1 = 1$. (f) These images were assessed with respect to $\hat{CNR}$ and $\hat{SH}$, where $w_1 > w_2 > w_3$ are three different high-pass cut-off frequencies used in measuring $\hat{SH}$. Optimal trade-off between $\hat{CNR}$ and $\hat{SH}$ occurs at an intermediate value of $c_1$, that may require sample-specific tuning [196].

in table 4.2. The resulting hybrid image preserves the contrast between Si particles and the eutectic, while also providing sharper interfaces for quantitative analysis [196].

Furthermore, spatial resolutions calculated using the power spectral density (PSD) approach are in good qualitative agreement with the relative sharpness estimates [196]. Fig. 5.12 shows the calculation of this resolution criterion, where $|C(w)|^2$ is the spectral power of the detected signal, $\mu_s$ is the noise baseline, and $w_{res}$ is the maximum spatial
Figure 5.12. Measurement of resolution for a line profile in (a) PFBP image and (b) PAG image where $|C(k)|^2$ is the spectral power of the detected signal, $\mu_s$ is the noise baseline, and $k_{res}$ is the maximum spatial frequency. Spatial frequencies are given in units of inverse pixels, px$^{-1}$. The PFBP image has a resolution approx. 40% greater than the PAG image [196].

frequency from Eq. 5.11. The PSDs shown in Fig. 5.12(a) and Fig. 5.12(b) have been calculated for line profiles (see inset images) in PFBP and PAG images, respectively. It can be observed that the PFBP image has a spatial resolution, $x_{res}$, that is roughly 40% greater than that of the corresponding PAG image; as such, the PFBP image provides a natural source of image sharpening, but at a cost of CNR (Fig. 5.11).

The enhanced resolution of the PFBP image can be understood by exploiting the Wiener-Khintchine theorem [243], which states that the autocorrelation function is the Fourier transform of the power spectrum (i.e., autocorrelation and PSD are a Fourier transform pair). According to Fig. 5.12(a), then, the PSD of the PFBP image shows high autocorrelation for long wavelengths. For this reason, $w_{res}$ for $\mu_{PFBP}$ is greater than $k_{res}$.
for $\mu_{PAG}$. This correlation in pixel intensity values over large distances is expected since only high-frequency, interfacial fringes manifest in the PFBP reconstructions [196].
CHAPTER 6

Segmentation Methods

In computer vision, segmentation is the process by which a digital image is partitioned into multiple sets of pixels. The goal of segmentation is to simplify an image into something that is meaningful to analyze. For instance, image segmentation is often used to locate objects and boundaries, e.g., the interface between Si particle and eutectic in our reconstructions. For a review of the conventional segmentation approaches, see Ref. [190]. However, due to the complexity of the microstructure and the sensitivity of our measurements, we require a more robust image processing procedure. Moreover, the growing size of data collected during the XRT experiments, typically on the order of ten terabytes, renders manual segmentation impractical. For these reasons, we propose a suite of semi-automated segmentation algorithms that can be applied to attenuation and phase-based XRT experiments alike, and with minimal sample-specific tuning.\footnote{The subject matter of this chapter is adapted in part from Ref. [196] by A. J. Shahani and coworkers.}

For instance, in datasets #1 and #2 (Table 4.2), we aim to characterize the evolution of primary Si particles in an Al-Si(-Cu) system. Conventional image processing techniques, such as histogram thresholding and k-means clustering, fail to provide reliable results; for example, the “halo effect”, described in Section 5.2, leads to spurious edges in the PFBP images [171]. Meanwhile, smoothing of the interfaces in the PAG images (section 5.2) makes it difficult to determine the interfacial morphology. Advanced image processing techniques, such as the Expectation Maximization/Maximization of Posterior Marginals
Figure 6.1. (a) Hybrid image, $\mu_+$, subject to (b) Otsu thresholding [172] and (c) Expectation Maximization with Maximization of Posterior Marginals (EMMPM) algorithm [38, 207]. We need to segment only the primary Si particles (dark gray), which requires the removal of the Si lamellae in the eutectic [196]. Neither of the algorithms differentiate between structures of different size, nor do they preserve Si particle interiors.

(EM/MPM) algorithm [38, 207], fails to segment the images using their current image models, see Fig. 6.1. As a result, this approach does not allow us to characterize the primary Si particles that require the removal of the smaller fluctuations in the matrix. In the ex situ experiment (#1), these fluctuations are a result of the eutectic lamellae that appear with the same intensity level as the primary particles, and are an artifact of the quenching process. In the in situ experiment (#2), the noise that we perceive is not due to eutectic lamellae in the quenched samples, but rather to Nyquist undersampling and ring artifacts; the latter artifact may be a result of miscalibrated detector pixels [98]. Thus, it is necessary to enhance the edges of the primary Si particles while suppressing the low-frequency noise, in order to obtain a robust segmentation. The segmentation algorithms listed below are the ones that we use to achieve this goal. It is anticipated that this toolbox of segmentation algorithms can be tailored for various materials systems.
6.1. Noise-Adaptive Diffusional Filters

6.1.1. Nonlinear Diffusion Filter

Blurring the eutectic constituent and enhancing the interfaces of the primary Si particles (dataset #1 in Table 4.2) can be accomplished by using a nonlinear diffusion filter, such as a regularized Perona-Malik filter (RPM) [34, 176], which is applied on all 2D \((x, y)\) slices of the 3D \((x, y, z)\) dataset. In this method, a filtered image \(u(x, y, t)\), where \(t\) is the number of iterations, is obtained as the solution of the diffusion equation

\[
\frac{\partial}{\partial t} u_\sigma(x, y, t) = \text{Div} \left( D \left( |\nabla u_\sigma(x, y, t)|^2 \right) \nabla u_\sigma(x, y, t) \right)
\]

where

\[
D \left( |\nabla u_\sigma(x, y, t)|^2 \right) = \exp \left( -\frac{|\nabla u_\sigma(x, y, t)|^2}{\kappa^2} \right)
\]

\[
\left. \begin{array}{c}
 u_\sigma(x, y, t) = K_\sigma \otimes u(x, y, t) \\
u(x, y, 0) = \mu_+(x, y)
\end{array} \right\}
\]

The notation \(D \left( |\nabla u_\sigma(x, y, t)|^2 \right)\) is the nonlinear diffusion coefficient, \(\kappa\) is the gradient threshold parameter, \(K_\sigma\) is Gaussian structuring element with standard deviation \(\sigma\), and \(\otimes\) denotes the convolution operation [34]. The input of the algorithm is the hybrid image \(\mu_+\), see Eq. 5.8. Eqs. 6.1-6.2 suggest that the Perona-Malik model resembles forward diffusion for gradients whose absolute value is larger than the threshold \(\kappa\) and backward diffusion for gradients smaller than \(\kappa\) [107]. If the flux function is defined as \(\Phi = \nabla u \cdot D(|u_x|^2)\), it can be shown that the diffusion equation \(u_t = \nabla \left( D \left( |\nabla u|^2 \right) \nabla u \right)\) can be re-cast in terms of \(\Phi\) as \(u_t = \Phi \cdot u_{xx}\). Thus, the sign of the derivative of the flux function
Figure 6.2. Schematic plot of flux function $\Phi = \nabla u \cdot D(|u_x|^2)$ versus image gradient $|\nabla u|$. Note that the sign of $\Phi'$ will determine whether forward (+) or backward (−) diffusion will take place, since $u_t = \Phi' \nabla^2 u$ by the diffusion equation. For $|\nabla u| < \kappa$, where $\kappa$ is the gradient threshold, the system undergoes forward diffusion or “smoothing,” while for $|\nabla u| > \kappa$, the system undergoes backward diffusion or “edge enhancement” [107, 176].

$\Phi$ determines whether forward ($\Phi' > 0$) or backward ($\Phi' < 0$) diffusion will take place, see Fig. 6.2. This behavior is explicitly intended because it ensures that the filter smoothes over the lamellae in the eutectic while decreasing the widths of the interfaces of the primary Si particles. Furthermore, the iterative convolution of the image $u(x, y, t)$ with $K_\sigma$, in Eq. 6.2, regularizes the Perona-Malik model such that RPM is robust against local noise at scales smaller than or equal to $\sigma$ [34]. This means that gradients that result from lamellae are effectively removed, given that they are smaller than the Gaussian kernel. To minimize the local fluctuations in the eutectic, the images are also pre-processed with a combination of morphological and median filters [190].

The gradient threshold parameter, $\kappa$, is commonly fixed at a user-defined value [176]. A fixed $\kappa$ that is too small, however, may misinterpret large gradients due to noise as edges it should preserve, while a $\kappa$ that is too large may delete edges and small structures
Figure 6.3. (a) Plot of $\kappa$ versus number of iterations of RPM algorithm. Static $\kappa$ is fixed at a value of 0.05 which dynamic $\kappa$ is given by Eq. 6.3, where $\kappa_0 = 0.1$ and $\omega = 0.05$. The filtered images produced using static $\kappa$ and dynamic $\kappa$ after 250 iterations are shown in (b) and (c), respectively. Dynamic $\kappa$ preserves the edges of the Si particles better than static $\kappa$ [196].

during the diffusion process [107], see Fig. 6.3. Thus, $\kappa$ is updated such that it is proportional to the average noise in $u(x, y, t)$ at any given time. Noise can be estimated from morphological filters, see Refs. [190, 230]; however, these morphological operations, e.g., erosion and dilation, are computationally expensive and thus we estimate noise as

$$\kappa(t) \approx \kappa_0 \, \text{Exp}(-\omega t)$$

where $\omega$ is a user-selected constant. Eq. 6.3 suggests that the noise in the image drops exponentially under many applications of the RPM filter. In this way, the gradient threshold parameter $\kappa$ self-adapts to the image $u$ after every iteration of the RPM algorithm.
6.1.1.1. Parameter Selection. The parameter $\sigma$ (Eq. 6.2) is set in reference to the standard deviation of grayscale intensity values in the eutectic; $\kappa_0$ and $\omega$ (Eq. 6.3) are found from a nonlinear fit of the image noise \cite{190, 230} versus the number of iterations \cite{196}. It is important to note that the quality of the filtered images is most sensitive to the gradient threshold parameter, see Fig. 6.3. Time-varying or dynamic $\kappa$ preserves edges during the diffusion process. We find that after 1000 iterations (order of magnitude) of the RPM filter, the image converges to a steady-state \cite{196}.

6.1.2. Nonlinear, Anisotropic Diffusion Filter

In addition, we can use prior knowledge of materials structure to enhance semantically important interfaces. For instance, reconstructed Ge platelets in an Al-Ge eutectic (dataset #4 in Table 4.2) may appear rough on the mesoscale, due to the presence of speckle noise, when in fact they are crystallographically smooth along \{111\} (section 2.1). For this reason, we can introduce anisotropy in the Perona-Malik model by smoothing, in 3D, along the two directions of lowest grayscale fluctuations. The effect of this operation is to enhance coherent plate-like objects. Mathematical details are sketched out below.

Define the $3 \times 3$ structure tensor $J$ (per voxel) as \cite{107, 126, 240}

$$J = K_\sigma \otimes (\nabla u \cdot \nabla u^T) \tag{6.4}$$

where $K_\sigma$ is Gaussian structuring element with standard deviation $\sigma$ (as before), and the superscript $T$ indicates matrix transpose. The eigenvalues of $J$ are $\mu_1 \geq \mu_2 \geq \mu_3$ with corresponding eigenvectors $v_1, v_2,$ and $v_3$. Physically, the eigenvector $v_1$ describes the
Figure 6.4. Simulated datasets before and after application of a 3D anisotropic, nonlinear diffusion filter [107, 240]. Insets show 2D cross-sections of the datasets. (a) By smoothing along the direction of lowest grayscale fluctuation (where $\mu_1, \mu_2 \gg \mu_3$), we can enhance rod-like objects; if instead we smooth along the two directions of lowest grayscale fluctuations (where $\mu_1 \gg \mu_2, \mu_3$), we can enhance plate-like objects.

direction of highest gray-level fluctuation, and $v_3$ the direction of lowest contrast. Thus, to enhance coherent structures, we must smooth along (at least) $v_3$ [107, 126, 240].

As in RPM filtering, the image $u$ is evolved under application of the diffusion equation (Eq. 6.1). In this case, however, the diffusivity $D$ is nonlinear and anisotropic. The
eigenvectors of $D$ are $v_1$, $v_2$, and $v_3$, while the eigenvalues $\lambda$ are determined by the microstructure. For instance, eigenvalues that result in plane-enhancement are \[ \lambda_1 = c_1 \]
\[ \lambda_2 = c_1 + (1 - c_1) \exp \left( -\frac{c_2}{(\mu_2 - \mu_3)^2} \right) \]
\[ \lambda_3 = c_1 + (1 - c_1) \exp \left( -\frac{c_2}{(\mu_1 - \mu_3)^2} \right) \]
where $c_1$ and $c_2$ are user-defined constants. The expression $(\mu_1 - \mu_3)$ is a measure of local coherence [107, 240]; note that the diffusivity $\lambda_3$ along $v_3$ increases with respect to the coherence $(\mu_1 - \mu_3)$. In similar fashion, we can enhance rod-like objects along a single direction only by replacing $\lambda_2$ in Eq. 6.5 with a constant $c_1$ [126]. Examples of the anisotropic diffusion filter on simulated datasets are given in Fig. 6.4.

6.2. Bias-Field Corrections using Fuzzy Logic

The diffusion-filtered images are characterized by uneven background illumination. Intensity inhomogeneities or the bias field, arise from the extrinsic diffusional characteristics of RPM filtering as well as the intrinsic dark-light fringes suggested by Eqs. 5.7-5.8. This effect often results in under or over segmentation for fixed histogram threshold values [196]. In order to estimate the bias field of an image, Ref. [5] introduced an algorithm based on fuzzy logic, known as bias-corrected fuzzy C-means (BCFCM). Before discussing the mechanics of the BCFCM algorithm, it is worthwhile to introduce fuzzy logic below, in the context of the conventional fuzzy C-means (FCM) algorithm.
6.2.1. Fuzzy C-Means

FCM is a method of clustering data into two or more clusters [51, 22]. It is based upon minimization of the objective function $J$ (not to be confused with the structure tensor),

$$ J = \sum_{i=1}^{c} \sum_{k=1}^{N} u_{ik}^p \| x_k - \nu_i \|^2 $$  

(6.6)

where $c$ is the user-determined number of clusters, $N$ is the number of pixels, $x_k$ is the $k$-th pixel of measured data, $u_{ik}$ is the degree of membership of $x_k$ in cluster $i$, $p$ is the “fuzziness coefficient,” and $\nu$ are the cluster centroids. Theoretically, $u_{ik}$ and $p$ are defined in the ranges $[0,1]$ and $[1,\infty]$ [22], respectively, although the ideal value of $p$ is problem-specific.

The notation $\| * \|$ is the distance between $x_k$ and centroid $\nu_i$. Data are bound loosely to each cluster by means of a membership function $u_{ik}$, which represents the “fuzzy” behavior of the algorithm. For instance, consider the 1D clustering example shown in Fig. 6.5: twenty datapoints (grey circles) and two clusters are used to initialize the FCM algorithm. The membership function (in red) follows a smooth line to show that every datapoint may belong to multiple clusters with different probabilities [22, 51]. In practice, the algorithm proceeds by minimizing $J$ subject to $\{u_{ik} \in [0,1] \mid \sum_{i=1}^{c} u_{ik} = 1 \forall k\}$.

It is important to emphasize that the picture in Fig. 6.5 is quite different than a step-function characteristic of the more deterministic k-means (KM) clustering algorithm [190]. The objective function (Eq. 6.6) is identical in both cases; however, in FCM, each datapoint has a weighting associated with a particular cluster. A datapoint doesn’t belong to a single cluster, as much as it has a strong or weak association to the cluster,
Figure 6.5. Schematic of 1D fuzzy c-means (FCM) algorithm: data (gray circles) along the x axis are grouped into two clusters, \( c_1 \) and \( c_2 \), where \( u \) refers to the membership function. The partitioning is “fuzzy” since data can belong to both clusters, and hence \( u \) may be between 0 and 1 [22, 51].

Given by its inverse distance to the cluster centroid [22, 51]. Thus, shorter distances to the cluster centroid would result in a high value of the membership function.

In addition, most clustering algorithms (such as FCM and KM) group datapoints according to some notion of proximity between the points. Thus, the choice of a particular distance function should reflect the nature of the dataset. For instance, in Eq. 6.6, Euclidean distance is applied in the FCM algorithm. Clustering can also be accomplished on a unit hypersphere; in this non-euclidean geometry, the “distance” measured between a centroid vector \( \vec{\nu} \) and a data vector \( \vec{x} \) is the cosine dissimilarity given by \( (1 - \vec{x} \cdot \vec{\nu}) \), assuming both \( \vec{x} \) and \( \vec{\nu} \) are normalized [48, 151]. It can be shown that the squared Euclidean distance \( \|x_k - \nu_i\|^2 \) is directly proportional to this dissimilarity function [151].

### 6.2.2. Bias-Corrected Fuzzy C-Means

In order to estimate the bias field of an image, Ref. [5] modified \( J \) as

\[
(6.7) \quad J = \sum_{i=1}^{c} \sum_{k=1}^{N} u_{ik}^p \|x_k - \nu_i\|^2 + \frac{\alpha}{N_R} \sum_{i=1}^{c} \sum_{k=1}^{N} u_{ik}^p \left( \sum_{x_r \in N_k} \|x_r - \nu_i\|^2 \right)
\]
where $N_k$ is the set of neighbors of $x_k$, $N_R$ is the cardinality of $N_k$, and $\alpha$ is a weighting parameter [5]. The first term of Eq. 6.7 is the standard fuzzy C-means expression (Eq. 6.6, while the second term accounts for the fact that each pixel is influenced by its local neighborhood. More specifically, the regularizing effect of a pixel’s local neighborhood is controlled by the parameter $\alpha$ [5]. Thus, the goal of BCFCM algorithm is to divide the data into two clusters, that of the primary silicon particles and that of the eutectic constituent, while taking into account the slow-varying bias field of the images.

BCFCM was originally developed for magnetic resonance imaging, though it can be applied to our data by modeling the image after the RPM filter has been applied as

$$y_k = x_k + \beta_k$$

where $x_k$ and $y_k$ are the true and observed intensities of the $k$-th pixel, respectively, and $\beta_k$ the bias field at the $k$-th pixel. Inserting $x_k$ in Eq. 6.7 and minimizing $J_m$ with respect to constraints on membership, $u$, leads to an expression for $\beta_k$ [5]. The bias-corrected image $x_k$ has a bimodal histogram and therefore can be robustly segmented using conventional histogram-based segmentation methods, such as Otsu’s method [172].

6.2.2.1. Parameter Selection. In the BCFCM algorithm, we use a cardinality $N_R$ (Eq. 6.7) of eight and 5000 iterations in order to represent the image using two clusters, corresponding to the Si particles and the matrix [196]. The neighborhood parameter $\alpha$ is estimated as the inverse of the signal-to-noise ratio in the RPM-filtered image. Theoretically, $p \in [1, \infty)$ although the ideal value is problem-specific and was empirically selected for our dataset (#1 in Table 4.2). However, increasing $p$ beyond two causes the clusters to overlap significantly such that cluster boundaries become ill-defined [196].
6.3. Digital Image Inpainting

BCFCM algorithm assumes a two-phase system. Presence of voids in the microstructure, which appear as dark regions in the image, result in misinterpretation of bias field of the image \[196\]. Thus, prior to the bias-field correction, it is necessary to determine if a given image has voids, and if so, to camouflage these voids. Hartigan’s dip test (HDT) is a statistical measure of the deviation of a distribution from unimodality \[89\]. It is a useful tool since statistically significant voids manifest as a separate peak in the image histogram. For each image, if HDT determines that the histogram is not unimodal to a confidence level of 95%, the voids are inpainted by solving the steady-state diffusion equation with constant diffusivity (i.e., Laplace’s equation), only within the void, see Refs. [21, 140] for details. Following inpainting, the images associated with dataset #1 (Table 4.2) are processed using RPM filtering and BCFCM algorithm, respectively \[196\].

