In Situ Studies of Pattern Formation and Evolution In Complex, Multi-Phase Alloys

by

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For my beloved family and friends who support me every day

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ABSTRACT

This dissertation delves into the growth and coarsening of three-phase eutectics and off-peritectics, employing $A1-Ag_2A1-A_12Cu$ and $Zn-AgZn_3$ alloys as representative systems. The investigation seeks a comprehensive understanding of pattern formation, exploring the interplay among local composition, crystalline anisotropy, and growth velocity. Through state-of-the-art experimental methods, the study conducts a thorough microstructural analysis during solidification and coarsening, leveraging recent advancements in X-ray transmission microscopy and machine learning tools.

The research provides new insights into the four-dimensional $(i.e.,$ three-dimensional space- and time-resolved) morphological and crystallographic evolution of these materials. The outcomes lay the foundation for theoretical development and refinement, offering, e.g., real-time perspectives on the formation of a three-phase eutectic microstructure along the surface of a primary phase; a 4D view of the morphological and crystallographic evolution of three-phase eutectic; and in situ observations of the directional solidification of a metallic off-peritectic alloy.

Broadly, these studies bring to light the importance of growth competition in shaping multi-phase patterns. For example, we observed *pseudo-2D* dendritic 'finger' formations on primary Al_2Cu rods due to local microsegregation of Al and Ag, in turn influencing pattern formation in the Al-Ag-Cu eutectic. Similar effects were found in $Zn-AgZn₃$ alloys, leading to a distinct partially banded morphology. Crystallographic anisotropy also played a significant role in pattern formation and evolution, with primary $\rm Al_2Cu$ rods dominating the surrounding morphology and crystallography of the Al-Ag-Cu eutectic. Likewise, the interplay of multiple phases and their associated phase-interfaces led to a remarkable complexity in the patterns that formed. Take for instance the Al-Al₂Cu and Ag₂Al-Al₂Cu interphase boundaries, which influenced eutectic morphology and suppressed the coarsening rate of Ag_2Al . Additionally, our work highlights the impact of alloy composition and growth conditions on pattern stability, demonstrated by a composition-velocity eutectic stability field for the Al-Ag-Cu ternary system. In directionally solidified $Zn-AgZn₃$, the solidification time emerged as a critical parameter influencing pattern selection, particularly with reference to solid-state coarsening of primary $AgZn₃$ columns, which eliminated trapped liquid channels within which the peritectic could nucleate and grow.

By focusing on the model alloy systems of $A1-Ag_2A1-Ag_2Cu$ and $Zn-AgZn_3$, this dissertation aims to advance our understanding of pattern formation and evolution in three-phase eutectics and off-peritectic materials. The insights gained may hold potential implications for the manufacture of natural composite materials with various commercial and industrial applications.

Part I

Motivation and Background

CHAPTER I

Introduction

1.1 Natural multi-phase materials

One of the pivotal intellectual advancements in human history was our ability to extract and alloy metals, enhancing their properties. This is evident in how historians and anthropologists categorize distinct eras, such as the Bronze Age and the Iron Age [\[25,](#page-274-0) [26\]](#page-274-1). Through experimentation, we crafted alloys that were both stronger and more easily manufacturable than pure elemental metals [\[27\]](#page-274-2). Microscopy revealed the microstructural hierarchy of these alloys, with metals composed of grains, which are large clusters of specifically oriented atoms [\[25,](#page-274-0) [28\]](#page-274-3). Furthermore, the images showed multiple phases in many widely used metal alloys, such as brass, steel, bronze, debased silver, pewter, cast iron, and others [\[25\]](#page-274-0).