Fig. 6.6(a) shows a flowchart of segmentation methods applied to our PCT images. An example in 1D is given in Fig. 6.6(b). It can be seen that successive iterations of the RPM filter allow for the removal of intra-phase noise while still preserving interface positions \[196\]. The interface width decreases with iterations of RPM filter because these stronger fluctuations are above the gradient threshold \(\kappa(t)\) and thus diffusion is inhibited (see also Fig. 6.2). With RPM filtering, it is possible for diffusion and edge detection to interact in one process. The final result with bias-field corrections is shown at the top of Fig. 6.6(b) \[196\]. In addition, Fig. 6.7 summarizes the segmentation steps in 2D, where we have used a combination of digital image inpainting, noise-adaptive diffusional filters, and bias-field corrections with fuzzy logic to process dataset #1 in Table 4.2.
6.4. Evaluation of Segmented Images

Similar to section 5.4, in which two metrics were used to evaluate the quality of the tomographic reconstructions, this section is concerned with the quantitative assessment of the proposed segmentation algorithms. The evaluation of the segmentation results, e.g., Figs. 6.6(b) and 6.7(f), is difficult since the “ground truth” is unknown. However, in
supervised evaluation, the segmented image can be compared to the manually segmented image in terms of the adjusted rand index (ARI). ARI describes the similarity between the two methods, and varies between $-1$ and $1$, where $1$ indicates a perfect match:

$$ARI = \frac{\sum_{ij} \binom{n_{ij}}{2} - \left( \sum_i \binom{a_i}{2} \sum_j \binom{b_j}{2} \right) / \binom{n}{2}}{\frac{1}{2} \left( \sum_i \binom{a_i}{2} + \sum_j \binom{b_j}{2} \right) - \left( \sum_i \binom{a_i}{2} \sum_j \binom{b_j}{2} \right) / \binom{n}{2}}$$

(6.9)

where

$$a_i = \sum_j n_{ij}, \quad b_j = \sum_i n_{ij}, \quad \text{and} \quad n = \sum_{ij} n_{ij}$$

(6.10)

and where $n_{ij}$ is the number of voxels belonging to class $i$ in the manual segmentation, and to class $j$ in the automated approach [99, 179]. For datasets #1 and #2 (Table 4.2), there are two classes corresponding to the Si particles and the eutectic matrix (or liquid phase). The notation $\binom{\cdot}{\cdot}$ represents the binomial coefficient. Manual segmentation is conducted by tracing out the interfaces of the hybrid images. For instance, we find for dataset #1 that we can achieve an ARI value of $0.91 \pm 0.02$ using the proposed segmentation suite (Figs. 6.6 and 6.7) [196]. This ARI value is not intended to make a statement on the absolute accuracy of the automated segmentation, but to provide a relative comparison to the manual case. As such, the high ARI value indicates that using the proposed automated method, we can achieve results similar to that of manual segmentation with significantly less effort and much greater reproducibility [196].

On the other hand, unsupervised evaluation enables the objective comparison of segmentation methods without human intervention (e.g., manual segmentation) [255]. For instance, given an image of a 100% solid alloy sample, we can compare the nominal alloy
composition with that calculated from the segmented image. This is the procedure by
which we evaluate five segmentation approaches on a solid Al-56wt%Ge eutectic dataset
(#4 in Table 4.2), see Fig. 6.8. Here, we find that the “comp. dilated” method, based on
the dilation filter [190], captures the nominal composition and is the one used to segment
the dataset. In general, unsupervised methods incorporating such prior knowledge can
enable the tuning of algorithm parameters based on the evaluation results [255].
Figure 6.7. Segmentation steps on (a) 2D hybrid image: (b) pre-processing step with inpainted void, (c) isotropic, non-linear diffusion smoothing, (d) bias-field estimation and (e) subtraction from RPM filtered image, and (f) Otsu-thresholded output. Interface positions are preserved [196].

Figure 6.8. (a) Evaluation of five segmentation approaches on a 100% solid Al-56wt%Ge eutectic dataset. The segmentations are compared with respect to the nominal alloy composition. The “comp. dilated” method (i.e., based on the dilation filter [190]) captures closely the nominal composition and is used to segment the dataset. The Al-Ge eutectic during growth is shown (b) before and (c) after application of the “comp. dilated” method. Black pixels correspond to Ge, light blue to Al, dark blue to the liquid phase, and red to regions of the liquid phase sandwiched between Al and Ge. The “comp. dilated” method reduces these red artifacts.
CHAPTER 7

Microstructural Analysis Methods

The focus of this chapter is on the collection of analytical tools that are applied on the segmented images. There are two classes of analytical tools: those that measure global properties that describe the entire microstructure, and those that measure local properties of a small section of interface. The global quantities are surface area per unit volume $S_{v^{-1}}$ and volume fraction $V_{v}$, which can be determined from the tomography data itself or by stereological means. The local properties of interest are the local curvatures, orientations, and velocities, which can only be measured computationally using the 4D XRT data.

7.1. Mesh Generation and Smoothing

For the subsequent analyses, the digitized surfaces are meshed. That is, the solid-liquid interfaces are represented as a sequence of triangles and vertices, see Fig. 7.1. Each triangle on the mesh and its three vertices $v$ will hereafter be referred to as a patch [198]. Measurement of global and local properties make use of mesh face and vertex positions, as discussed below. To remove any meshing artifacts (e.g., staircasing) prior to analysis, we smooth the mesh by mean curvature flow [25, 47]. Curvature flow smooths the surface by moving along the surface normal $\hat{n}$ with a speed given by the mean curvature $H$:

\begin{equation}
\frac{\partial v}{\partial t} = -H \hat{n}
\end{equation}
where $t$ is time. Using this approach, a sphere should stay spherical under mean curvature flow as the curvature is constant [47]; in this way, the interfacial morphology is preserved during the smoothing process. Even so, curvature smoothing tends to shrink volume [198], especially for more aggressive smoothings. For this reason, we apply the least amount of curvature smoothing for each structure to maintain the integrity of the interface. The effect of mesh smoothing on the subsequent analysis is discussed below.

Fig. 7.2(a) shows a plot of the logarithm of inverse surface area per unit volume of dataset #1 (Table 4.2) at time $t = 10$ min., versus number of iterations of triangular mesh smoothing. As the number of iterations of smoothing increases from 0 to 120, the measured $\ln[S_v^{-1}/\mu m]$ increases by 0.3 or almost 10%). Figs. 7.2(b-f) show the tomographic reconstruction (gray) superimposed with edges from the segmented image (black lines) as well as mesh vertices intersecting the 2D plane (red lines), for different levels of mesh smoothing. Subtle variations in the location of mesh vertices may result in appreciable
Figure 7.2. (a) Logarithm of inverse surface area of the Si particles per unit volume at time $t = 10$ min. during isothermal coarsening, versus number of iterations of mesh smoothing. As the number of iterations of smoothing increases from 0 to 120, the measured $\ln[S_v^{-1}/\mu m]$ increases by 0.3 or almost 10%. (b) Tomographic reconstruction (gray) superimposed with edges from the binary image (black) as well as the mesh vertices intersecting the 2D plane (red). While the segmentation and triangulation appear to accurately represent the interfaces at the scale of this image, a closer examination may reveal otherwise. (c-f) Magnified boxed region at different levels of mesh smoothing: 0, 20, 60, and 120 iterations, respectively [198].

differences in $S_v$. In practice, we use 15 iterations of mesh smoothing, which optimally reduces the staircasing artifacts while preserving the integrity of the interface. Similarly,
the interfacial normal and curvature are highly sensitive to the level of mesh smoothing, since they are computed as the first and second derivative of the interface, respectively.

7.2. Surface Area per Unit Volume \( S_v \)

Surface area per unit volume is an important measure of length scale during both growth and coarsening. For instance, during diffusion-limited growth, we would expect \( S_v^{-1} \) to vary parabolically with time \((i.e., S_v^{-1} \propto t^{1/2}, \text{see Eq. 6.1})\); on the other hand, during diffusion-limited coarsening, we would expect the relationship \( S_v^{-1} \propto t^{1/3} \) to hold (Eqs. 3.15 and 3.16). Note that the volume \( V \) can either be that of the full ROI or of the solid phase. In dataset #1 (Table 4.2), \( V \) is that of the full ROI during isothermal coarsening \([198]\), while in the dataset #2, we normalize the surface area, \( S \), with respect to the volume of the solid phase. This is because the volume fraction of the solid phase decreases by over 40\% during coarsening due to sedimentation of particles out of the ROI \([199]\). During growth (datasets #3 and #4), the volume of solid phase is a better option since the interfacial area increases due to additional solid forming or due to other morphological changes \([67]\). \( S \) and \( V \) can be calculated from the mesh as

\[
S = \frac{1}{2} \sum_i \| \vec{e}_{i,1} \times \vec{e}_{i,2} \|
\]

\[(7.2)\]

\[
V = \frac{1}{6} \left| \sum_i (\vec{v}_{i,1} \times \vec{v}_{i,2}) \cdot \vec{v}_{i,3} \right|
\]

where \( i \) is the index of the triangular patch; \( \vec{e}_{i,1}, \vec{e}_{i,2}, \text{and} \vec{e}_{i,3} \) are its three edge vectors; \( \vec{v}_{i,1}, \vec{v}_{i,2}, \text{and} \vec{v}_{i,3} \) are its three vertices; \( \| \ast \| \) indicates vector norm; and \( | \ast | \) is absolute value. The equation for \( V \) assumes that the surface is closed, and that the vertex order is
consistent for all faces, e.g., \( \vec{v}_{i,1} \rightarrow \vec{v}_{i,2} \rightarrow \vec{v}_{i,3} \), see Ref. [254] for details. Using Eqs. 7.2, we calculate \( S_v \) for all time-steps for datasets #1 [198], #2 [199], and #3 [197].

Due to time-constraints at the beamline, samples were only annealed for short times (a few hours or less). Furthermore, the segmented ROI is only a few hundred micrometers in length. Therefore, to reinforce the findings of the tomography experiment, \( S_v \) was calculated using optical metallography for datasets #1 and #2 (Table 4.2). New as-cast samples of composition Al-29.9wt%Si and Al-32wt%Si-15wt%Cu were used for the isothermal annealing experiments and stereological evaluation. Annealing times in the range of several days combined with the much larger ROIs for optical microscopy, in the millimeter range, provide reliable data to check for consistency. \( S_v \) can be calculated from the optical micrographs via the line-intercept method [13, 224]: first, a grid of “test lines” is superimposed on the micrograph; next, the number of points generated per unit length of test lines, \( P_L \), is determined. These “points” consist of intersections made by test lines with the interfaces of the Si particles. Then, \( S_v \) is calculated as

\[
S_v = 2 P_L 
\]

The above expression shows that \( S_v \) is related to \( P_L \) by a factor of 2, which is due to the theoretical restriction of random orientation [224]. Thus, we measure \( S_v \) via quantitative stereology for several time-steps over the course of a few days [198, 199].

A critical parameter in the above stereological evaluation is the spacing between the test lines. Lines that are spaced far apart may not accurately reflect the length scale of the Si particles; on the other hand, lines that are finely spaced would result in higher accuracy at the expense of speed. In Fig. 7.3, we test various grid spacings to determine
Figure 7.3. (a) Convergence test of (b) rectangular and (c) diagonal grid spacings. Convergence is measured by plotting the spacing between lines of a grid versus the stereologically measured $S_v$. The dashed line in (a) corresponds to the "ground truth" value of $S_v$. Errors due to counting statistics improve with finer grid spacings. In practice, we use a fractional grid spacing of 0.09 in our stereological analysis, which is within error.

$S_v$ via Eq. 7.3. We find that convergence is reached for both rectangular and diagonal grids when a fractional grid spacing of 0.09 is used in our stereological analysis. This grid spacing is within error of the "ground truth" value of $S_v$ determined at finer spacings.

### 7.3. Interfacial Shape Distributions

Despite being morphology-independent, the length scale $S_v^{-1}$ is an average over the system and cannot account for any localized evolution of the microstructure. In order to measure these microstructural details, we determine the evolution of curvature of a patch of interface during the phase transformation. In particular, the principal curvatures $\kappa_1$
and $\kappa_2$ are geometric properties that completely describe a surface. They are defined as the inverse of the principal radii of curvature, and hence have units of inverse length. In addition, $\kappa_2 \geq \kappa_1$; for this reason, $\kappa_1$ and $\kappa_2$ are known as the minimum and maximum principal curvatures of the interface, respectively. From differential geometry, $\kappa_1$ and $\kappa_2$ are the eigenvalues of the two-by-two curvature (Hessian, $\mathcal{H}$) matrix [128]. The two important invariants of this curvature matrix are the mean and Gaussian curvatures, defined as half the trace and the determinant of the curvature matrix, respectively [128]:

$$H = \frac{1}{2} \text{tr} [\mathcal{H}] = \left( \frac{\kappa_1 + \kappa_2}{2} \right)$$

$$K = \det [\mathcal{H}] = \kappa_1 \kappa_2$$

where $\text{tr}$ indicates trace and $\det$ indicates determinant. Recall that the mean curvature $H$ has physical significance: it is linked via Eq. 3.9 to the driving force for the coarsening evolution of isotropic structures. However, the Si particles of this study are clearly not isotropic (see section 2.1). Due to the presence of both faceted and smooth interfaces, there is no direct connection between $H$ and the interfacial composition. So, using a probability plot in $H$-$K$ space to represent the distribution of interfacial curvatures is not necessarily the best option [198]. We seek another classification scheme of the interfacial morphologies during the growth and coarsening evolution of the Si particles.

There are several methods to determine $\kappa_1$ and $\kappa_2$ from 3D images. Refs. [54, 112, 113, 152, 153] used the finite-element/finite-volume approach developed by Guillaume et al. [80]. On the other hand, Refs. [67, 69] use the level set algorithm for extracting the mean and gaussian curvatures from a signed distance function [75]. Here, we determine principal curvatures $\kappa_1$ and $\kappa_2$ by using a surface fitting algorithm as illustrated in Fig. 7.4.
We fit each patch and its nearest neighbors to a conic section, $f(x, y)$, of the form

$$f(x, y) = ax^2 + by^2 + cxy + dx + ey + f$$

with respect to the local coordinate system $(x, y)$ of the patch [128]. Specifically, the local coordinate system is defined by the $x$ and $y$ coordinates in the plane of the patch, and $z$ normal to the patch, pointing towards the liquid. In practice, we use first, second, and third order nearest neighbor patches, see Figs. 7.4(b-c). Fitting is done using least-squares.

Then, the eigenvalues of the Hessian (curvature) matrix $\mathcal{H}$ can be found as

$$\kappa = \frac{1}{2} \left( a + b \pm \sqrt{(a - b)^2 + 4c^2} \right)$$

This process is repeated for all patches in the ROI (i.e., on the order of $10^6$ patches).
Figure 7.5. (a) Map of local interfacial shapes in a “classical” ISD, where $\kappa_1 = 1/R_1$, $\kappa_2 = 1/R_2$, and $\kappa_2 \geq \kappa_1$ by definition [54, 112, 113, 152, 153]. (b) The new ISD, where interfacial shapes are represented using the shape index $\mathcal{I}$ and curvedness $C$ proposed by Koenderink and van Doorn [121].

Table 7.1. Classification of local interfacial shapes in both the classical ISD ($\kappa_1$ vs. $\kappa_2$, Fig. 7.5(a)) and the new version ($\mathcal{I}$ vs. $C$, Fig. 7.5(b)).

<table>
<thead>
<tr>
<th>$\kappa_1$</th>
<th>$\kappa_2$</th>
<th>Interfacial Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>Planar</td>
</tr>
<tr>
<td>0</td>
<td>+</td>
<td>Solid Cylinder</td>
</tr>
<tr>
<td>−</td>
<td>0</td>
<td>Liquid Cylinder</td>
</tr>
<tr>
<td>−</td>
<td>−</td>
<td>Cup</td>
</tr>
<tr>
<td>−</td>
<td>+</td>
<td>Saddle</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>Cap</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\mathcal{I}$</th>
<th>$C$</th>
<th>Interfacial Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[-1, +1]$</td>
<td>0</td>
<td>Planar</td>
</tr>
<tr>
<td>$[-1, -\frac{7}{8}]$</td>
<td>+</td>
<td>Cup</td>
</tr>
<tr>
<td>$[-\frac{5}{8}, -\frac{3}{8}]$</td>
<td>+</td>
<td>Rut</td>
</tr>
<tr>
<td>$[-\frac{1}{8}, +\frac{1}{8}]$</td>
<td>+</td>
<td>Saddle</td>
</tr>
<tr>
<td>$[+\frac{3}{8}, +\frac{5}{8}]$</td>
<td>+</td>
<td>Ridge</td>
</tr>
<tr>
<td>$[-\frac{7}{8}, +1]$</td>
<td>+</td>
<td>Cap</td>
</tr>
</tbody>
</table>
Once the principal curvatures are determined, the curvature space can be visualized by plotting a bivariate histogram of $\kappa_1$ versus $\kappa_2$, or $H$ versus $K$, as mentioned above [113, 152]. This construction is known as the interfacial shape distribution (ISD), which provides the probability of locating an interfacial patch for a given range of curvatures. A map of the local interfacial shapes possible in the “classical” ISD is given in Fig. 7.5(a). However, we make use of an alternative classification of curvature proposed by Koenderink and van Doorn, namely that of $\mathcal{S}$ versus $\mathcal{C}$ space [121], where

\begin{align}
\mathcal{S} &= \frac{2}{\pi} \tan^{-1} \left( \frac{\kappa_2 + \kappa_1}{\kappa_2 - \kappa_1} \right) \\
\mathcal{C} &= \sqrt{\kappa_1^2 + \kappa_2^2}
\end{align}

and $S \in [-1, 1]$ and $C \in [0, \infty)$. Note that $\tan^{-1}(\ast)$ is needed in the definition for $\mathcal{S}$ such that the shape index scale is “well tempered” [121]. For instance, if shapes are drawn at random in the $(\kappa_1, \kappa_2)$ plane, the distribution of $\mathcal{S}$ would be uniformly covered. This follows from the fact that $\mathcal{S}$ is proportional to the angle with the $\kappa_1 + \kappa_2 = 0$ axis. The major advantage of this representation is that shape and length scales are decoupled: the “shape index”, $\mathcal{S}$, specifies shape independently of length scale, whereas the “curvedness”, $\mathcal{C}$, specifies the characteristic length [121] and is related to the inverse diffusion distance during coarsening [55]. As such, $\mathcal{C}$ has units of inverse length.

In this classification, patches have a liquid cylindrical-like shape when $\mathcal{S} = -\frac{1}{2}$, a saddle-like shape when $\mathcal{S} = 0$, and a solid cylindrical-like shape when $\mathcal{S} = \frac{1}{2}$. However, for a planar patch, $\mathcal{S}$ is indeterminate while $\mathcal{C} = 0$ [121, 198]. Fig. 7.5(b) shows a map of the distribution of shapes possible in $\mathcal{S}$ versus $\mathcal{C}$ space; in addition, Table 7.1 and Fig. 7.6 provide further details on the curvature classification scheme adopted in
The shape ($S$) index scale, divided into nine categories: spherical cup for $S \in [-1, -\frac{7}{8})$, trough for $S \in [-\frac{7}{8}, -\frac{5}{8})$, rut for $S \in [-\frac{5}{8}, -\frac{3}{8})$, saddle rut for $S \in [-\frac{3}{8}, -\frac{1}{8})$, saddle for $S \in [-\frac{1}{8}, \frac{1}{8})$, saddle ridge for $S \in \left[\frac{1}{8}, -\frac{3}{8}\right)$, ridge for $S \in \left(\frac{3}{8}, \frac{5}{8}\right)$, dome for $S \in \left[\frac{5}{8}, \frac{7}{8}\right)$, and spherical cap for $S \in \left[\frac{7}{8}, 1\right]$. Shown shapes are of identical curvatures, $C = 1$ [121].

Figure 7.6. The shape ($S$) index scale, divided into nine categories: spherical cup for $S \in [-1, -\frac{7}{8})$, trough for $S \in [-\frac{7}{8}, -\frac{5}{8})$, rut for $S \in [-\frac{5}{8}, -\frac{3}{8})$, saddle rut for $S \in [-\frac{3}{8}, -\frac{1}{8})$, saddle for $S \in [-\frac{1}{8}, \frac{1}{8})$, saddle ridge for $S \in \left[\frac{1}{8}, -\frac{3}{8}\right)$, ridge for $S \in \left(\frac{3}{8}, \frac{5}{8}\right)$, dome for $S \in \left[\frac{5}{8}, \frac{7}{8}\right)$, and spherical cap for $S \in \left[\frac{7}{8}, 1\right]$. Shown shapes are of identical curvatures, $C = 1$ [121].

this work. Using Eqs. 7.7, a bivariate histogram of $S$ versus $C$ can be plotted for all time-steps, thereby providing quantitative snapshots of the morphological evolution.

7.4. Interfacial Normal Distributions

The directionality in the microstructure can be determined by creating a stereographic projection of the interfacial patch normals. By scaling the stereographic projection with the patch area, these plots represent the probability of locating an interfacial patch with particular spatial orientation, referred to as the IND [54, 113, 152]. It is important to note that the IND is constructed in the laboratory coordinates, and not the coordinates
of the *crystal* lattice. Thus, due to the independent particles in the bulk microstructure, the IND represents a superposition of many single crystal patterns [198].

In order to construct an IND of a given microstructure, the first step is to determine the unit normals of each patch of interface. We adopt the thermodynamic convention for calculating interface normals, where the normals consistently point from the solid to liquid. This requirement is enforced by switching the direction of an edge vector for any two triangles that share the same edge. Note, however, that this approach does not apply to “non-orientable” surfaces such as the Klein bottle or the Möbius strip. The interface normal \( \hat{n} \) of a mesh triangle with edge vectors \( \vec{e}_1 \) and \( \vec{e}_2 \) is defined as

\[
(7.8) \quad \hat{n} = \frac{(\vec{e}_1 \times \vec{e}_2)}{\|\vec{e}_1 \times \vec{e}_2\|}
\]

The orientation of a patch of interface is then specified by the point of intersection of \( \hat{n} \) with the unit hypersphere [41], see Fig. 7.7(a). These normals are then projected onto a pre-defined projection plane, tangent to the unit hypersphere, using angular relationships, see Ref. [141]. Conventionally, the upper and lower projection planes are used to fully quantify the directionality in the northern and southern hemispheres of the unit hypersphere, respectively. This stereographic construction is shown in Fig. 7.7(b).

To avoid having to show two INDs of a given microstructure, we project the normals onto a single cylinder, tangent to the unit hypersphere at its equator [198], see Fig. 7.7(c). The coordinates \((\theta', \phi')\) of this Mercator projection are given by

\[
(7.9) \quad \begin{align*}
\theta' &= \theta - \theta_0 \\
\phi' &= \ln \left[ \tan \left( \frac{\pi}{2} - \frac{\phi}{2} \right) \right]
\end{align*}
\]
where \((\theta, \phi)\) are the azimuth and elevation coordinates on the unit hypersphere, respectively, and \(\theta_0\) is an arbitrarily centered meridian. The mapping of Eq. 7.9 represents an angle-preserving projection although there are distortions towards the north and south poles of the unit hypersphere, \(i.e.,\) as \(\phi \to \{0, \pi\}\). If the normals are equatorial, however, then there is little discernible distortion in the projection. Furthermore, it should be noted that the normals are binned on the hypersphere and not on the Mercator projection to avoid any artifacts arising from the nonequal-area nature of the projection [113, 198].

In addition, it is possible to index the predominant poles in the IND using the following procedure [197, 198]. First, it is necessary to cluster the patches that belong to the same facet. This is necessary because, unlike in a perfectly smooth interface, the faceted particles of this study have finite roughness due to small segmentation errors or noise in the data. This corresponds to a finite (albeit, narrow) distribution of patch orientations in the IND [198]. Clustering is accomplished on the unit hypersphere using the spherical k-means (SKM) algorithm [48], presented in brief in section 6.2.1. Once cluster centroids

Figure 7.7. (a) The normals of a cube are projected from the origin onto the reference sphere, revealing the \(\{100\}\) poles [41]. These points along the 3D reference sphere can then be projected on a 2D plane in two ways: by creating a (b) stereographic [41] or (c) Mercator [77] projection.
Figure 7.8. Relationship between the specimen coordinate system $C_S$ denoted by the $X$, $Y$, and $Z$ axes, and the crystal coordinate system $C_C$ given by the [100], [010], and [001] directions. The cosines of the angles $\alpha_1$, $\beta_1$, and $\gamma_1$ give the first row of the orientation matrix $g$ [180].

have been determined via SKM algorithm, the next step is to compute the angles between all centroids and compare to the dihedral angle of a single monocrystal. The angle $\alpha_{ij}$ between centroid vectors $i$ and $j$, both of unit length, is given by

\begin{equation}
\alpha_{ij} = \cos^{-1} (h_i h_j + k_i k_j + l_i l_j)
\end{equation}

For instance, the interior angle of a monocrystal bounded by \{111\} habit planes is either 70.53°, 109.47°, or 180°. If the angle between two given cluster centroids $\alpha_{ij}$ matches any one of these angles, the two corresponding poles are indexed as \{111\}. Because this simple procedure may (by chance) match two unrelated planes in the ROI, the \{111\} assignments are confirmed by visually inspecting the surfaces in the real-space reconstructions. It should be noted that this angle matching procedure is computationally tractable since there are (in general) only a few particles in the region-of-interest [197, 198].
7.5. Crystallographic Normal Distributions

Using the above information, we can rotate the specimen coordinates $C_S$ onto the crystal coordinates $C_C$, as shown schematically in Fig. 7.8. We must specify an orientation matrix $g$ such that $C_C = g \cdot C_S$ [180]. The three-by-three orientation matrix $g$ describes the three rotations by the Eulerian angles $\phi_1$, $\Phi$, and $\phi_2$, necessary to bring $C_S$ into coincidence with $C_C$. Thus, the interface normal of a triangle in the crystallographic frame is $\hat{n}' = g \cdot \hat{n}$. The point group $m3m$ of the diamond structure has 48 symmetry elements; so, to generate all of the crystallographically-related solutions we premultiply the orientation matrix $g$ by each of the 48 three-by-three symmetry operators $T_j$ [58, 180]. Thus, the crystallographic orientation of the solid-liquid interface is given by

\begin{equation}
\hat{n}' = (T_j \cdot g) \cdot \hat{n}
\end{equation}

Once $\hat{n}'$ is calculated for all mesh triangles, the distribution of $\hat{n}'$ is plotted as a stereo-graphic projection (inverse pole figure) along $\langle 100 \rangle$, hereby referred to as a crystallographic (interface) normal distribution (CIND) [197]. According to crystal symmetry it is not necessary to show the entire distribution, but one unit triangle suffices. In this way, each orientation from a sample population is represented only once [180]. This well-known unit triangle or “fundamental zone” is bounded by $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ and is shown in the yellow outline in Fig. 7.9. For all time-steps the standard triangle can be plotted, thereby providing quantitative snapshots of the textural evolution during the growth process. Our method of characterizing crystallographic orientation is similar to that first popularized by Rohrer and colleagues [182, 183, 184], except these authors look at the
Figure 7.9. (a) Stereographic projection of cubic material along the ⟨100⟩ zone axis [3]. (b) An example distribution of crystallographically-related solutions $C'_S$ along the ⟨100⟩ zone axis, revealing a {111} texture. Due to the crystal symmetry, it is necessary to display in the CIND only the fundamental zone (FZ, yellow outline) bounded by ⟨100⟩, ⟨110⟩, and ⟨111⟩.

internal boundaries in a material, while we consider only the external, solid-liquid interfaces visible in our tomographic data [197]. Rowenhorst [188] uses a similar approach in his CIND construction, but does not account for crystallographic symmetries.

It remains to determine the orientation matrix $g$ in order to apply Eq. 7.11 to the experimental data. The analysis of facet crystallography (and hence $g$) can be performed ex situ via EBSD [180] (section 4.4), but we describe below that $g$ can be easily determined using our tomography data [197]. Our analysis relies on prior knowledge of the structure of Si polycrystals: namely, that the kinetic and equilibrium Wulff shapes are dominated by {111} planes (section 2.1). Thus, the broad, flat facets of the Si polycrystals can be indexed as {111}, using the procedure described in the preceding section (7.4). Once the facet planes have been confirmed as {111} orientations, the optimal rotation matrix $g$ is
calculated using the Kabsch algorithm [110] which is based on singular value decomposition (SVD). Shechtman [204, 205] used an analogous procedure to identify facet planes in diamond films produced by chemical vapor deposition (CVD). His analysis requires only standard scanning electron microscopy (SEM) and is based upon an understanding of the nature of diamond twins. Nevertheless, it is often worthwhile to cross-check the identity of the twins observed via XRT with those found via high resolution EBSD.

### 7.6. Interfacial Velocity Measurements

The rapidly improving temporal resolution of XRT makes it now possible to extract interfacial velocities from our data. Positive velocity corresponds to particle growth and negative velocity to particle dissolution. In past work [2, 69], interfacial velocities have been determined using level set methods, in which interface locations are represented by a signed distance function. However, we demonstrate below that interfacial velocities can also be calculated using the mesh [199]. Our method relies on the k-nearest neighbors (k-NN) algorithm [45] and offers substantial speed-up over the conventionally used, mesh-based Möller-Trumbore ray-triangle intersection (MT) algorithm [159].

It is instructive to first review the MT method. According to its nomenclature, the “ray” $R$ is measured from the mesh at time $t$, with origin set by the patch centroid and direction specified by the patch normal; the “triangle” refers to any patch belonging to the mesh at time $t + \Delta t$. If there are $N$ rays (corresponding to $N$ triangular patches) at time $t$, and $M$ triangular patches at time $t + \Delta t$, we must compute a total of $NM$ ray-triangle intersections in order to determine how far the interfaces have traversed in some time $\Delta t$ [199]. If the point of intersection $p$ lies within the triangle, the barycentric
coordinates \((\alpha, \beta, \gamma)\) of \(p\) must satisfy \(\alpha + \beta + \gamma = 1\) and \(\alpha, \beta, \gamma \geq 0\), i.e., \(p\) is a weighted average of the vertices of the triangle. To find \((\alpha, \beta, \gamma)\) in the MT approach, we must build and apply a transformation matrix that maps the ray \(R\) in the specimen coordinate system to another basis that uses two edges of the triangle, and another well-chosen vector [159]. We then use Cramer’s rule to solve for \((\alpha, \beta, \gamma)\), see Ref. [159] for details.

Solving for \(NM\) barycentric coordinates is a computationally expensive operation that involves at least two cross products and two dot products per ray-triangle iteration. Thus, we propose an alternative method to approximate interfacial velocity, without calculating the barycentric coordinates. In our approach, we find the first nearest neighbor (NN) mesh vertex at time \(t + \Delta t\) for each mesh centroid at time \(t\) via the k-NN algorithm [45]. The k-NN algorithm proceeds as follows: first, we calculate the distance between the centroid at time \(t\) and all vertices at time \(t + \Delta t\); then, we sort these distances using a k-d tree, and pick the shortest, NN distance within the list. For meshes in this study, triangle areas are relatively small (approx. \(5 \times 10^{-5}\) % of the surface area \(S\)) so the distance between the actual, barycentric point of intersection and the NN vertex is almost imperceptible [199]. Note that the difference in the magnitude between the velocity vectors calculated from the NN and MT approaches is proportional to \(\cos \theta\), where \(\theta\) is the angle between the two vectors. Since \(\cos \theta\) goes as \(\theta^2\) for small \(\theta\), the difference is second-order if \(\theta\) is small.

In general, the accuracy of our NN method depends on the “coarseness” of the mesh at time \(t + \Delta t\). We define coarseness as the ratio of the average surface area of the mesh triangle to \(S\) [199]. To improve the accuracy of the NN algorithm for relatively coarse-grained meshes, it is possible to refine the mesh at time \(t + \Delta t\) by including “fictitious points” along the triangle edges and medians, see the inset in Fig. 7.10. These
Figure 7.10. Performance of Möller-Trumbore (MT) [159] and nearest neighbor (NN) algorithms applied to a simulated dataset of spherical particles with radius $R$ at time $t$ and radius $2R$ at time $t + \Delta t$. Regardless of $R$ (or the number of patches), the NN method is approx. five times faster than the MT method. (inset) To improve the accuracy of the NN computation, we refine the mesh at time-step $t + \Delta t$ by introducing fictitious points along the triangle medians (dashed lines) and edges (solid lines). Fictitious points are in blue while the original mesh vertices are in white [199].

16 fictitious points (in blue) contribute to an increased vertex density in the mesh at time $t + \Delta t$. To demonstrate the speedup and scalability of our approach, we measure the compute time using the MT and NN methods using simulated data of spheres with radius $R$ at time $t$ and radius $2R$ at time $t + \Delta t$, see Fig. 7.10. In the NN method, we
refine the mesh at time $t + \Delta t$ by including the 16 fictitious points per triangle. The results indicate that, on average, the NN method is over five times faster than the MT method, regardless of the size of $R$ (or the number of mesh triangles) [199].

In order to connect the velocity of an interface to its morphology, we can plot $V$ vs. $\mathcal{C}$ and $V$ vs. $\mathcal{S}$ as bivariate probability distributions. As an example, we define the distribution $P(\mathcal{C}, V)$ where $P(\mathcal{C}, V) d\mathcal{C} dV$ is the probability that an interfacial patch will have curvedness $\mathcal{C}$ (Eq. 7.7) moving at velocity $V$. For instance, we use the MT and NN methods on our real data to obtain plots of $\mathcal{C}$ versus $V$ during coarsening (dataset #2 in Table 4.2). The probability distributions in Fig. 7.11 are nearly identical, indicating that we can achieve results similar to that of the MT method with a fraction of the compute time [199]. Thus, we use the NN method to compute $V$ at all time-steps.
Figure 7.11. Comparison of $\gamma/dS_v^{-1}/dt$ vs. $\mathcal{C}/S_v$ histograms at 5889 seconds during the coarsening process of Si particles in an Al-Si-Cu liquid, where interfacial velocities are computed using both (a) the NN approach and (b) the MT algorithm [159]. The limits of the color-bar of the distribution are fixed so that the two plots can be compared. Within each distribution, white contour lines correspond to probabilities $P(\mathcal{C}/S_v, \gamma/dS_v^{-1}/dt)$ equal to 0.005, 0.01, 0.05, 0.1, and 0.25. The results indicate that a nearly identical curvature-velocity distribution can be obtained using our nearest neighbor approach, with a significantly shorter compute time [199].
Part 3

Results and Discussion
CHAPTER 8

Coarsening of Si Particles in Al-Si

The coarsening of anisotropic systems is more complex than in systems in which the interfacial energy and interfacial mobility are both isotropic. The focus of this chapter is to gain insights into the coarsening mechanisms of fully-faceted, complex, and interconnected systems. Specifically, I present experimental results on the coarsening evolution of highly anisotropic Si particles in an Al-Si alloy (dataset #1 in Table 4.2).\(^1\) The equilibrium and kinetic Wulff shapes of Si are dominated by \{111\} planes, see section 2.1. The coarsening behavior of such particles at elevated temperature but below the eutectic temperature (576 °C) has been widely reported, see Ref. [109] and references therein. However, the morphological evolution of primary Si above the eutectic temperature, which is critical to the semi-solid processing of the alloy [117], remains poorly understood.

Hypereutectic Al-Si alloys of composition Al-29.9wt%Si were investigated via ex situ PCT at the TOmographic Microscopy and Coherent rAdiology experimenTs (TOMCAT) beamline of the Swiss Light Source (Paul Scherrer Institut, Switzerland) [208]. As introduced in section 4.2.1, phase-based imaging is advantageous for imaging systems consisting of elements with similar atomic numbers (e.g., Al and Si in an Al-Si alloy). The sample was placed in a custom-made furnace, and the primary Si particles were allowed to coarsen isothermally at 590 °C, just above the eutectic temperature (575 °C, see the

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\(^1\) The subject matter of this chapter is adapted in part from Ref. [198] by A. J. Shahani and coworkers.
Figure 8.1. 3D microstructure coarsening in time. Light gray regions are the primary Si particles while the dark gray background is the eutectic. The as-cast sample in (a) was coarsened in furnace at 590°C for (b) 10 min., (c) 20 min., (d) 30 min., (e) 40 min., and (f) 50 min. Imaging was conducted via ex situ PCT. A ROI of 296 × 296 × 159 μm³ is shown [82, 196, 198].

Phase diagram in Fig. 4.2(a)). After 10 minutes, the sample was quenched to room temperature, and tomographic projections were collected when the sample was fully solid. Subsequently, the sample was reheated to 590 °C for another 10 minutes, continuing the coarsening of the primary Si particles. This cycle was repeated six times. Following the PCT experiment, the datasets were reconstructed using the hybrid approach presented in section 5.3 and segmented using the suite of algorithms described in chapter 6 [196]. Each dataset measured 1525 × 1525 × 1598 μm³, with a voxel size of 0.74 × 0.74 × 0.74 μm³.
The microstructural evolution during coarsening is shown in the 3D reconstructions in Fig. 8.1, first published in Refs. [82] and [196]. The light gray particles are Si and the eutectic is transparent. Qualitatively, the increase in size scale of the structure is consistent with a coarsening process and the increasingly isotropic structure can be clearly observed [198]. While the structures grow less interconnected and more isotropic, some degree of faceting can still be observed at later times. This suggests the presence of \{111\} facets along the solid-liquid interfaces that do not evolve as fast as other orientations, as previously observed in Refs. [17, 82, 162, 165]. In other words, the broad faces of a given particle, suggested to be of \{111\} type, appear to be growing much slower with respect to the edges of the particle, giving rise to the observed structural changes [82]. The morphological evolution of the particles is characterized in this chapter using INDs and ISDs, the results of which are supported by EBSD orientation mapping.

8.1. Surface Area per Unit Volume $S_v$

Fig. 8.2 shows (a) a comparison of the metallography and tomography results, as well as (b-e) optical micrographs of some coarsened structures and their corresponding annealing times. In order to determine the coarsening exponent and rate constant, $K$, we fit the data to Eq. 3.16. Slopes of $0.29 \pm 0.03$ and $0.28 \pm 0.03$ were obtained from the metallographic and tomographic datasets, respectively, which are both far closer to the $S_v^{-1} \propto t^{1/3}$ relationship of bulk diffusion than the $S_v^{-1} \propto t^{1/2}$ relationship of interfacial reaction [198]. Worth noting is the displacement of the tomographic results relative to the metallographic results: this is most likely due to artificial smoothing in the tomographic
Figure 8.2. (a) Log-log plot of inverse surface area per unit volume at different coarsening times for Al-29.9wt%Si. Blue data points are measured from XRT, and the orange are measured from optical metallography (section 7.2). In the tomography data, error bars are estimated from the number of mis-classified voxels, in comparison to a few hand-segmented images [196] (section 6.4), while in the metallography data, error bars are determined from counting statistics during stereological analysis. (b-e) Optical micrographs collected at the same magnification during the coarsening evolution of silicon particles (black) in a eutectic matrix (white) [198].

data during the segmentation process [196] and mesh generation, see section 7.1 for details. It could also be due to the fact that the annealing temperature in the metallography experiments was 10 °C higher than in the tomography experiments [198]. This would lead to a difference in measured absolute values of around 10 %, but not a difference in measured slopes. The average coarsening rate constant $K$ is $15 \pm 2 \mu m^3/min.$, where the error accounts for the relative offset (standard deviation) between the tomographic and metallographic results. The volume fraction for all time steps is consistently around the expected value of $0.30 \pm 0.05$. Errors in the measurement of $S_v$ from the tomography data
are predominantly due to mis-classified voxels during the segmentation process, in comparison to a few hand-segmented images [196], while errors in $S_v$ from the metallography data are due to counting statistics during stereological analysis [198].

The exponent of $1/3$ measured from both tomography and metallography suggest that long-range diffusion is an important factor during the coarsening process [198]. However, one should note that the relatively immobile \{111\} planes, which are the broad faces of the particles, are still governed by interfacial kinetics, more specifically, the attachment and detachment of solute (see also sections 3.1.2 and 3.5.2). This implies that the growth of the primary Si particles during coarsening is determined principally by growth at the curved particle edges. This conclusion is discussed further in section 8.5.