Within this rich history, eutectic alloys stand out as a prominent class of multiphase materials, utilized since antiquity. The term 'eutectic' derives from the Greek $ευ$ -(eû), meaning 'well,' and $τηξις$ (têxis), meaning 'melting' [\[29\]](#page-274-4). These alloys, formed by the fusion of two or more components, solidify into discrete phases from a pure liquid, displaying minimal freezing ranges at low melting temperatures [\[30,](#page-274-5) [31\]](#page-274-6). Examples such as Fe-C [\[32\]](#page-274-7), Al-Si [\[33\]](#page-274-8), Pb-Sn [\[34\]](#page-274-9), Cu-Sn [\[35\]](#page-274-10), and Sn-Ag-Cu [\[36\]](#page-274-11) are particularly suitable for casting and soldering applications. The naturally complex and often periodic microstructural patterns of eutectic alloys contribute to unique electrical, optical, magnetic, and mechanical properties, resembling those found in engineered composite materials [\[37\]](#page-274-12). The correlation between patterns and properties motivates us to explore higher-order three-phase eutectic alloys [\[38\]](#page-274-13).

Likewise, peritectics represent another fascinating category of natural composite materials. They arise from the reaction between a liquid and primary solid phase to yield a secondary or peritectic solid phase [\[30\]](#page-274-5). The Greek prefix $\pi \epsilon \rho_l$ -(per), conveying 'about' or 'around,' offers insight into this process as the secondary phase is thought to nucleate along the surfaces of primary grains at the solid-liquid interface [\[39\]](#page-275-0). This process creates a skin around the primary crystals, often arresting the consumption of the grain and yielding a distinctive two-phase morphology [\[40\]](#page-275-1). In contrast to eutectics, where solid phases share comparable melting temperatures and exchange constituents in the liquid, the primary phase in a peritectic reaction may have a melting temperature well above the peritectic temperature. Additionally, the peritectic and primary phases reject the same component into the liquid (*i.e.*, there is no cooperation between them). Finally, the primary phase is frequently an intermetallic with favorable strength properties inherited by the two-phase alloy [\[40\]](#page-275-1). Paired with the typically ductile peritectic phase, these materials often exhibit strength and durability [\[41\]](#page-275-2).

The mechanisms through which eutectic and peritectic alloys develop their unique morphologies, and by extension their desirable properties, is a topic of scientific research [\[42,](#page-275-3) [43\]](#page-275-4). Theoretical and experimental research has illustrated the driving forces that contribute to the formation of their morphologies [\[40,](#page-275-1) [44,](#page-275-5) [45\]](#page-275-6) and the kinetics that determine the growth process [\[46,](#page-275-7) [47\]](#page-275-8). Preliminary studies employed postmortem two-dimensional optical microscopy to characterize the eutectic and peritectic alloy microstructures, extrapolating formation pathways by systematically altering the growth parameters in directional solidification $[48-50]$ $[48-50]$. In situ characterization on transparent organic systems also provided insight into the coupled relationships during solidification, used to develop generalized growth models [\[45,](#page-275-6) [51–](#page-275-11)[55\]](#page-276-0). More recently, X-ray imaging provides the capabilities to observe dynamic behavior, such as solidification, in opaque, metallic materials in real-time and in three-dimensions [\[17,](#page-273-5) [56](#page-276-1)[–59\]](#page-276-2). In parallel, advancements in artificial intelligence and machine learning tools [\[60\]](#page-276-3) open the door to using big data analysis techniques in the field of solidification and processing science.

In this dissertation, we harness the contemporary advancements in characterization and computation to visualize, reconstruct, and analyze the solidification and coarsening dynamics of three-phase eutectic and two-phase peritectic metallic systems, in unprecedented detail. To my knowledge, this is the first experimental measurement and characterization of dynamics of three-phase eutectic growth about a primary phase and the morphological and crystallographic evolution at sub-micrometer resolution of a three-phase eutectic during annealing.

1.2 Dissertation Outline

This dissertation is structured into three parts, spanning ten chapters. The initial part, encompassing chapters 1-4, offers an in-depth exploration of classical theories pertaining to eutectic and peritectic solidification and coarsening. Serving as a foundational framework, this section lays the groundwork for the subsequent discussions in the dissertation. The following two chapters delve into the various characterization and experimental techniques employed to capture materials solidification and solidstate evolution, followed by an exploration of the computational and analytical tools used to process the results.

Part II, comprising chapters 5-8, elaborates on specific questions, experiments, and computational methods employed in this work. These chapters include manuscripts that have undergone peer review and one submitted for publication, representing the substantial portion of my research tenure at the University of Michigan from 2018 to 2024.