8.2. Interfacial Normal Distributions

Fig. 8.3 shows the IND for the as-cast sample ($t = 0$ min.), depicted as a Mercator projection of the unit hypersphere. While dendritic samples ($\Delta S_m \leq 2$) are typically characterized by smoothly varying INDs [54, 112, 113, 152, 153], the Si facets in this study correspond to sharp peaks in the IND. This indicates a high degree of directionality in the as-cast microstructure. Poles in the IND can be indexed as \{111\} using the post hoc procedure described in section 7.4, which involves first clustering the unit hypersphere. The results of SKM clustering are given in Fig. 8.4 [198]. There are 17 such clusters identified. By computing the angles between the cluster centroids (via Eq. 7.10, i.e., a total of $17 \times 17$ angles), we determine that the four poles A-D are of \{111\} type and belong to the same connected component, denoted ABCD. “Connected component” refers to several interconnected particles, as opposed to a single, isolated structure [82].
Figure 8.3. Interface normal distribution (IND) for the as-cast sample, $t = 0$ min., depicted as a Mercator projection (section 7.4). The IND contains several poles indicating a highly faceted structure. Those poles that are boxed (A-D) belong to the same connected component and to the $\{111\}$ family (see Fig. 8.4), and are used in subsequent analysis [198].

In Figs. 8.5 and 8.4, it can be seen that poles A and C, and B and D are $180^\circ$ apart due to inversion symmetry in $\{111\}$. Physically, this means that these pole pairs correspond to two opposite faces of a given particle in the connected component [198].

We can track the evolution of Mercator poles A-D as a function of coarsening time, see Fig. 8.5 [198]. Fixing the range of the color bar and the range of values ($\theta', \phi'$ in Eq. 7.9) that are indicative of each of the four facets allows for the comparison of multiple coarsening times. In general, pole intensities decrease with time for facets A-D, relative to the total surface area; however, the intensities appear to decay faster for poles B and D compared to A and C. This is because particle BD is smaller than particle AC and
Figure 8.4. Results of spherical k-means (SKM) clustering of the interface normals from the as-cast microstructure (Fig. 8.3). Different colors indicate different clusters; black points are the locations of the centroid vectors, \{hkl\}. We identify a total of 17 clusters, labelled A through Q [198].

therefore has fewer \{111\} patches. The decrease in pole intensity with time is consistent with the structures becoming increasingly rounded during the coarsening process [198].

The range of values (\(\theta', \phi'\)) depicted in Fig. 8.5 can be segmented with an appropriate threshold (4 \times 10^{-4}), to give those bins in the (\(\theta', \phi'\)) histogram corresponding to \{111\} poles A-D. Then, the interfacial patches belonging to these bins can be illuminated on the microstructure, creating a so-called Specific Microstructural Location (SML) figure [54]. The SML for connected component ABCD is shown in Fig. 8.6, depicting the segmented \{111\} patches in red. Fig. 8.6(a) shows two particles that intersect at a 70.5° \(<110>\) symmetrical tilt grain boundary in the as-cast sample. The edges of both particles evolve much faster than the broad \{111\} faces during the microstructural evolution [198].
Figure 8.5. Evolution of $\{111\}$ Mercator poles (A-D) with coarsening time. Fixing the range of the color bar and the range of values $(\theta', \phi')$ that are indicative of each of the four facets allows multiple coarsening times to be compared. In general, pole intensities decrease with time [198].

The ratio of the area of these $\{111\}$ red patches in connected component ABCD, $A_{\{111\}}$, to the total surface area of the ROI, $S$, is plotted versus time in Fig. 8.7. The plot shows a decrease in fractional area, $A_{\{111\}}/S$, with time, indicating that $A_{\{111\}}$ decays faster than $S$. This suggests that the Si particles are evolving away from their equilibrium Wulff shape during the first 50 min. of coarsening. Hypothetically, a single crystal of Si coarsening near equilibrium would change volume but still preserve aspect ratio [233], or in this case, $A_{\{111\}}/S$. However, the complex, interconnected structures of this study are not evolving through a series of equilibrium shapes, and thus the surfaces of primary
Figure 8.6. Specific Microstructural Location (SML) figures [54], depicting \{111\} patches (A-D) in red, for the (a) as-cast sample, and after (b) 10 min., (c) 20 min., (d) 30 min., (e) 40 min., and (f) 50 min. of coarsening at 590°C. The mesh patches belonging to \{111\} poles A-D were determined by segmenting those poles on the unit hypersphere with a threshold of $4 \times 10^{-4}$. The misorientation between the two particles is $70.5^\circ <110>$, as indicated in (a). The misorientation axis points out of the page [198].

Si do not have constant chemical potential with respect to the liquid phase. Thus the mechanism for the disappearance of the \{111\} facets is not the motion of the \{111\} facet itself, but instead, it is the much faster evolution of the surrounding non-faceted interfaces.

8.3. Interfacial Shape Distributions

ISDs of the microstructures are given in Fig. 8.8. They are read with the help of Figs. 7.5(b) and 7.6. To compare multiple time steps, we scale the $C$ axis by the time-dependent length scale, $S_v$, and also fix the range of the color bar. In the as-cast
Figure 8.7. (a) Patch triangles belonging to the \{111\} orientation are indicated in red. These patches were identified by summing over bins in the IND which had values above the threshold of $4 \times 10^{-4}$, see Fig. 8.6. (b) By summing the area $A$ of each \{111\} patch in connected component $ABCD$, we can track $A_{\{111\}}$ over total surface area, $S$, versus coarsening time. Errors bars are due to binned patches that do not belong to connected component $ABCD$, but rather to similarly-oriented particles (roughly 5-8% error) [198]. The trend indicates that the Si particles evolve away from their equilibrium Wulff shape (section 2.1) during coarsening.

sample, $t = 0$ min., two concentrated peaks, i.e., $P(\mathcal{I}, \mathcal{C}/S_v) \geq 0.4$, are evident: the first is located at $\mathcal{I} \approx 0.5$ and $\mathcal{C} \approx 0.5 S_v$, and the second at $\mathcal{I} \approx 0.5$ and $\mathcal{C} \approx 2.5 S_v$. The latter peak represents the particle edges, while the former accounts for patches with near-planar shape. To confirm this notion, we illuminate the patches belong to these two peaks on the microstructure, see Fig. 8.9. Thus, the as-cast microstructure has two characteristic length scales $\mathcal{C}$, at values that are 0.5 and 2.5 times $S_v$. The large tail in the distribution at $\mathcal{I} = 0.5$ indicates a dispersion in the sizes of the solid cylindrical-like shapes; the reason for this tail is that interfacial patches must connect these two peak
Figure 8.8. Interface shape distributions (ISDs, section 7.3) using the alternative $\mathcal{I}$ versus $\mathcal{C}$ classification [121], for the same microstructures shown in Fig. 8.1: (a) $t = 0$ min. and $S_{v}^{-1} = 19 \mu m$, (b) $t = 10$ min. and $S_{v}^{-1} = 31 \mu m$, (c) $t = 20$ min. and $S_{v}^{-1} = 42 \mu m$, and (d) $t = 50$ min. and $S_{v}^{-1} = 53 \mu m$ [198]. Scaling the curvedness, $\mathcal{C}$, by $S_{v}$ and fixing the range of the color bar allow multiple coarsening times to be compared. Dashed lines at $\mathcal{I} = \{-0.5, 0, 0.5\}$ serve as markers for liquid cylinders (“ruts”), saddle shapes, and solid cylinders (“ridges”), respectively [198].
Figure 8.9. SML figures [54], depicting (a) the two peaks in the ISD corresponding to the as-cast sample (see also Fig. 8.8(a)). Boxed in green is the peak located at $S = 0.5$ and $C/S_v = 2.5$, and in blue the peak located at $S = 0.5$ and $C/S_v = 0.5$. (b-c) Patches belonging to these boxed regions are colored on the microstructure: the green patches illuminate the lath edges, while the blue patches illuminate the near-planar facets. For this reason, there is a distribution in $C$ required to connect these green and blue patches, hence the long “tail” in the ISD for $S = 0.5$.

regions to form a continuous interface, and therefore must have a wide variety of “curvedness.” As time increases, patches that are concave towards the solid ($S < 0$) almost completely disappear, and both the average shape index and average curvedness appear to increase, relative to $S_v$. For instance, at $t = 50$ min., a peak is evident at $C \approx 3 S_v$ and $S \approx 0.75$, indicating that patches have cylindrical-like and spherical-like shape (see also Fig. 7.6), consistent with the microstructure in Fig. 8.1(f). Since these ISDs are scaled by $S_v$, it is important to note that the variations of $S$ and $C$ are not due to the increased size-scale of the microstructure, but rather due to morphological changes alone [198].

We can consider shapes of patches independent of length scale, see Fig. 8.10. The histogram labels match those of Table 7.1 and Fig. 7.6. Since there is no length scale associated with these distributions, they should be invariant with time if the system is
Figure 8.10. The probability of finding a patch of a given shape as a function of time, where (a) is 0 min., (b) is 10 min., (c) is 20 min., and (d) is 50 min., of elapsed coarsening time. These plots are for the same microstructures measured in Fig. 8.8. We use the shape index scale of Fig. 7.6, see Fig. 7.6. The fractions of domes and spherical caps increase with time, suggesting that the coarsening evolution of primary Si particles is not self-similar [198].

coarsening in a self-similar fashion, akin to the solid Sb particles in a Pb-Sn eutectic (Fig. 3.11). However, in our case, the probability of finding a patch with dome-like ($\mathcal{S} \in [\frac{5}{8}, \frac{7}{8}]$) or cap-like shape ($\mathcal{S} \in [\frac{7}{8}, 1]$) increases with coarsening time. Thus, even though the microstructures are evolving according to the $S_v^{-1} \propto t^{1/3}$ relationship (see Fig. 8.2), the structures are clearly not self-similar. The lack of self-similarity is due to the loss of morphological anisotropy during the microstructural evolution [198].
8.4. Electron Backscatter Diffraction Analysis

Figs. 8.11(a-c) show three representative orientation maps of primary Si particles that have coarsened for two days at 600 °C. The mean crystallographic orientation
of each grain of Si is colored according to the standard stereographic triangle on the bottom-right of Fig. 8.11(a), while non-indexed regions belonging to the eutectic are colored black [198]. The grain boundaries were smoothed via five iterations of constrained Laplacian smoothing in MTEX software [12]. The Si particles consist of multiple grain boundaries ("bands") that run along the long axes of the particles and that intersect the solid-liquid interface at the particle edges. Qualitatively, these interfaces between grains in a given particle suggest the presence of coherent annealing twins [180, 139].

In order to quantify this observation, we measure the uncorrelated misorientation distribution function (MODF) using the discretized EBSD data taken from the interior region of a representative particle, as shown in Fig. 8.11(d) [198]. The MODF can be represented as angle and axis (inset) distributions in Fig. 8.11(e), which then requires cross-referencing between particular angles and axes [180]. The peak in the angle distribution near 0° corresponds to low-angle, intra-granular misorientation noise, while the high probability of near 60° angles corresponds to ⟨111⟩ misorientation axes. Together, the 60° ⟨111⟩ combination represents a Σ3 coincident site lattice (CSL, see section 3.2.2), also known as a coherent twist grain boundary [164]. This angle-axis pair agrees with the IND results, since a 70.53° symmetric tilt about ⟨110⟩ (Fig. 8.6(a)) is structurally indistinguishable from the 60° twist around ⟨111⟩: both configurations produce a Σ3 CSL [164]. Consistent with the work of Ratanaphan et al. [181], our results demonstrate the high incidence of coherent twin boundaries in the polycrystalline Si particles.
8.5. Defect-Mediated Coarsening Mechanism

During the coarsening of Si particles, we found that $S_\alpha^{-1}$ varies as $t^{1/3}$, see Fig. 8.2, suggesting that long-range diffusion of solute is an important factor during the coarsening process [198]. However, unlike classical coarsening theories [133, 236] (section 3.5.2), the microstructural evolution in this case is not governed by the interfacial free energy of the $\{111\}$ planes. If the driving force is the reduction in total interfacial energy, then the particle structure would approach the equilibrium Wulff shape; correspondingly, the fractional area of $\{111\}$ planes would increase with time and plateau at a value given by the Wulff construction. However, the opposite trend is reported here (Fig. 8.7(b)). In general, the particle structure becomes less faceted and more isotropic with time, as seen in the INDs and ISDs of Figs. 8.3 and 8.5, and Figs. 8.8 and 8.10, respectively [198].

The Si particles of this study have “mixed interfaces”, i.e., partially faceted and partially rounded. From the 3D reconstructions in Figs. 8.1 and 8.6, we see that the $\{111\}$ facets are slow-moving during the microstructural evolution. Since the interfaces are evolving during coarsening, the driving forces at $\{111\}$ planes are small compared to those encountered during rapid crystal growth, and thus the kinetic limitations of step formation can be particularly difficult to overcome without the benefit of defects [82, 198]. In other words, the $\{111\}$ interfaces behave as poor sources and sinks, and as such, the coarsening rate at the $\{111\}$ interfaces depends on the rate of atom attachment and detachment at the interfaces. More specifically, the Jackson $\alpha$ factor [103] for Si $\{111\}$ is 2.7 [17]; the relatively high value of $\alpha$ ($\alpha_{\{111\}} > 2$) indicates that the $\{111\}$ surface is atomically smooth and exhibits a barrier to nucleation [17, 103], see also section 2.3.
On the other hand, the particle edges appear non-faceted and thus provide the kink sites necessary for interfacial propagation. The exposure of these less close-packed planes of Si to the liquid results in rapid lateral growth and a decrease in the area of the broad, equilibrium \{111\} facets. These more rapidly moving interfaces could be either (1) atomically rough, or (2) highly defective, with a high incidence of dislocations or re-entrant twin grooves at the edges of the faceted crystals. However, the particle edges are neither thermodynamically rough [19], since the annealing temperature (590 °C) is well below that of the roughening transition (757 °C [213]), at which steps are spontaneously created on Si \{111\}; nor are they kinetically rough [216, 215], due to relatively slow interfacial velocities during coarsening. Instead, EBSD measurements provide evidence for twin defects, which may contribute significantly to the observed microstructural evolution [198].

In particular, we find that \(\Sigma 3\) (twin) boundaries intersect the solid-liquid interface, see Fig. 8.11. These coherent annealing twins may have formed during the solidification of the primary silicon particles from the melt. According to the growth accident hypothesis of twin boundary formation, twins are formed and terminated by errors in the stacking of \{111\} planes during grain growth, which happens in a stochastic manner [26, 31, 32, 72]. It is also conceivable that the coherent twins arise naturally during the coarsening process. For instance, the particle thickness (in the direction perpendicular to the long axis) increased by roughly 20 % or 10 μm in 10 min., see Fig. 8.7. In this time interval, growth accidents on the \{111\} facets may have promoted the formation of coherent twin boundaries, whose spacing may be on the order of a few micrometers, as shown in Fig. 8.11.

To explore this possibility, consider the following scenario: an unperturbed, single crystal is octahedrally bounded by \{111\} habit planes. Assume that twinning can occur with
equal likelihood on the four available \{111\} facets (excluding inversion symmetry) \[92\].

Then, after one \((n = 1)\) twinning event, there are five possible orientations. Of the four first-order twin configurations, each one can, in turn, produce four second-order \((n = 2)\) twin configurations, one of which is that of the original crystal. Thus, there are 12 new configurations after second-order twinning, culminating in a total of 17 unique crystallographic orientations. In general, the total number of orientations possible \(N(n)\) after the \(n\)th-order twinning event can be described by the geometric series

\[
N(n) = 4 \sum_{t=1}^{n} 3^{t-1} + 1
\]

for \(n \geq 1\). Consequently, after \(n = 8\) repeated twinning events, there are a total of \(N(8) = 13121\) unique orientations that cover uniformly the \(\langle 100 \rangle\) stereographic projection, as shown in Fig. 8.12. Thus, it is indeed plausible that the structure of the originally unperturbed Si crystal may appear random or isotropic due to multiple twinning events. Because this analysis assumes that the low index \{111\} orientation is the dominant twinning orientation, it represents only a lower bound on \(N\). However, twinning in Si is also possible on \{221\} \(\Sigma 9\) and \{511\} \(\Sigma 27\) boundaries \[181\], and hence the total number of orientations \(N\) can be much higher than that predicted by Eq. 8.1.

The presence and orientation of these twin planes gives rise to re-entrant edges and grooves where the twin planes intersect the solid-liquid interface. In the twin plane re-entrant edge (TPRE) mechanism (section 3.2.2), provided that the bulk crystal has at least two such twin defects, growth on the re-entrant corners generates more re-entrant corners, thereby providing unlimited steps for interfacial attachment and detachment \[85, 237\]. Thus, the rate of growth at the multiply twinned particle edges is
Figure 8.12. (a-h) The influence of multiple twinning events on the \( \langle 100 \rangle \) stereographic projection. The number of \{111\} orientations (triangles) possible after \( n \) twinning events is given by the geometric series \( 4 \sum_{t=1}^{n} 3^{t-1} + 1 \) for \( n \geq 1 \). After \( n = 8 \) subsequent twinning events (h) the stereographic projection is uniformly covered, indicating an isotropic structure.

limited by the rate at which solute atoms diffuse to the surface. This implies that the growth of the particle is determined principally by growth at its edges, hence why \( S_v^{-1} \) varies as \( t^{1/3} \). In the limit of very long coarsening times, it is anticipated that the particle edges would completely overgrow the relatively immobile facets, leading to a completely isotropic structure \[198\]. In other words, the morphology of the defective crystals could be isotropic and thus distinct from the equilibrium Wulff shape of Si, a tetrakaidecahedron dominated by large \{111\} facets and smaller \{100\} surfaces \[52\] (section 2.1).
CHAPTER 9

Coarsening of Si Particles in Al-Si-Cu

In chapter 8, the coarsening evolution of primary Si particles in a binary Al-29.9wt%Si alloy, held isothermally in the solid-liquid regime, was discussed. The results given were based on an ex situ X-ray phase contrast tomography (PCT) experiment. It was reported \cite{198} that the Si particles do not evolve toward their fully-faceted Wulff shape during coarsening; instead, the complex, interconnected structure becomes increasingly spherical or isotropic over time. Due to the difficulty of resolving contrast between the Si and liquid at temperature, Refs. \cite{82, 196, 198} quenched their samples to room temperature and collected images when the sample was fully solid. This anneal-and-quench procedure was repeated for six time-steps. This method is prohibitive for two reasons: first, the effects of the repeated thermal cycling on the microstructural evolution are unknown; secondly, the ex situ nature of the experiment makes it impossible to track the evolution of the solid-liquid interfaces with sufficiently high temporal resolution.

To circumvent these experimental challenges, we “dope” the hypereutectic Al-Si alloy with a heavy element, e.g., Cu, which serves as an agent to generate X-ray absorption contrast, see section 4.1.\footnote{The subject matter of this chapter is adapted in part from Ref. \cite{199} by A. J. Shahani and coworkers.} The role of the dissolved Cu during coarsening is addressed in section 9.1, using a combined experimental-theoretical approach. Thus, it is now possible to study the coarsening evolution of primary Si particles in the Al-Si-Cu system via in situ X-ray absorption contrast tomography (ACT), without needing to repeatedly
quench the alloy sample. This technique not only removes any uncertainty associated with the thermal cycling, but also provides highly time-resolved measurement of the interfacial dynamics in the system [199]. As such, the complex and interconnected coarsening morphologies of the primary Si particles, including topological singularities that occur during the microstructural evolution, will be presented and discussed in this chapter.

Alloys of composition Al-32wt%Si-15wt%Cu (dataset #2 in Table 4.2) were placed in a resistive furnace held isothermally above the eutectic temperature, at 650 °C. As soon as the sample entered the field-of-view, 105 tomographic scans were collected in logarithmically increasing intervals: for the first 60 time-steps, projections were collected continuously over 20 minutes; for the next 20 time-steps, scans were spaced one minute apart; for the following 20 time-steps, scans were spaced five minutes apart; for the last five time-steps, the interval between scans increased to 11 minutes. Within each 20 second scan, 1000 projections were distributed evenly between 0 and π radians. The motivation for collecting the X-ray projections in this manner is that the system-average length-scale increases logarithmically with time during the coarsening process, see section 3.5.2. Therefore, this data collection scheme adequately captures the interfacial dynamics [199].

The microstructural evolution of the Al-32wt%Si-15wt%Cu alloy during coarsening is depicted in Figs. 9.1(a-f) for six representative time-steps, from \( t = 60 \) s to 12112 s. The orange particles are Si and the Cu-enriched liquid is black. The reconstructions show that the initially faceted and interconnected Si particles become increasingly isotropic over the course of five hours. However, some degree of faceting is still observed at late times, suggesting that these facets are of the low energy, low mobility \{111\} type [199]. Furthermore, the numbering indicates several features-of-interest: pinch-off events of (1)
Figure 9.1. 3D reconstructions during the coarsening evolution of silicon particles (orange) in a copper-enriched liquid (black). Shown are six time-steps: (a) 60 s, (b) 1495 s, (c) 2781 s, (d) 4214 s, (e) 7420 s, and (f) 12112 s. The numbering indicates several features-of-interest: pinch-off events of (1) liquid and (2) solid cylinders, see Fig. 9.6; (3) a sedimenting particle, see Fig. 9.2; and (4) stationary liquid inclusions, see Fig. 9.9 [199].

liquid and (2) solid cylinders, a zoomed view of which is shown in Fig. 9.6; (3) particle sedimentation; and (4) stationary liquid inclusions. Sedimentation, as shown in (3) and described in section 4.1, appears to occur as soon as the particles break off from the
interconnected, skeletal structure. As a result, the volume fraction of the solid Si phase decreases by over 40% over five hours, as shown graphically and pictorially in Fig. 9.2. In (4), the trapped liquid inclusions do not change volume during the time-scale of the experiment. This is to be expected because, under typical circumstances, diffusion through the solid phase is orders of magnitude slower than in the liquid.

9.1. Rate Constant Calculations

The rate constant for coarsening in a ternary system, $K$, is given by

\[ K = \zeta f(V_v) \left[ \frac{8 \sigma V_m^S}{9 \Lambda} \right] \]
where the bracketed term represents the classical rate constant $K_{LSW}$ predicted from multicomponent LSW theory [127] in the limit of infinitely dilute, spherical particles. The two terms to the left of the brackets, $\zeta$ and $f(V_v)$, are corrections for non-spherical morphologies and finite volume fraction of the coarsening phase, respectively (see section 3.5.2). Somewhat surprisingly, $\zeta$ is a constant even if the microstructural evolution during coarsening is not self-similar. This was demonstrated by Ref. [145], who studied the evolution of a dendritic structure to a spheroidal one. Thus, the coarsening rate is not affected by detailed changes in the phase morphologies. Returning to Eq. 9.1, $\sigma$ is the interfacial free energy, $V_s^S$ is the molar volume of solid (S) Si phase, and

$$\Lambda = \frac{\Delta C_{Al}^L}{D_{Al}^L} (\Delta C_{Al} G_{jAl}^L + \Delta C_{Cu} G_{jAlCu}^L)$$

$$+ \frac{\Delta C_{Cu}^L}{D_{Cu}^L} (\Delta C_{Cu} G_{jCuCu}^L + \Delta C_{Al} G_{jAlCu}^L)$$

(9.2)

Here, $D_i^L$ is the diffusivity of component $i$ in the liquid (L) phase, and $\Delta C_i = C_i^S - C_i^L \approx -C_i^L$, where $C_i^S$ and $C_i^L$ are the concentrations of component $i$ at a flat interface. Note that the solid Si is essentially pure and hence $C_{Al}^S, C_{Cu}^S \approx 0$. In addition, the partial derivatives of the Gibbs surface of the liquid phase, $G_{ij}^L$, have the form

$$G_{ij}^L = \frac{\partial^2 G^L}{\partial C_i \partial C_j} |_{C^L}$$

(9.3)

where $G_{ij}^L$ is evaluated at $C^L$, the equilibrium composition of the liquid (L) phase at a planar interface. In general, for an $N$ component system, Philippe and Voorhees [177] showed that Eq. 9.2 can be written as $\Lambda = (\Delta \overline{C})^T M^{-1} \Delta C^L$ where the vector $\Delta \overline{C} = \overline{C}_i^S - \overline{C}_i^L$ for $i = 2 \ldots N$, $\Delta C^L = C_j^L - \overline{C}_j^L$ for $j = 2 \ldots N$, and $M^{-1}$ is the inverse of a
diffusion mobility matrix. Thus, the thermodynamic and kinetic information contained in $\Lambda$ (Eq. 9.2) are related to the diffusion mobilities in the Al-Si-Cu melt [199].

In practice, all terms except $\sigma$ and $\zeta$ in Eq. 9.1 can be determined as follows:

- $K$ in the Al-32wt%Si-15wt%Cu alloy at 650 °C can be found by fitting Eq. 3.16 to the experimental data here. For purpose of comparison, $K$ in the binary Al-29.9wt%Si system at 610 °C can be retrieved from chapter 8 [198].
- $f(V_v)$ can be predicted from recent simulations and theories. Recall that $f(V_v) = V_v^{1/2}$ in the low volume fraction limit [231, 232] (section 3.5.2). Thus, for the aforementioned Al-Si and Al-Si-Cu alloy samples, where $V_v \approx 16\%$ and 23%, respectively, the influence of finite volume fraction on $K$ can be safely neglected.
- $\Lambda$ (Eq. 9.2) can be calculated by incorporating CALPHAD thermodynamic modeling of the Al-Si-Cu system [90], which provides both $\Delta C_i$ and $G_{i,j}^L$ for $i, j \in \text{Al}, \text{Cu}$; and ab initio molecular dynamics (AIMD) simulation, which predicts the diffusivities $D_{\text{Al}}^L$ and $D_{\text{Cu}}^L$ in an Al-Si-Cu liquid at 650 °C.
- $V_{m}^S$ can similarly be obtained from thermodynamic databases. We find that $V_{m}^S$ in these two samples are approximately equal (12.14 cm$^3$/mol.), because the solubility of Cu in Si is very low (< 1 ppm [50, 83]), as stated previously.

For spherical particles, $\zeta = (1/3)^n$ [138], where $n = 2$ or $n = 3$ in the interface-reaction or bulk diffusion limit, respectively (see section 3.5.2). However, in this study, the geometrical factor $\zeta$ is difficult to determine since the Si particles are highly interconnected and morphologically complex. Nevertheless, we can gain key insight into the influence of Cu on the diffusion mobilities (via $\Lambda$) and the rate constant for coarsening $K$. 
9.1.1. Thermodynamic Modeling

In the CALPHAD method, the liquid phase is treated as a substitutional solution. Then, the free energy of the Gibbs surface of the liquid phase, $G^L$, is given by the equation

$$G^L = C_{Al} \, 0G_{Al}^L + C_{Si} \, 0G_{Si}^L + C_{Cu} \, 0G_{Cu}^L + R \, T \left( C_{Al} \ln C_{Al} + C_{Si} \ln C_{Si} + C_{Cu} \ln C_{Cu} \right) + \varepsilon G^L$$

(9.4)

where $0G_i^L$ is the Gibbs free energy of component $i$ in the liquid phase relative to the standard element reference (SER) state (i.e., 25 °C and 1 bar), $R$ is the ideal gas constant, $T$ is temperature, and $\varepsilon G^L$ is the excess Gibbs free energy. $\varepsilon G^L$ given by

$$\varepsilon G^L = C_{Al} \, C_{Si} \, \mathcal{L}^{AlSi}_{AlSi} + C_{Al} \, C_{Cu} \, \mathcal{L}^{AlCu}_{AlCu}$$

$$+ C_{Si} \, C_{Cu} \, \mathcal{L}^{SiCu}_{SiCu} + C_{Al} \, C_{Si} \, C_{Ce} \, \mathcal{L}^{AlSiCu}_{AlSiCu}$$

(9.5)

where $\mathcal{L}^L$ represent the Redlich-Kister polynomials; they have been determined empirically in Ref. [90] for the Al-Si-Cu system. Likewise, the thermodynamic data of the pure phases Al, Si, and Cu are retrieved from the SGTE unary database [49].

9.1.2. Molecular Dynamics Simulation

The self-diffusion coefficients were calculated using AIMD simulation, as follows: first, the equilibrium molar volumes for each alloy composition of interest were determined. Then, NPT ensembles were employed using the projector augmented wave (PAW) method implemented in a version of VASP [123, 124, 125] capable of sampling time-averaged statistics under isothermal and isobaric conditions. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [175] was used for the exchange-correlation functional.
The ionic positions of atoms were evolved by computing the interatomic forces derived from the electronic structure approximation calculated from density functional theory (DFT). The interatomic forces were used in generating the trajectories used in the AIMD studies. The resulting time-averaged properties were extracted via

\[(9.6) \quad \psi(t) = \langle v_i(t) \cdot v_i(t = 0) \rangle\]

where \(v_i(t)\) are the position and velocity of atom \(i\) at time \(t\), and the angular brackets indicates the average over all time origins and atoms. The time integration of \(\psi(t)\) provides access to the self-diffusion coefficient \(D\) via the Green-Kubo relations [199].

9.1.3. Influence of Dissolved Copper

Fig. 9.3(a) shows a log-log plot of \(S_{v}^{-1}\) versus time, \(t\), for the metallography (denoted met.) and tomography (tom.) data of Al-32wt%Si-15wt%Cu and Al-29.9wt%Si alloy samples. Coarsening data on the binary alloy first appear in chapter 8 [198]. A fit of the tom. and met. data in Fig. 9.3 to Eq. 3.16 gives \(1/n = 0.30 \pm 0.02\) and \(K = 15.3 \pm 0.5 \ \mu m^3/min.\) for the ternary alloy; in comparison, Ref. [198] determined that \(1/n = 0.29 \pm 0.03\) and \(K = 15 \pm 2 \ \mu m^3/min.\) for the binary alloy. The coarsening exponent of \(n \approx 3\) indicates (Eq. 3.16) that the evolution of the solid Si particles is governed by diffusion in both systems. Furthermore, \(K\) is approximately equal for both alloy samples, suggesting that the 15wt%Cu does not affect appreciably the coarsening rate [199].

It should be noted that the coarsening experiments in this work involving Al-32wt%Si-15wt%Cu alloy samples were conducted at 650 °C [199], i.e., 40 °C higher than in similar investigations [82, 196, 198] of the binary Al-29.9wt%Si alloy samples.
Figure 9.3. (a) Log-log plot of inverse surface area per unit volume, $S_v^{-1}$, versus coarsening time, $t$, for Al-29.9wt%Si [198] and Al-32wt%Si-15wt%Cu [199] alloy samples analyzed using X-ray tomography (tom.) and optical metallography (met.) data. The annealing temperature is 610 °C for Al-29.9wt%Si and 650 °C for Al-32wt%Si-15wt%Cu. For both samples, the temporal exponent $n$ is nearly 3, indicating that the coarsening evolution of primary Si particles is diffusion-limited; the coarsening rate constant $K$ is $15 \pm 2 \mu m^3/min$ for Al-29.9wt%Si and $15.3 \pm 0.5 \mu m^3/min$ for Al-32wt%Si-15wt%Cu. (b) Plot of factor $\Lambda^{-1}$ versus mole fraction of Cu and Al in the alloy, denoted $C_{Cu}^0$ and $C_{Al}^0$, respectively; this plot is constructed by interpolating over the values of $\Lambda^{-1}$ in Table 9.1. The Cu constituent (15t% by weight) in the ternary alloy results in approx. 10% decrease in $\Lambda^{-1}$ compared to the binary Al-Si alloy at 650 °C [199].

In general, the rate constant $K$ varies with temperature $T$ as an Arrhenius relationship:

\begin{equation}
K \propto \exp \left( -\frac{E_a}{kT} \right)
\end{equation}

where $E_a$ is the activation energy for interdiffusion in the melt, and $k$ is the Boltzmann factor. Eq. 9.7 follows from the fact that diffusivity is strongly temperature dependent, compared to $\sigma$, $G_{ij}^L$, or $V_m^S$ in Eqs. 9.1 and 9.2. Typical values of $E_a$ are $280 \pm 70$ meV.
for self-diffusion in liquid Al [115] and 330 meV for interdiffusion in an Al-20at%Cu liquid [253]. Using $E_a \approx 300$ meV and Eq. 9.7 above, we estimate that $K$ for the ternary alloy at 610 °C is $13 \text{ } \mu \text{m}^3/\text{min}$. This “temperature-corrected” value of $K$ is still within the error of $K = 15 \pm 2 \text{ } \mu \text{m}^3/\text{min}$ measured for the binary alloy at 610 °C [199].

Additionally, we calculate the parameter $\Lambda^{-1}$ (Eq. 9.2) at 650 °C for four alloy compositions $C_0^0$ labelled 1-4 using parameters determined from CALPHAD and AIMD simulation, see Table 9.1. As the concentration (mol%) of Cu in the Al-Si-Cu alloy increases from $C_{Cu}^0 = 0$ to 20 with $C_{Al}^0$ fixed, $\Lambda^{-1}$ (cm$^2$/kJ s) decreases from $10.48 \times 10^{-7}$ to $6.20 \times 10^{-7}$. Consider that alloys with compositions along the same solid Si-liquid tie-line should, according to Eq. 9.2, have the same value of $\Lambda^{-1}$. Note that any influence of finite $V_v$ on $K$ is reflected in the parameter $f(V_v)$ alone. Thus, we calculate the parameter $\Lambda^{-1}$ for four distinct tie-lines in the solid-liquid regime. Empirically fitting these tie lines to a quadratic surface yields an expression for $\Lambda^{-1}$ in terms of $C_{Al}^0$ and $C_{Cu}^0$ [199],

\begin{equation}
\Lambda^{-1} = a C_{Al}^0 + b C_{Al}^0 + c C_{Al}^0 C_{Cu}^0 + d C_{Al}^0 + e C_{Cu}^0 + f
\end{equation}

where the coefficients $a-f$ of the second-order polynomial are given by $-6.34 \times 10^{-7}$, $8.71 \times 10^{-6}$, $3.56 \times 10^{-6}$, $6.84 \times 10^{-7}$, $-5.90 \times 10^{-6}$, and $8.83 \times 10^{-7}$, respectively. Eq. 9.8 is plotted in Fig. 9.3(b) in units of cm$^2$/kJ s over the solid-liquid regime. Also indicated are the alloy compositions of interest, Al-32wt%Si-15wt%Cu and Al-29.9wt%Si. The factor $\Lambda^{-1}$ is roughly 10% lower for the ternary compared to the binary alloy at 650 °C.

By using a combined experimental-computational approach, we have demonstrated that the dissolved Cu (15% by weight) does not modify detectably (1) the diffusion mobilities in the liquid phase (via the parameter $\Lambda$), nor (2) the coarsening rate $K$. Taken
Table 9.1. The factor $\Lambda^{-1}$ (Eq. 9.2) is calculated using parameters $C^L$ and $G^L_{ij}$ determined from CALPHAD, and diffusivities $D^L_i$ determined from AIMD simulation, where $i, j \in \text{Al, Cu}$. We evaluate $\Lambda^{-1}$ at 650 °C for four alloy compositions $C^0$ labelled 1-4, which contain varying amounts of Cu. Errors represent estimated standard uncertainties [199].

<table>
<thead>
<tr>
<th>i.d.</th>
<th>$C^0_{\text{Al}}$ (mol %)</th>
<th>$C^0_{\text{Cu}}$ (mol %)</th>
<th>$C^L_{\text{Al}}$ (mol %)</th>
<th>$C^L_{\text{Cu}}$ (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0</td>
<td>83.28</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>5</td>
<td>76.34</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>10</td>
<td>71.38</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>20</td>
<td>64.19</td>
<td>0.26</td>
</tr>
</tbody>
</table>

(a) Initial alloy compositions, $C^0$, and liquid compositions, $C^L$, at 650 °C.

<table>
<thead>
<tr>
<th>i.d.</th>
<th>$G^L_{\text{AlCu}}$ (kJ)</th>
<th>$G^L_{\text{AlAl}}$ (kJ)</th>
<th>$G^L_{\text{CuCu}}$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78.79</td>
<td>81.70</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>50.32</td>
<td>90.02</td>
<td>205.68</td>
</tr>
<tr>
<td>3</td>
<td>32.04</td>
<td>96.59</td>
<td>105.04</td>
</tr>
<tr>
<td>4</td>
<td>14.05</td>
<td>109.41</td>
<td>25.44</td>
</tr>
</tbody>
</table>

(b) Partial derivatives of the liquid phase, $G^L_{ij}$, with respect to components $i, j$.

<table>
<thead>
<tr>
<th>i.d.</th>
<th>$D^L_{\text{Al}}$ ($\times10^{-4}$ cm$^2$/s)</th>
<th>$D^L_{\text{Cu}}$ ($\times10^{-4}$ cm$^2$/s)</th>
<th>$\Lambda^{-1}$ ($\times10^{-7}$ cm$^2$/kJ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.59 ± 0.018</td>
<td>—</td>
<td>10.48 ± 0.32</td>
</tr>
<tr>
<td>2</td>
<td>0.54 ± 0.008</td>
<td>0.53 ± 0.012</td>
<td>9.00 ± 0.13</td>
</tr>
<tr>
<td>3</td>
<td>0.41 ± 0.011</td>
<td>0.48 ± 0.013</td>
<td>7.25 ± 0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.31 ± 0.008</td>
<td>0.39 ± 0.011</td>
<td>6.20 ± 0.15</td>
</tr>
</tbody>
</table>

(c) Diffusion coefficients, $D^L_i$, of components $i$ in the liquid phase at 650 °C.

altogether, these results suggest that the Cu constituent does not strongly affect the dynamics of Ostwald ripening. However, we are unable to calculate the interfacial free energy $\sigma$ via Eq. 9.1. This is because the geometric constant $\zeta$ is difficult to determine given the extraordinary morphological complexity of the Si particles (see Fig. 9.1).
9.2. Interfacial Shape Distributions

9.2.1. Initial State of System

Fig. 9.4 shows the “initial state” of the system, for (a) the Al-32wt%Si-15wt%Cu alloy of this study and (b) the Al-29.9wt%Si alloy of chapter 8. The first row (Figs. 9.4(a-b)) shows the ISDs for both alloys at or near time $t = 0$ min., i.e., before any coarsening takes place. Each region of the ISD along the $S$ axis is associated with a particular shape, e.g., trough, saddle rut, saddle ridge, dome, as indicated from left-to-right on Fig. 9.4(a). Refer to Table 7.1 and Fig. 7.6 for a more exhaustive description of the shape index scale, $S$. In order to compare the two ISDs, the $C$ axis is scaled by $S_v$ and the color-bar range is fixed [113, 152]. Regardless of axis scaling, however, it is evident that the two ISDs show significant difference: the probability distribution corresponding to the ternary alloy is nearly symmetric about $S \approx 0$, while that of the binary alloy is asymmetric and features a long tail at $S \approx 0.5, C/S_v > 0$ (see also Fig. 8.8(a)) [199].

The above trends can be cross-checked by coloring the mesh faces of both microstructures according to their characteristic length scale, $C/S_v$, refer to Figs. 9.4(c-d). It can be seen that the regions of high curvedness or $C$ correspond to the particle edges, which are considerably finer in size for the unmodified alloy. This could account for the tail in the distribution at $S \approx 0.5, C/S_v > 0$ in the ISD of the binary alloy. Differences in the solidification pathways, from undercooled liquid to as-cast solid, may result in differences in the interfacial morphologies between the two alloy samples [199].
Figure 9.4. Comparison of the “initial state” of the system in alloys of composition Al-32wt%Si-15wt%Cu [199] (left) and Al-29.9wt%Si [198] (right). (a-b) Interfacial shape distributions (ISDs) near time $t = 0$ s for the ternary and binary alloys, respectively. Insets in (a) show characteristic shapes along the $\mathcal{C}$ axis, from (far left) liquid spheres or “cups” to (far right) solid spheres or “caps” (see Table 7.1) [121]. In both cases (a-b), the inverse characteristic length-scale, $\mathcal{C}$, is scaled by the surface area per unit volume, $S_v$. The limits of the color-bar are identical, such that the two ISDs can be compared. The ISD of the ternary alloy is nearly symmetric about $\mathcal{C} = 0$, while the ISD of the binary alloy is asymmetric and features a long tail at $\mathcal{C} \approx 0.5$, $\mathcal{C}/S_v > 0$. (c-d) 3D reconstructions of the as-cast Si particles, where interfacial patches have been illuminated according to $\mathcal{C}/S_v$ [199].
9.2.2. Evolution of Interfacial Shapes

The ISDs of the six reconstructions shown in Fig. 9.1 are given in Figs. 9.5. The $C$ axis is scaled by $S_v$, and the color-bar range is fixed in order to compare all time-steps, as before. If left unscaled, the ISDs would depict the increase in length scale of the system with coarsening time, as the non-zero probability regions of the plots shrink towards the origin. Using scaled ISDs, then, allows for comparison of morphology without regard to length-scale. Initially, there is high probability of finding a patch with planar shape, $C/S_v \approx 0$. However, as time increases, convex solid patches almost completely disappear, while the probability of concave spherical-like and cylindrical-like patches increases. Qualitatively, this is consistent with the reconstructions given in Figs. 9.1 and also with the work of Ref. [198] (chapter 8) in their studies of the unmodified Al-Si alloy: the Si particles become increasingly isotropic during coarsening, thereby evolving away from their fully-faceted, equilibrium Wulff shape. Furthermore, the similarity of our in situ results with those of the past ex situ experiments suggests that repeated thermal cycling has negligible influence on the coarsening dynamics of the Si particles [199].

We can examine more closely the evolution of the liquid and solid cylinders (denoted A and B in Fig. 9.1), see Fig. 9.6. These reconstructions show the (b) growth and (d) dissolution of solid Si, respectively, compared to (a,c) models for both processes proposed by Moorthy and Howe [162]. In (b,d), the solid phase is orange-green, while the liquid phase is black. Both images show the superposition of three meshes at time-steps $t_1 < t_2 < t_3$, where $\Delta t \approx 140 \text{ s}$. The meshes at time-steps $t_1$ and $t_2$ are rendered at 50% transparency in order to visualize the surfaces and inner structures underneath. In both cases, the cross-section of the solid-liquid interface is circular or isotropic. Therefore,
Figure 9.5. (a-f) Interfacial shape distributions (section 7.3) corresponding to the six reconstructions given in Fig. 9.1. The inverse length-scale, $C$, is scaled by the surface area per unit volume, $S_v$. The limits of the color-bar of the distribution are fixed so that the ISDs at multiple time-steps can be compared. The ISDs indicate that the initially faceted particle structure, i.e., $C/S_v \approx 0$ (a), becomes increasingly isotropic or rounded over time, i.e., $I \approx 0.5$, $C/S_v > 0$ (f), consistent with the images shown Fig. 9.1 [199].

The morphological evolution may be symmetric upon solidification and melting. Defects may decorate the solid-liquid interfaces such that growth and dissolution are both continuous processes. The density of such defects, e.g., twins, may become so large that the solid-liquid interfaces appear curved at the microscale (Fig. 9.6(b,d)). For instance, Ref. [93] demonstrated that twin planes in Si may have nanometer spacing, so it is entirely conceivable that the interfaces are isotropic upon solidification and melting [199].
Figure 9.6. (a,c) Illustration of the suggested difference in the interfacial morphologies during growth and dissolution of a faceted particle, adapted from Ref. [162]. (b,d) Results from this investigation [199], showing the growth and dissolution of solid silicon, respectively. Both images show the superposition of three meshes at time-steps $t_1 < t_2 < t_3$, where $\Delta t \approx 140$ s. The meshes at time-steps $t_1$ and $t_2$ are rendered semi-transparent for clarity. In both cases, the cross-section of the solid-liquid interface is circular or isotropic, indicating that the solid is filled with multiple re-entrant twin defects, even for relatively small length-scales [199].

9.3. Interfacial Velocity Measurements

Fig. 9.7 shows probability distributions of (a-c) interfacial velocity $\nu$ versus curvedness $\mathcal{C}$ and (d-f) $\nu$ versus shape index $\mathcal{S}$, at three representative time-steps during coarsening. Velocity $\nu$ is scaled by $dS_v^{-1}/dt$ and $\mathcal{C}$ is scaled by $S_v$, as before. Also indicated are white contour lines corresponding to the probabilities $P(\mathcal{C}/S_v, \nu/dS_v^{-1}/dt)$ or $P(\mathcal{S}, \nu/dS_v^{-1}/dt)$ equal to 0.005, 0.01, 0.05, 0.1, and 0.25. At early stages of coarsening,
the distributions in Figs. 9.7(a,d) are concentrated about $C/S_v \approx 0$, and $\mathcal{V}/dS_v^{-1}/dt \approx 0$. Over time, however, interfacial patches with $\mathcal{S} \approx 0.5$ and $C/S_v \approx 1$ develop a large range of interfacial velocities, $\mathcal{V}/dS_v^{-1}/dt \in [-20, 15]$ as depicted in Figs. 9.7(c,f). In other words, planar patches with near-zero velocity are highly probable at early times, whereas curved patches with high velocity dominate the microstructure at the later stages of ripening. Observe also that the plots of velocity vs. curvature scales at long times (Fig. 9.7(c,f)) are not centered about the $\mathcal{V}/dS_v^{-1}/dt = 0$ axis. Instead, there is a higher probability of negative velocity. This implies that $dV/dt = \sum_i \mathcal{V}_i S_i$ is negative, i.e., the volume fraction of coarsening phase decreases over time. This is consistent with sedimentation of the microstructure out of the field-of-view (Fig. 9.2) [199].

We can represent the above information more succinctly using 3D contour plots of $\mathcal{S}$ vs. $C/S_v$ vs. $\mathcal{V}/dS_v^{-1}/dt$, see Fig. 9.8. Shown are three contours of the 3D probability ($P$) space rendered semi-transparent for clarity. The orthogonal projections $\mathcal{S}$ vs. $\mathcal{V}/dS_v^{-1}/dt$ and $C/S_v$ vs. $\mathcal{V}/dS_v^{-1}/dt$ are depicted in gray and match those in Fig. 9.7. While the plots in Fig. 9.8 are included for completeness, they will not be discussed in detail because further analysis using 3D semi-transparent contour plots is still necessary. Nevertheless, we observe qualitatively that the volume of probability space enclosed by the contour at $P = 20\%$ (in yellow) becomes larger over time, indicating that the Si particles adopt a large range of interfacial velocities as the coarsening proceeds.

The $C/S_v$ versus $\mathcal{V}/dS_v^{-1}/dt$ distributions (Fig. 9.7(a-c)) can be divided into three “zones,” in which patches have (1) low curvedness and low velocity ($C/S_v < 1$ and $\mathcal{V}/dS_v^{-1}/dt \approx 0$), (2) high curvedness and high velocity ($C/S_v > 1$ and $|\mathcal{V}/dS_v^{-1}/dt| > 2.5$), and (3) high curvedness and low velocity ($C/S_v > 1$ and $|\mathcal{V}/dS_v^{-1}/dt| < 2.5$).
The boundaries of each zone are selected arbitrarily. Interfacial patches that fall in zone (1) presumably belong to the broad \{111\} faces of the Si particles; along such facets, 2D nucleation is required to initiate growth of a new layer (section 3.1.2). Under weak supersaturation, this 2D nucleation rate is very low, hence, $\mathcal{V}/dS_v^{-1}/dt \approx 0$ [199].
Figure 9.8. Isosurfaces of the 3D probability space $P(\mathcal{S}, C/S_v, \mathcal{V}/dS_v^{-1}/dt)$ after isothermal coarsening for (a) 1495 s, (b) 5889 s, and (c) 12566 s. The dark green surface represents the isosurface $P = 60\%$, yellow-green is $P = 40\%$, yellow is $P = 20\%$, and gray is the projection of the 3D surfaces onto the 2D planes $C/S_v$ vs. $\mathcal{V}/dS_v^{-1}/dt$ and $\mathcal{S}$ vs. $\mathcal{V}/dS_v^{-1}/dt$.

On the other hand, patches falling in zone (2) correspond to the highly curved solid-liquid interfaces; such patches are expected to evolve rapidly since the driving force for coarsening is proportional to the mean curvature via the Gibbs-Thomson equation (Eq. 3.9). On the corresponding $\mathcal{S}$ vs. $\mathcal{V}/dS_v^{-1}/dt$ figures, e.g., Fig. 9.7(e,f), it is evident that these high velocity interfaces have cylindrical-like shape, since $\mathcal{S} \approx 0.5$. Microscopically, this curvature may originate from rough, high index orientations that evolve rapidly and eventually cease to exist. Another possibility, first pointed out in chapter 8 [198], is that a high density of twin boundaries that intersect the Si particle edges may act as a source of steps, providing the kink sites (re-entrant grooves) necessary for interfacial propagation. In light of these findings, one may link the observed high curvature to a rapidly evolving interface that may be filled with defects [199].

The last zone (3), comprising patches with high curvedness and low velocity, is not predicted by the above logic and thus warrants further exploration. This region of curvature-velocity space is boxed in red in Fig. 9.7(b). The interfacial patches belonging
to these bins in the $C/S_v$ versus $\mathcal{V}/dS_v^{-1}/dt$ histogram can be illuminated on the mesh, creating an SML figure [54], see Fig. 9.9(a). Patches that fall in zone (3) are depicted in red. Approx. 40% of such patches comprise liquid inclusions, which do not evolve over the course of the five hour experiment; the remainder span the length of the junction between rough and faceted interfaces, see the magnified view in Fig. 9.9(a). The evolution of this boxed region is shown in Figs. 9.9(b-e) at four representative time-steps. The region to the right of the crimson segment (in the magnified view) is termed “rough” because such interfaces, which are initially highly curved (Fig. 9.9(b)), evolve rapidly during ripening ($|\mathcal{V}/dS_v^{-1}/dt| > 5$); thus, steps and kinks must facilitate the interfacial propagation. On the other hand, the region to the left of the crimson segment represents a faceted interface that remains relatively immobile ($\mathcal{V}/dS_v^{-1}/dt \approx 0$). The pinning of microstructure where a rough interface meets a faceted one is analyzed in detail in section 9.4 [199].

9.4. Analysis of Microstructural Singularities

The highly time-resolved nature of our in situ investigation allows us to characterize for the first time the local evolution of interfaces during the coarsening process. In particular we observe “pinning” of the microstructure at the highly curved junction between rough interfaces and smooth ones. It is unlikely that lattice defects, e.g., screw dislocations, stacking faults, and twin boundaries, intersect the solid-liquid interface at this junction because such defects would generate a self-perpetuating source of steps. If this were the case, growth would occur continuously and the interfacial velocity would be nonzero. Instead, we assume, below, that the junction is defect-free. Using the analogy of cars (steps) on a road (crystal surface) [134], there must be another explanation for the “traffic
Figure 9.9. (a) Specific Microstructural Location (SML) figures [54], depicting solid-liquid interfacial patches with $\mathcal{C}/S_v > 1$ and $|\mathcal{V}/dS_v^{-1}/dt| < 2.5$ in red, at 5889 s during the coarsening process (see Fig. 9.7). Approx. 40% of such patches comprise liquid inclusions, and the remainder lie at the junction between rough and faceted interfaces, see boxed inset. (b-e) Evolution of this boxed region at (b) 1495, (c) 2066, (d) 2494, and (e) 5506 s during ripening. At each time-step, scaled velocities, $\mathcal{V}/dS_v^{-1}/dt$, are illuminated on the interface, where positive velocity corresponds to particle growth and negative velocity to dissolution. The highly curved, rough region evolves rapidly while the facet remains relatively immobile. The arrow in (e) points to the aforementioned high curvature, low velocity interface that “pins” the microstructure, as explained in Fig. 9.10 [199].

jam” of steps at the rough-smooth junction. We explain the interfacial dynamics in the vicinity of this rough-smooth junction using a step flow model, illustrated in Fig. 9.10.

Initially, the rough interface in Fig. 9.10 is “S”-shaped (gray isochrone). Over time, however, the upper segment melts away while the lower segment grows into the liquid (black isochrone). Step trains that are provided by the rough interface are unable to traverse the lower facet during growth. Since the facet remains essentially stationary during ripening, there is enough time for an adsorption equilibrium to be established
Figure 9.10. Illustration of interfacial evolution at the junction between faceted and rough interfaces. Two isochrones of the solid-liquid interface are given, at times $t_1$ and $t_2$ where $t_1 < t_2$. The grey isochrone at $t_1$ matches the interfacial profile shown in Fig. 9.9(b), while the black isochrone corresponds to that of Fig. 9.9(e). During growth, steps that are provided by the rough interface are unable to propagate across the left-most facet because impurity atoms (denoted by red spheres) may inhibit step flow. This may explain the high curvature, low velocity regions (in purple, see also Figs. 9.7 and 9.9) that “pin” the microstructure during coarsening. On the other hand, the steps need only to recede during dissolution, hence why melting is a continuous process and involves no such microstructural singularities [199].

between impurity precipitates (red spheres in Fig. 9.10) and the crystal surface. Thus, the concentration of impurities may be high on the faceted interfaces [57, 143]. The latter may inhibit strongly the propagation of steps across the facet [57, 143], resulting in a “traffic jam” of steps at the rough-smooth junction. This may explain the existence of the high curvature, low velocity regions (Fig. 9.7). On the other hand, steps need only to recede during dissolution, hence why melting is a continuous process and involves no such pinning events on the upper facet in Fig. 9.10. This suggests that, for defect-free crystals, the morphological evolution is asymmetric upon growth and dissolution.

All generalizations are dangerous, and in principle one can conceive of circumstances in which growth and dissolution are both continuous processes. Indeed, such behavior is
possible in highly *defective* crystals, see, *e.g.*, Fig. 9.6. This observation is supported by Tepper and Briels [217], who addressed in their molecular dynamics simulations the role of lattice imperfections along \{100\} FCC interfaces. They noted that the asymmetry in the interface response disappears in defective crystals [217]. Our results on the coarsening of Si particles in a liquid support this conclusion. Thus, the interfacial response is contingent on the prevalence of lattice defects along the solid-liquid interfaces.
CHAPTER 10

Growth of Si Particles in Al-Si-Cu

While the results presented in chapters 8 and 9 demonstrate that defects are central to the coarsening evolution of Si particles, it remains to be determined exactly how defects (such as twins) facilitate the growth process. Many controversial models have been proposed for twin-mediated crystal growth, including those by Wagner [237], Hamilton and Seidensticker [85] (denoted WHS) and Fujiwara and coworkers [60] (denoted F, see section 3.2.2), most of which lack experimental verification. Here, we probe the real-time interfacial dynamics of polycrystalline Si particles growing from an Al-Si-Cu liquid via synchrotron-based XRT (section 4.2).\(^1\) Our subsequent analysis of interfacial texture allows us to quantify unambiguously the habit plane and grain boundary orientations during growth, from which we validate with high precision the aforementioned twin-mediated growth mechanisms. To the best of our knowledge, this is the first time that time-dependent crystallographic information has been obtained from XRT.

During the experiment [197], hypereutectic alloys of composition Al-32wt%Si-15wt%Cu were heated in a resistive furnace to above the liquidus and allowed to equilibrate at 910 °C. Then, the samples were cooled at a rate of 1 °C/min while projections were recorded. The sampling parameters are given for sample #3 in Table 4.2. For the first 20 minutes, projections were collected continuously at a rate of 50 frames/s, with

\(^1\) The subject matter of this chapter is adapted in part from Ref. [197] by A. J. Shahani and coworkers.
1500 frames distributed evenly in every 180° rotation; these parameters provide a temporal resolution of 30 s between each of the 40 reconstructions. For the next 120 minutes, 40 tomographic scans with the same parameters were spaced 150 s apart. The motivation for this data collection scheme is that the growth rate of the particle is inversely proportional to its system-average length-scale in the bulk diffusion controlled limit \([233]\); as such, one scan every three minutes during the late stages of growth is adequate to keep up with the interfacial dynamics. The remainder of the data processing and microstructural analyses is based on the techniques described in chapters 6 and 7, respectively.

10.1. Attenuation-Based Reconstructions

The evolution of the sample at six representative time-steps is shown in Fig. 10.1. White regions correspond to the primary Si particles, and the dark blue background to the Al-Si-Cu liquid. Visible in Fig. 10.1 are four Si particles that grow from the oxide skin into the melt. Two of the particles appear to be in contact at the latest time. These reconstructions reflect the extraordinary morphological and topological complexity of the primary Si particles during crystallization. Note that the weight fraction of the Si phase versus temperature in this experiment is almost coincident with predictions at equilibrium, see Fig. 10.2. However, the shapes of the Si particles in Fig. 10.1 do not resemble the equilibrium Wulff shape of the crystal, a tetrakaidecahedron dominated by \{111\} habit planes \([52]\) (section 2.1). Instead, defects (e.g., twins) that perturb the solid-liquid interfaces may lead to a rich variety of polycrystalline growth forms \([197]\).

We consider the boxed particle in Fig. 10.1(b) for subsequent analysis. Fig. 10.3 shows the 3D interfacial morphologies of this particle at a more local scale, during the early stages
Figure 10.1. 3D reconstructions showing the growth process of Si particles (white) in a Cu-enriched liquid (dark blue). Six representative time-steps during the \textit{in situ} XRT scan are given: (a) 840 s, (b) 1200 s, (c) 2476 s, (d) 3865 s, (e) 7238 s, and (f) 9023 s. The time $t = 0$ s (approx. 910 °C) corresponds to the onset of the XRT scan, at which the sample is entirely liquid. The field-of-view measures $1664 \times 1664 \times 715 \, \mu\text{m}^3$ (Table 4.2). The boxed particle in (b) is considered for further analysis [197].

of growth. The time interval between the reconstructions is 20 s. The Si particle grows from the oxide skin (not pictured) into the melt (in white). Interestingly, the particle is initially fully-faceted, but develops concave (negative) curvature relative to the solid phase during growth (see Fig. 10.3(e)). We attribute this morphological instability to the formation of twin defects during growth [197], as explained further in section 10.5.1.
Figure 10.2. Weight fraction of primary Si, $X_{Si}$, versus temperature, $T$, during growth in an alloy of composition Al-32wt%Si-15%Cu. $X_{Si}$ is calculated from the experimental data over the entire field-of-view and is shown in blue, while equilibrium and Gulliver-Scheil simulations are determined from CALPHAD and plotted as a red line and black stars, respectively. All three curves are coincident, indicating that the growth rate of the solid can keep up with the quench rate. Errors in the measurement of $X_{Si}$ from the experimental data due to segmentation are negligible [197].

Figure 10.3. The Si particle boxed in Fig. 10.1(b) grows from the oxide skin (not pictured) into the melt (in white). Shown are four time-steps during growth: (a) 900 s, (b) 1110 s, (c) 1476 s, and (d) 1873 s. (e) 3D reconstructions of the same particle are given from a worm’s eye view. Five time-steps $t$ are superimposed where $\Delta t$ is 20 s. The initially faceted solid-liquid interface, in purple, develops curvature during growth [197].
10.2. Surface Area per Unit Volume, $S_v^{-1}$

Recall from sections 3.1.1 and 3.1.2 that the growth rate of the Si particle may be limited by either the diffusion of growth species from the bulk to the growth surface, or the adsorption of the growth species onto the growth surface. If the growth process is controlled by diffusion, then the particle length-scale $S_v^{-1}$ varies parabolically with time $t$; on the other hand, $S_v^{-1}$ varies linearly with $t$ for interface-reaction-limited growth [145, 233]. Thus, assuming growth follows a power law relationship, $S_v^{-1}$ varies as

$$S_v^{-n}(t) - S_v^{-n}(t_0) = K (t - t_0)$$

(10.1)

where $S_v(t_0)$ is the specific surface area at time $t_0$, representing the onset of steady-state growth; $K$ is a rate constant that depends on materials parameters; and $n = 1$ in the interface-reaction limit or $n = 2$ in the diffusion limit. This is the analogue of Eq. 3.16 previously encountered in coarsening theory (section 3.5.2). To adequately represent the kinetics of particle growth, we measure $S_v$ at each time-step according to Eqs. 7.2.

A plot of $S_v^{-1}$ versus $t$ for the same particle is given in Fig. 10.4(a). Then, a nonlinear least-squares fit to the three parameters $t_0$, $S_v(t_0)$, and $K$ in Eq. 10.1 is used to analyze this data. Two lines-of-best-fit are plotted in Fig. 10.4(a): a line of constant slope ($n = 1$), in red, corresponding to growth in the interface-reaction limit, and a line varying as $t^{1/2}$ ($n = 2$), corresponding to growth in the bulk diffusion-limit. We find that at early times, growth is interface-reaction-limited, while at later times, it is diffusion limited. The transition between these two epochs occurs between 4500 and 5500 s [197].
Figure 10.4. (a) Inverse surface area per unit volume $S_v^{-1}$ versus time $t$ for the boxed particle in Fig. 10.1(a). To the experimental data, in blue, we fit two lines-of-best-fit: a line of constant slope, in red, corresponding to interface-reaction-limited growth, and a line varying as $t^{1/2}$, in green, corresponding to diffusion-limited growth. At early times, growth is interface-reaction-limited, while at later times, it is diffusion-limited. The transition between these two regimes occurs between 4500 and 5500 s. (b) Patches along the solid-liquid interfaces are indexed as $\{111\}$ if the orientation of such patches falls within the yellow region of the IPF (see inset). The total area fraction, $A_A$, of these $\{111\}$ patches belonging to the Si particle is plotted over time $t$ (in blue). The black curve represents a cubic spline interpolation of the data. $A_A \{111\}$ passes through a maximum of approx. 0.45 at 3200 s, suggesting that $\{111\}$ facet growth at early times ($t < 3200$ s) competes with the proliferation of twin defects at later times ($t > 3200$ s). Twin defects provide the kink sites necessary for interfacial propagation, hence why growth is diffusion-limited at late times [197].

10.3. Crystallographic Normal Distributions

In order to further elucidate the structure of the solid-liquid interfaces, we characterize the distribution of crystallographic orientations along the particle surfaces during growth. Fig. 10.5 gives the distribution of interfacial normals in the specimen frame at an early stage in the growth process. Normals are plotted in spherical coordinates $(\theta, \phi)$ such that
Each value in \((\theta, \phi)\)-space is associated with a unique hue in the color spectrum. The black contoured peaks in the \((\theta, \phi)\) distribution (Fig. 10.5(a)) represent the orientations of the three largest facets (by area) in the Si particle. In Fig. 10.5(b), the interfaces of the Si particle are illuminated according to the \((\theta, \phi)\)-map of surface orientations. For example, the three broadest facets are colored blue, red, and green, and are plotted individually in Figs. 10.5(c-e). The red facet is 180° away from the green facet; thus, the red and green poles in Fig. 10.5(a) are related by inversion symmetry. In addition, we index the prominent blue and green facets to the \(\{111\}\) family. This is plausible because the kinetic [251] and equilibrium Wulff shapes [52] of Si are bounded by \(\{111\}\) planes. As explained in section 7.5, provided that these two facets—which are adjacent to one another—have no defects between them, they must belong to the same monocrystal. To verify the above, we calculate the angle between these two facets as 70.5°, which matches the 70.53° dihedral angle of a monocrystal bounded by \(\{111\}\) habit planes [197]. This information can now be used to construct the orientation matrix \(g\), such that all crystallographic orientations can be measured relative to this particular monocrystal (section 7.5).

Once the crystallographic normals are calculated for all interfacial patches at all time-steps, we can track the textural development of the solid-liquid interfaces during the growth process. Fig. 10.6 (top row) displays the Si particle at five representative time steps, illuminated according to the standard triangle given in Fig. 10.6(a). While the broadest facets have the \(\{111\}\) orientation (in blue), other crystallographic orientations are certainly evident, indicative of polycrystallinity. For instance, the boxed region in Fig. 10.6(e) shows multiple monocrystalline grains that meet at lamellar grain boundaries. This microstructure resembles that of parallel annealing twins in FCC metals [139],
Figure 10.5. (a) Interface normal distribution (IND, see section 7.4) of the Si particle at 2675 s during growth, in which the surface normals are plotted in spherical coordinates ($\theta, \phi$). Each color in ($\theta, \phi$)-space represents a unique orientation of the solid-liquid interface. The black peaks in the distribution represent the orientations of the three largest facets of the Si particle. (b) The corresponding 3D microstructure of the Si particle illuminated according to the orientation of the surface normals in ($\theta, \phi$)-space. The green facet in the IND is nearly 180° from the red facet, i.e., they are on opposite sides of the Si particle. We assign the blue and the green facets to the $\{111\}$ family, and assuming that there are no defects (e.g., grain boundaries) between these facets, they must belong to the same monocrystal (see section 7.5). As a consistency check, the angle between the blue and green facets is 70.5°, which matches the 70.53° dihedral angle of a monocrystal bounded by $\{111\}$ habit planes [197]. (c-e) The dominant blue, red, and green facets are illuminated individually onto the particle, respectively.
a possibility that is explored further in Fig. 10.7. The bottom row in Fig. 10.6 shows the five corresponding inverse pole figures (IPFs). The limits of the color-bar range are fixed such that multiple IPFs can be compared. It can be seen that the probability $P$ of the \{111\} orientation first increases and then decreases during the growth process [197].

Quantitatively, patches of interface are indexed as \{111\} if the orientation of the patches falls within the yellow region of the IPF, see the inset in Fig. 10.4(b). The boundary of this yellow region is selected somewhat arbitrarily. Then, the total area fraction, $A_A$, of these \{111\} patches belonging to the Si particle is plotted over time $t$. We find that the maximum areal coverage of the \{111\} orientation (relative to the monocrystal identified in Fig. 10.5) is around 45% and occurs at approx. 3200 s. For $t < 3200$ s, the high mobility facets grow out and cease to exist such that the crystal is asymptotically bounded by the low mobility \{111\} planes [17, 251]. This kinetic behavior accounts for the regime of \{111\} facet growth observed for $t < 3200$ s. On the other hand, the proliferation of defects, \textit{e.g.}, twin boundaries, at later times ($t > 3200$) leads to the formation of new grains that have divergent orientations from that of the original, \{111\}-bounded monocrystal. This explains the decrease in the areal coverage of the \{111\} orientation. The plot of $S_V^{-1}$ versus $t$ (Fig. 8.2(a)) can now be understood in the context of $A_A$ \{111\} ((Fig. 8.2(b)): when $A_A$ \{111\} is high, such as in the early stages of growth, 2D nucleation on \{111\} is needed to initiate new layers and thus growth is interface-reaction limited. Conversely, growth is governed by the bulk diffusion of solute at late times provided that there are enough defects to facilitate the growth process [197].

We can examine more closely the aforementioned lamellar (parallel) grain boundaries (Fig. 10.6(e)) using our 4D XRT data, as follows: at each time-step, we measure several
Figure 10.6. Evolution of the solid-liquid interfacial texture during growth: the top row displays the crystal facets of the Si particle illuminated according to the standard triangle in (a), and the bottom row depicts the corresponding inverse pole figures (IPFs). Shown are five time-steps during growth: (a) 930 s, (b) 1476 s, (c) 3071 s, (d) 5254 s, and (e) 8230 s. The limits of the color-bar range are fixed such that multiple IPFs can be compared. The probability $P$ of the $\{111\}$ orientation, $P(\{111\})$, first increases and then decreases during growth. The boxed region in (e) consists of lamellar grain boundaries, which are characterized in Fig. 10.7 [197].

points along the grain boundaries by hand; then, we fit the grain boundaries to 3D surfaces. Figs. 10.7(a-b) show the semi-transparent microstructure of the Si particle overlaid with the grain boundaries (in green and blue). The mesh surfaces of these boundaries are nearly planar, indicating a high degree of coherency between the adjoining monocrystalline grains. Boundaries are termed incoherent if there exists any lattice curvature that must be accommodated plastically through dislocations, which is not the case here. In Fig. 10.7(b), the grain boundary in blue makes an angle of approx. $110^\circ$ with respect to the facet planes, which corresponds very nearly to the $109.47^\circ$ angle between two $\{111\}$ interfaces of the same family. In addition, the angle of the concave triple junction measures $150^\circ$; this is within 10% error of the $141.06^\circ$ re-entrant groove angle centered at a $\Sigma3$ twin plane (see Fig. 3.5(a) for an idealized schematic). From these angular relationships,
we are able to classify the lamellar grain boundaries as \{111\} \Sigma 3 coherent (twin) boundaries [197]. Furthermore, the grain boundary misorientation measured here via 4-D XRT is consistent with that measured using EBSD for the case of coarsened Si particles in a eutectic matrix, see Fig. 8.11 [198]. In chapters 8 and 9, it was determined that multiple \{111\} \Sigma 3 twin boundaries intersect the “rough” edges of the Si particles.

The propagation of this doubly-twinned interface is depicted in Fig. 10.7(c). Five semi-transparent isochrones are plotted (\(\Delta t \approx 600\) s) together with points along the two twin boundaries, labelled I and II and colored in blue and green, respectively. The interfacial morphology is identical between time-steps, i.e., the concave re-entrant groove does not disappear during growth. This picture is consistent with the WHS model (refer to Fig. 3.6), and incongruous with the F model (Fig. 3.7), as will be discussed in section 10.5.2. In particular, we do not see the appearance and disappearance of 60° triangular corners (at the length-scale of the crystal) expected from the F model.

In general, five macroscopic parameters are needed to classify a grain boundary [180]. Three parameters define the orientation relationship between the two adjacent grains, usually in terms of the Eulerian angles \(\phi_1\), \(\Phi\), and \(\phi_2\). Two more parameters define the inclination of the grain boundary plane, expressed as the plane normal \(\langle uvw \rangle\). In our work [197], we determine all five parameters from our tomography data: grain orientations are found from the crystallographic interface normal distribution (CIND) construction (Fig. 10.6) and the boundary plane orientation from the interfacial isochrones (Fig. 10.7). All intrinsic properties of the grain boundaries are functions of these parameters [76]. For instance, the growth direction of the twinned interface is fixed by the geometry of the re-entrant groove, see Fig. 10.8(a). Denote the growth direction as \(\langle hkl \rangle\), and re-entrant
Figure 10.7. Characterization of grain boundaries using 4-D XRT data [197]. (a) Semi-transparent 3D microstructure of Si particle overlaid with meshes of the nearly planar grain boundaries (in blue and green). (b) Magnified bird’s eye view of the boxed region in (a). The planarity of the grain boundaries suggests a high degree of coherency between the adjoining grains. The boundaries make an angle of approx. 110° with respect to the facet planes, which corresponds to the angle between two \( \{111\} \) interfaces of the same family. Thus, the lamellar grain boundaries are coherent \( \{111\} \Sigma 3 \) (twin) boundaries. The angle of the re-entrant groove is 150°. (c) Propagation of the twinned interface in (b) during growth. Five semi-transparent isochrones are plotted (\( \Delta t \approx 600 \) s) together with points along the two twin boundaries, labelled \( I \) and \( II \) and colored in blue and green, respectively. The morphology of the twinned interface appears nearly identical between the five time-steps, i.e., the re-entrant groove does not disappear during growth, consistent with the WHS model [85, 237].
angle as $\alpha$. The facet planes on either side of the groove have the \{111\} orientation. The growth direction $\langle hkl \rangle$ must satisfy the following two geometric constraints:

\[
\langle hkl \rangle \cdot \langle 0\bar{1}1 \rangle = 0
\]

\[
\langle hkl \rangle \cdot \langle 111 \rangle = \sqrt{3} \cos \left(90 - \frac{\alpha}{2}\right)
\]

where $\vec{a} \cdot \vec{b}$ indicates the dot product between vectors $\vec{a}$ and $\vec{b}$. According to the first equation, the growth direction $\langle hkl \rangle$ must lie normal to the zone or symmetry axis ($\langle 0\bar{1}1 \rangle$) between the two \{111\} facet planes; the second indicates that $\langle hkl \rangle$ must make an angle of $90 - \alpha/2$ with the \{111\} plane. Eqs. 10.2 assume that $\langle hkl \rangle$ is normalized.

Solving the simultaneous equations (Eqs. 10.2) gives $\langle hkl \rangle = \langle n11 \rangle$ where

\[
n = \frac{4 + 3\sqrt{2} \sin \alpha}{1 - 3 \cos \alpha}
\]

Thus, for a re-entrant angle of 141.06°, caused by the intersection of a \{111\} $\Sigma3$ boundary with the surface, the growth direction is $\langle 211 \rangle$. Note that growth direction satisfies the Weiss zone law, since $\langle hkl \rangle$ lies in the plane of the twin boundary (i.e., $\langle 211 \rangle \cdot \langle \bar{1}11 \rangle = 0$). This function $n(\alpha)$ is plotted on the standard triangle in Fig. 10.8(b) as $\alpha$ varies from 70.53° to 180° (dashed line). Note that $\alpha = 180°$ represents a flat \{111\} facet growing in the $\langle 111 \rangle$ direction. Also plotted are the growth directions for a \{111\} $\Sigma3$ boundary ($\alpha = 141.06°$), a \{221\} $\Sigma9$ boundary ($\alpha = 109.47°$), and the experimental data ($\alpha = 150°$, see Fig. 10.7). Thus, the twinned interface in our study grows along the $\langle 211 \rangle$ direction. It has been suggested [203] that the second-order $\Sigma9$ boundary may appear at very high growth rates, but we do not observe any such twinning configuration. In addition, we find no evidence for cozonal twins [203] with effective $\langle 110 \rangle$ or $\langle 100 \rangle$ fiber axes.
Figure 10.8. (a) Schematic showing the morphology of a twinned interface near a re-entrant groove. The groove has angle $\alpha$ and is bounded by two \{111\} habit planes. The generalized growth direction is denoted $\langle hkl \rangle$. (b) The growth direction of a twinned interface $\langle n11 \rangle$ is plotted on the stereographic triangle, where $n$ varies with $\alpha$ according to Eq. 10.3, and $\alpha \in (70.53^\circ, 180^\circ)$. Also plotted are the growth directions for a \{111\} $\Sigma 3$ boundary ($\alpha = 141.06^\circ$), a \{221\} $\Sigma 9$ boundary ($\alpha = 109.47^\circ$), and the experimental data ($\alpha = 150^\circ$, see Fig. 10.7). Thus, the twinned Si particle in our study grows along the $\langle 211 \rangle$ direction [197].

Figure 10.9. 3D microstructure of the Si particle during the late stages of growth, illuminated according to interfacial velocity $\mathcal{V}$. Shown are three time-steps: (a) 4856 s, (b) 6047 s, and (c) 8230 s. The velocity $\mathcal{V}$ is scaled by $dS_v^{-1}/dt$ and the range of the color-bar is fixed such that the three plots can be compared. The numbering in (b) indicates microstructural features-of-interest: (1) \{111\} facet plane, (2) ridge structure, and (3) re-entrant groove. It can be seen that $\mathcal{V}_\text{groove} > \mathcal{V}_\text{ridge} \gg \mathcal{V}_\text{facet}$ [197].
10.4. Interfacial Velocity Measurements

Twin-mediated growth theories [59, 61, 85, 106, 131, 155, 225, 237] predict that re-entrant grooves serve as preferential attachment sites for solute atoms during crystal growth. We confirm this notion by illuminating interfacial patches according to normal velocity \( \mathcal{V} \), as shown in Fig. 10.9 at three representative time-steps. \( \mathcal{V} \) is scaled by \( dS_v^{-1}/dt \) and the color-bar range is fixed such that the three plots can be compared. The numbering in (b) indicates microstructural features-of-interest: (1) \{111\} facet plane, (2) ridge structure, and (3) re-entrant groove. Recall that the ridge structure is convex while the re-entrant groove is concave with respect to the solid Si phase. In general, we detect that \( \mathcal{V}_{\text{groove}} > \mathcal{V}_{\text{ridge}} \gg \mathcal{V}_{\text{facet}} \), as one would expect based on the bonding arguments presented in section 3.2.2. Thus, we have established unequivocally via 4-D XRT the properties of the twinned interface, including its crystallography and dynamics [197].

10.5. Kinetics of Defect Generation and Growth

10.5.1. Formation of Twin Defects

It has long been recognized [23] that, due to the relatively low stresses experienced by the crystal during growth, the formation of twin defects (Fig. 10.3) cannot be of a mechanical origin and must therefore be related to solidification, and hence to some phenomenon occurring at the solid-liquid interface. There has been much debate on when and where such growth twins form, i.e., whether the critical nucleus originally contains a twin boundary [195, 238] or whether the twin boundaries form after nucleation [30, 31, 62]. Our results in Fig. 10.3 suggest the latter possibility, that multiple twin defects perturb the initially faceted surface of a Si monocystal during bulk crystal growth. According to the
“growth accident” hypothesis [31], twins are formed and terminated by errors of the stacking of the \{111\} planes. Moreover, the twinning probability is negatively correlated with the stacking fault energy (SFE). For instance, \Sigma 3 \{111\} boundaries possess very low SFE (30 mJ/m²) [122, 181], less than one-fifth of the SFE of other grain boundaries, and hence appear most frequently in grain boundary character distributions [181]. Ref. [62] proposed a mechanism by which growth accidents on Si \{111\} lead to the formation of parallel \Sigma 3 \{111\} boundaries. While we observe lamellar twins in our work (see Fig. 10.7) [197], the formation of such defects involves sub-micrometer scale dynamics that are well below the spatial resolution of our current XRT experimental results. Future improvement in higher resolution XRT would provide more conclusive evidence [248].

It should be noted that crystal twinning is also sensitive to the chemical environment. According to the “impurity induced twinning” (IIT) mechanism proposed by Lu and Hellawell [137], the adsorption of impurity atoms at monolayer steps may contribute to an alteration of the stacking sequence of \{111\} planes, and thus to the formation of twins. Geometrical considerations [137] require a specific radius ratio of impurity to Si for IIT to take place. However, neither Al not Cu in the Al-Si-Cu alloys of this study satisfies this condition. Instead, Timpel and colleagues [218] suggest that it is not the geometrical size factor that plays a major role in IIT but rather the chemistry of the co-segregations. Thus, we cannot rule out the possibility of intermetallic Al-Si-Cu adsorbents [197].

10.5.2. Growth of Twinned Polycrystal

The morphology of a twinned crystal results from a complex interplay between nucleation at the re-entrant groove and lateral growth of the layers so initiated. Let the nucleation
rate be denoted by \( \dot{N} \) and lateral growth by \( V_l \). The lateral growth rate, \( V_l \), which is *tangential* to the faceted interface, should not be confused with the growth rate *normal* to the interface, \( \mathcal{V} \), presented in Fig. 10.9. Consider the following three regimes illustrated in Fig. 10.10: (a) \( \dot{N} \leq V_l \), (b) \( \dot{N} > V_l \), and (c) \( \dot{N} \gg V_l \). In case (a), the lateral growth of layers away from the groove can keep pace with the nucleation rate at the re-entrant; as such, the corners of the crystal remain large, with wide terraces and flat interfaces. This “birth-and-spread” of new layers, emanating from the type I re-entrant groove, is the model most frequently encountered in the literature [85, 237]. If instead \( \dot{N} > V_l \) (case (b)), many layers emerge from the re-entrant. The lateral growth cannot keep up with the nucleation rate and the interface resembles a multiply tiered “wedding cake” centered at the twin boundary. By increasing \( \dot{N} \) further relative to \( V_l \) (case (c)), the re-entrant accumulates a multitude of layers that are stacked one above the other. At the macroscale, this configuration may have the appearance of a triangular mound projecting into the melt. Clearly, then, a continuum of polycrystalline growth forms can be obtained based on the kinetics of the materials system investigated [197].

Our results (Figs. 10.6, 10.7) show that the type I re-entrant groove does not disappear during growth, suggesting that the lateral growth of layers, \( V_l \), keeps pace with the nucleation rate, \( \dot{N} \), i.e., \( \dot{N} \sim V_l \). This is consistent with the WHS picture of twin-mediated crystal growth [85, 237] (Fig. 3.6). On the other hand, the F model (Fig. 3.7) predicts the formation of triangular 60° corners at the type I groove [59, 61]. Differences between the F and WHS approaches can be rationalized based on nucleation rates at the type I re-entrant, noting that, in general, \( \dot{N} \) depends strongly on temperature, undercooling, and the associated energy barrier [97]. While the nucleation barrier is not well known, and
Figure 10.10. Morphology of twinned interface under different growth conditions: (a) nucleation rate $\dot{N}$ at the re-entrant groove is of same order of magnitude as lateral growth rate $V_l$ of layers so initiated, (b) $\dot{N} > V_l$, and (c) $\dot{N} \gg V_l$. A continuum of growth morphologies is attainable.

may itself be a function of alloy composition, it is worth mentioning that the experiments performed by Fujiwara et al. \cite{59, 61, 249, 250} were conducted at temperatures much higher than in this investigation. In particular, Fujiwara et al. studied the crystallization of pure Si (melting temperature of 1414 °C) while we observed the growth of Si in an Al-Si-Cu melt (liquidus temperature of 910 °C) \cite{197}. If we consider the influence of absolute temperature on $\dot{N}$ alone, we might expect $\dot{N}$ to be considerably larger in the experiments performed by Fujiwara et al., resulting in the pancake stacking of layers at the type I groove (cases (b) or (c) above). Thus, a single growth mechanism may be inadequate to explain interfacial phenomena over the entire ($\dot{N}, V_l$) parameter space. Instead, the F model may be operant in the limit of large $\dot{N}$ while the classical WHS model may be more appropriate in the limit of small to moderate $\dot{N}$ (relative to $V_l$) \cite{197}. 
CHAPTER 11

Eutectic Solidification in Al-Ge

The focus of this chapter is on irregular eutectic solidification, in which one of the two phases is faceted ($\Delta S_m \geq 2$) and grows with significant kinetic undercooling. Eutectics between semiconductors and metals typically fall into this class. It is generally well established that in such systems the solid-liquid interface is non-isothermal, and the eutectic spacing is non-periodic (see section 3.4.2 and Figs. 3.9 and 11.1). While great insights have been gained into the structure and crystallography of irregular eutectics, their interfacial dynamics have remained an enigma for the past 50 years.

Previous studies have been limited to “quench-and-look” experiments wherein a completely solid alloy sample is analyzed post mortem, such as the eutectic Al-Si alloy sample shown in Fig. 11.1(a) [92]. However, it is well known that the quenching needed to convert the liquid to solid can distort the morphology of the solid-liquid interface from that present during crystallization. To circumvent these challenges several researchers have investigated via optical microscopy the growth of transparent organic films sandwiched between two glass slides [56, 101, 130], such as that shown in Fig. 11.1(b). Yet many details of the microstructural evolution remain unclear because of the effects of the constraint imposed by the thin film on an inherently 3D phenomenon. Furthermore, the ability of organic materials to accurately mimic the growth process of faceted phases has not been ascertained, even though they may share a similar $\Delta S_m$ [200].
Figure 11.1. Comparison of irregular eutectic growth morphologies. (a) Quenched growth front of an Al-12.7wt%Si eutectic, where an envelope of Al encloses the faceted Si crystals [92]. According to Hellawell, this metallic “skin” could not have been present at temperature and must have formed during the quench [92]. (b) Growth front of a eutectic mixture of borneol (faceted minor constituent) and succinonitrile [104] (see also Fig. 3.9(d)). (c) Growth front of an Al-51.6wt%Ge, this work [200]. The solid-liquid interfaces in (c) share some semblance to that of (a) in that a volume of melt is trapped between highly branched plates of Ge (orange) [200].

Figure 11.2. Two competing viewpoints of textural development during irregular eutectic growth: (a) the “re-nucleation” hypothesis [150], whereby “islands” of the nonfaceted phase (e.g., Al) are repeatedly nucleated on the faceted phase (e.g., Ge); (b) the Fisher-Kurz [56] picture (see also Fig. 3.9(d)), supported by Hellawell and coworkers [92], in which the nonfaceted phase advances continuously across the exposed facets.
Thus, it is no surprise that the growth morphology of an irregular eutectic is still not altogether settled. There have been two schools of thought, the first of which is the “re-nucleation” hypothesis and the other is the Kurz-Fisher model. According to the “re-nucleation” hypothesis proposed by Hogan and coworkers [150], the non-faceted phase may nucleate heterogeneously and repeatedly on exposed surfaces of the faceted flakes, as shown in Fig. 11.2(a). According to these authors, the “re-nucleation” of grains accounts for the observed polycrystallinity of the non-faceted phase in irregular eutectic alloys [96, 120, 202]. In contrast to this picture is the model proposed by Fisher and Kurz [56] and supported by Hellawell and coworkers [92], see Fig. 11.2(b). According to the Fisher-Kurz model, the nonfaceted phase advances continuously across the exposed facets (see also the discussion in section 3.4.2). The question therefore arises of whether epitaxial nonfaceted-faceted relationships develop during nucleation (i.e., the re-nucleation hypothesis) or during growth (i.e., the Kurz-Fisher model).

To shed light on the growth mode of irregular eutectics, we investigate via XRT the growth process in Al-Ge alloys of eutectic composition (51.6wt%Ge, dataset #4 in Table 4.2). In the experiment, we cool a 1 mm diameter rod sample from above the eutectic temperature (420 °C) to 3 °C below. The sample is held at this temperature isothermally while X-ray projections are recorded continuously. The minimal “driving force” or undercooling of 3 °C ensures that we can temporally and spatially resolve the interfacial dynamics [200]. We reconstruct the resulting dataset using the TIMBIR approach (section 5.1.2) which offers clear gains in the reconstruction quality over the conventionally used Gridrec algorithm [144] (Fig. 5.8). Due to the excellent interphase contrast

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1 The subject matter of this chapter is adapted in part from Ref. [200] by A. J. Shahani and coworkers.
between Al and Ge, as shown in Fig. 11.3, segmentation is relatively straightforward: we use a combination of morphological filters [190] to trinarize the grayscale dataset into Al, Ge, and liquid phases. In evaluating the segmented images, we note that they are able to reproduce the nominal volume fractions of Al and Ge in the fully-solidified alloy (see Fig. 6.8). The 2D images are then combined to reveal the 3D volumes.
11.1. Analysis of Reconstructions

Fig. 11.4(a) gives a snapshot of the full region-of-interest at 180 seconds after the start of solidification. Shown are Ge in orange, Al in white, the melt in dark blue, and the oxide skin in translucent-gray. One eutectic colony is boxed and isolated for subsequent analysis. By definition, a “colony” refers to the portion of the microstructure that nucleated at a single site [70]. The front (0°), back (180°), and side (90°) snapshots of this eutectic colony are displayed in Figs. 11.4(b-d). The outline of the colony is rectangular, indicating that the anisotropy of the faceted phase is an important factor during the growth process. Interestingly, the faceted Ge lamellae may be arranged in a regular pattern, see the arrow in Fig. 11.4(d), anomalous for an irregular eutectic alloy. Structural regularity is discussed in section 11.3. In general, the side profile (Fig. 11.4(d)) resembles that of the Kurz-Fisher model [56] (Fig. 11.1(b)) in that a volume of liquid is trapped between highly branched plates of Ge that extend deeper into the melt. On the other hand, the front and back views in Figs. 11.4(b-c) appear to support the “re-nucleation” hypothesis [150], wherein pockets of Al cover the exposed Ge surfaces. We reconcile these two competing viewpoints by tracking the growth of the eutectic colony in 4D [200].

Fig. 11.5 shows the morphology of the eutectic colony at five representative time-steps during the growth process. As each time-step, we view the colony from its front (0°), back (180°), and side (90°), as before. While plates of Ge are evident at the earlier stages of growth, bulbous-like domains of Al envelope its surfaces at longer times. One might suppose that these bulbs of Al impede the growth of the colony in the lateral (horizontal) direction, since the Ge crystals cannot grow through the solid metal layer. However, even before the emergence of the outermost bulbs of Al, the colony is unable to extend laterally.
Figure 11.4. Irregular eutectic microstructures across length scales. (a) Snapshot of the full tomographic region-of-interest during the growth process, where Ge is orange, Al is white, and the melt is blue. One eutectic colony is boxed and isolated for subsequent 3D imaging. (b-d) The front (0°), back (180°), and side (90°) views of this eutectic colony. The yellow arrow in (d) points to a region of high structural regularity, wherein the Ge lamellae are nearly parallel. The front and back views (b-c) suggest that pockets of Al cover the exposed Ge surfaces. (e) In some cases, defects cause holes or gaps within the Ge plates; then, the Al can grow through these holes and spread across the Ge {111} facets [200].
Figure 11.5. Morphology of the eutectic colony at (a) 100, (b) 140, (c) 180, (d) 220, and (e) 260 seconds after the start of growth. Shown are the front (0°), back (180°), and side (90°) views of the eutectic colony per time-step. The arrow in (d) points to another eutectic colony that impinges upon the one of interest. When viewed from either the front or the back, the interfacial morphology is markedly different from that predicted by Fisher and Kurz [56]: bulbs of Al envelope the surfaces of Ge, perhaps reminiscent of the “re-nucleation” hypothesis (Fig. 11.2(a)) [200].
In fact, throughout the growth process, interfacial velocities are roughly ten times lower in the lateral direction compared to the transverse (vertical), see Fig. 11.6. Velocities are measured at several points along the lateral and transverse directions of the colony, and the average velocities along both directions are plotted in Fig. 11.6(a). Any nonzero growth rate in the lateral direction at long times may be due to the growth and coarsening of the outermost Al bulbs, since the Ge plates do not become any thicker [200].
11.2. Interplanar Twin-Mediated Growth

The above trends can be rationalized by considering the critical role of defects during irregular eutectic solidification. Both Si and Ge have relatively low stacking fault energies [4, 11], and are thus expected to twin frequently. For instance, when viewed from the front, plates of Ge that run parallel to the transverse axis are filled with holes or gaps; according to the growth accident hypothesis [26, 31, 32, 72], these defects may result from errors in the stacking sequence of \{111\} planes. Note that the holes are not artifacts arising from the segmentation procedure. Upon visual inspection, the 3D microstructure in the vicinity of a given hole defect is indeed consistent with the grayscale reconstructions, see Fig. 11.7. Furthermore, our 3D reconstruction of the Ge phase (Fig. 11.8) bears some similarity to the optical micrograph of the extracted Si flake from Hellawell [92]; both images show that the faceted phase is filled with holes, because, as Hellawell notes, the faceted plates “contain multiple twin traces” [92]. Thus, our in situ results prove that the holes visible in Hellawell’s image (Fig. 11.8(b)) are not a result of the chemical etching required to isolate the Si flake, but are due to the structure within the plates themselves.

As a result of this interplanar twin defect, the kinetically mobile metallic phase can then grow through these holes and spread across the \{111\} facets. An example is shown in Fig. 11.4(e), in which Al makes it way through a hole in Ge \{111\}. An important distinction between the “re-nucleation” hypothesis [150] and our results is that the metallic phase is not nucleating on the plates; rather, the metal emerges from holes within the plates. The contact angle at the trijunction between the Al-Ge-liquid phases is greater than 0°, and thus the Al spreads across the Ge plates as isolated domains. This defect-mediated
growth mechanism is responsible for the bulbs of Al that cover the exposed Ge surfaces, when the colony is viewed from the front (Figs. 11.4(b) and 11.5) [200].

11.3. Intraplanar Twin-Mediated Growth

Defects also lead to the formation of complex regular crystals, in which parallel lamellae connect to a common spine. Such geometrical structures have been documented in Si, Ge, and Bi, see the work by Refs. [40, 46, 53, 91, 92, 165]. In particular, according to Hellawell’s “double twin” model, a \{100\} spine is related to \{111\} lamellae by twinning across axial and non-axial \{111\} planes, thereby producing an angle of 62.5° between lamellae and spine [46, 91, 92]. These twinning relationships are conveyed on a \langle 110 \rangle
Figure 11.8. (a) Front view of the eutectic colony, showing the Ge phase in orange. The gaps or holes indicate frequent twinning events within the Ge plate [200]. (b) Extracted eutectic Si flake, from Hellawell [92], showing multiple twin traces. Holes are indicated with an orange outline.

stereographic projection in Fig. 11.9(a). Evidence for twinning comes from optical metallography, in which cusps are observed where the lamellae join the interconnecting spine, as pointed out by Hellawell in Fig. 11.9(b) [46, 91, 92]. It follows that the periodicity of the lamellae is set by the spacing of the twins along the {100} spine.

In this work, we measure the angle between lamellae and transverse spine as 61.4±1.7°, see Fig. 11.10, which agrees well with Hellawell’s model (Fig. 11.9(a)). Note that the angular relationship between {100} and {111} in a perfect and singly-twinned crystal is 54° and 70°, respectively. Our result matches neither of these orientation relationships. Instead, the indexed {100} spine and {111} lamellae in Fig. 11.10(b) are related by double
“Double Twinning” Model
Hellawell (1968)

Figure 11.9. (a) Hellawell’s double twin model [46, 91, 92]: twinning about axial (#1) and non-axial (#2) \{111\} planes can produce a \{100\} spine, the trace of which makes an angle of approx. 63° with untwinned \{111\} lamellae. Twinning relationships are plotted on a \langle110\rangle projection, where blue, green, and yellow poles represent the untwinned, first twinned, and second twinned configuration [91]. (b) Metallographic evidence for twinning comes from cusps where lamellae join the spine [46, 91, 92].

twinning events between the lamellae and spine. Since individual lamellae are planar and run the length of the spine, as shown in Fig. 11.11, the \{100\} spine itself is likely defect-free. This is in contrast to the \{111\} plates discussed in section 11.2, which are filled with hole defects. Worth noting is that the lamellae too are untwinned within the plate, as confirmed in back-reflection Laue photographs [91]. Because there is no such growth advantage for the lamellae, the metal overgrows and eventually engulfs the faceted phase. For this reason, we see bulbs of Al cap the lamellae on the back side of the colony (Figs. 11.4(c) and 11.5). The sluggish kinetics of the faceted lamellae at early times,
Figure 11.10. (a) Distribution of lamella-spine angles, with mean angle of 61.4 ± 0.7°. This matches Hellawell’s double-twin model [46, 91, 92]. (b) Back side of eutectic colony, showing Ge phase in orange. The junction between \{111\} lamellae and \{100\} spine is indicated [200].

together with the Al bulbs impeding growth at later times, explain why the colony is unable to extend laterally throughout the growth process (Fig. 11.6).

The above insights suggest that twinning leads to holes within Ge plates (section 11.2), as well as branching events between Ge plates (section 11.3) [200]. These two defect-mediated growth mechanisms are summarized in Figs. 11.8 and 11.11. In both cases, defects bring about the “decoupling” of the Al and Ge phases at the growth front, such that steady-state growth can no longer be maintained. When this occurs, the metallic phase precedes the faceted phase. Only when two or more twin planes are parallel to the growth direction, as in the twin-plane re-entrant edge (TPRE) mechanism [85, 237], are the interfaces sufficiently mobile that cooperative growth is possible and the Fisher-Kurz model [56] is valid. Using this logic, we expect that the Ge plates grow rapidly in the
Figure 11.11. (a) Side view of the eutectic colony, showing the Ge phase in orange. (b-d) Three views of a single, regularly-arranged lamella (see yellow outline in (a)). Since the lamella is planar and runs the length of the spine, the \{100\} spine itself is likely defect-free. Any “roughness” in the plane of the lamella is due to small segmentation errors [200]. (e) Comparison to the complex regular structure documented by Elliott [53].

transverse direction compared to the lateral (Fig. 11.6) because the tips of the transverse plates contain several twins that give rise to the TPRE mechanism [200].
CHAPTER 12

Conclusions

The coarsening and solidification behaviors of highly anisotropic systems have been investigated via 4D XRT. Such investigations are finally possible due to major strides in data sampling and reconstruction, computer hardware and storage, and algorithms for processing Big Data in a massively parallel environment. The growing size of data collected during the experiments renders manual processing and analysis impractical. For these reasons, we have developed a suite of algorithms for reconstruction, segmentation, and microstructural characterization [82, 196, 198]. In the cases presented below, the interfacial dynamics were assessed by measuring in 4D the evolution of local curvatures, velocities, and orientations along the solid-liquid interfaces. A summary of the coarsening results is given first, followed by a summary of the solidification results.

12.1. Coarsening Experiments

4D XRT experiments were performed ex situ on an Al-29.9wt%Si alloy during coarsening, when the sample was held isothermally in the solid-liquid regime [198]. While the morphology of the primary Si particles is faceted, the morphologies at later times are less faceted and more isotropic. This suggests that the structures are not evolving in a self-similar manner, as quantitatively confirmed in the ISDs and the INDs. However, we still observe that the system-average length-scale $S_v^{-1}$ varies with time $t$ as $t^{1/3}$. More specifically, the Si particles are not evolving towards their equilibrium Wulff shape, a
tetrakaidecahedron dominated by \{111\} habit planes. Instead, the particle edges more rapidly due to the prevalence of defects, and eventually overgrow the relatively immobile \{111\} faces. The defect structure of the Si particles has been confirmed via EBSD [198]. In addition, higher resolution orientation mapping via plasma focused ion beam on the as-coarsened samples is well underway at Carnegie Mellon University.

Somewhat analogously, the coarsening process of Si particles in an Al-32wt\%Si-15wt\%Cu alloy has been imaged via \textit{in situ} 4D XRT [199]. By supplementing our XRT data with CALPHAD modelling and AIMD simulation, we find that the Cu constituent does not influence appreciably the coarsening rate constant nor the diffusion mobilities in the liquid phase (compared to the above binary Al-29.9wt\%Si alloy). Furthermore, the morphological evolution of fully-faceted Si particles away from their equilibrium Wulff shape observed in this \textit{in situ} investigation is qualitatively similar to that seen in the above \textit{ex situ} study, suggesting that thermal cycling has negligible influence on the coarsening dynamics. The highly time-resolved nature of this \textit{in situ} investigation is also beneficial for uncovering the dynamics of microstructural singularities, \textit{e.g.}, the junction between rough and smooth interfaces [199]. We find that step flow may be “pinned” at this junction due to impurities adsorbed on the facets.

### 12.2. Solidification Experiments

From the coarsening studies, we have determined that defects are central to the microstructural evolution. However, the morphology of the twinned interface during growth has remained a mystery due to the lack of 4D experiments. Thus, we probe the free growth of Si particles in alloys of composition Al-32wt\%Si-15wt\%Cu [197]. Our 4D data
collected *via in situ* XRT has made it possible to quantify the local velocities and crystallographic orientations of the solid-liquid interfaces during growth. Our results show, unambiguously, that the concave, type I re-entrant groove does not disappear during the continuous propagation of a doubly twinned interface, consistent with the classical mechanism proposed by Wagner, Hamilton and Seidensticker [85, 237] over 50 years ago. Such growth morphologies are attainable when the nucleation rate at the type I re-entrant groove is comparable to the lateral growth of layers so initiated [197]. The successful characterization of a twinned interface during solidification is a major accomplishment of this work. To the best of our knowledge, this is the first time that time-dependent crystallographic information has been extracted from 4D XRT; the novel experiment and analysis method provide a unique vision into the growth behavior of polycrystalline materials.

We have also examined the solidification process of irregular eutectic alloys of composition Al-51.6wt%Ge. Similar to Si, Ge has a relatively high entropy of fusion ($\Delta S_m \approx 3$) and a relatively low stacking fault energy. Through our time-resolved XRT experiments, we have resolved a longstanding controversy in the field and demonstrate that none of the existing models [56, 137, 150] are fully adequate for describing the rich variety of anisotropic patterns that arise during crystallization. In particular, we find that frequent twinning contributes to holes within Ge plates, as well as branching events between Ge plates [200]. In both cases, the twin defects lead to the decoupling of the Al and Ge at the growth front, such that the metallic phase precedes the faceted phase and steady-state growth can no longer be maintained [200]. These experimental results identify a new mechanism for the growth of an irregular eutectic microstructure.
As can be seen from this work, the characterization of increasingly complex microstructures will lead to the validation of increasingly complex models. In particular, our 4D characterization of highly faceted materials allows for the critically needed testing of phase field methods (in a manner similar to Ref. [2]) that incorporate anisotropy in the interfacial mobility and the interfacial free energy. In addition, it is possible to use the experimental results not only as benchmark data but also as initial conditions for the phase field simulations. The coupling of experimental and simulation methods will enable progress in solving some of the most challenging problems in microstructural evolution, thereby impacting our ability to predict underlying materials behavior in engineered systems.
References