In Part III (chapters 9-10), we present the conclusions of this dissertation, accompanied by perspectives on opportunities for future scientific inquiry. A bibliography is included at the end of Part III.
CHAPTER II

Formation and Evolution of Eutectics and **Peritectics**

2.1 Background

The eutectic point is the composition, among two or more elements, with the lowest melting temperature [\[30,](#page-274-0) [31\]](#page-274-1). Eutectic materials exhibit alternating patterns of multiple phases upon solidification, resulting in composite-like mechanical and electrical properties [\[37,](#page-274-2) [61\]](#page-276-0). This characteristic makes them advantageous for engineered materials in cast parts. The periodicity, length-scales, and morphologies are significantly influenced by the solidification pathways [\[49,](#page-275-0) [62\]](#page-276-1). Understanding how eutectic patterns form from a liquid state is crucial for optimizing their use in technologically relevant materials. Below, we explore the theory and experimental background of two- and three-phase eutectic alloys, covering their formation, growth, and subsequent evolution upon annealing in the solid-state.

As mentioned earlier, the eutectic point, is characterized by the eutectic temperature (T_e) , where a liquid of the eutectic composition (C_e) transforms into multiple solid phases (a reference binary eutectic phase diagram is shown in Fig. [2.1\)](#page-38-0). However, if a liquid of composition C_e is held at a constant temperature of T_e , it would take an infinite amount of time to form a solid eutectic microstructure. To initiate this phase transition, a driving force is essential. This driving force is the *under*cooling (ΔT) , representing the amount by which a liquid cools below its freezing point without solidifying. In eutectic alloys, lateral solute transport through diffusion plays a critical role in determining the required undercooling for solidification and the resulting microstructure [\[3,](#page-272-0) [63\]](#page-276-2).

In addition to diffusion, steady-state eutectic growth is governed by interface atom attachment kinetics and the volume fraction of the component phases. Metallic systems exhibit rapid interface kinetics, whereas in semiconductors and ceramics, atomic attachment is slow and can be rate-limiting [\[3,](#page-272-0) [63\]](#page-276-2). An effective criterion for predicting the interphase morphology of a specific phase is the dimensionless 'alpha factor,' introduced by Jackson in 1958 [\[2\]](#page-272-1). Within eutectic alloys, the alpha factor, denoted as α , classifies the regularity or periodicity of morphological features into two categories: 'regular' or 'irregular.' α is defined as the ratio $\zeta \Delta S_f/R$, where ζ is a crystallographic factor, ΔS_f is the entropy of fusion of one of the eutectic solids, and R is the universal gas constant. Regular eutectic alloys (e.g., rod or lamellar morphologies, based on volume fraction) often exhibit $\alpha < 2$ with a microscopically rough solid/liquid interface at the atomic scale. In contrast, irregular eutectic alloys (e.g., branched or plated structures, based on volume fraction) typically display $\alpha > 2$ and a faceted solid/liquid interface at the microscopic scale [\[3\]](#page-272-0). A graphical representation of eutectics and their classification is shown in Fig. [2.2.](#page-40-0)

As previously mentioned, the volume fraction of the solid phases can heavily influence the eutectic morphology. Regular eutectics may undergo lamellar-to-rod or rod-to-lamellar transitions as the volume fraction varies (see, e.g., Fig. 8 in Ref. [\[17\]](#page-273-0)). These changes become thermodynamically favorable when the stored free energy density (associated with the solid-solid interfaces) can be reduced by altering morphology. For a given eutectic pattern, there exists a critical free energy where these changes occur. In turn, the relationship between free energy and volume fraction means that

Figure 2.1:

Binary eutectic phase diagram: This schematic illustrates a binary phase diagram depicting the thermodynamic conditions that result in a twophase eutectic composed of α and β phases. The eutectic transformation occurs at a specific temperature (T_e) and composition (C_e) . The diagram includes the key interfacial compositions (assuming local equilibrium at low solutal Peclet numbers [\[1\]](#page-272-2), as well as key temperatures such as the solutal temperature (T_C) and capillary temperature (T_R) .

there exists a critical volume fraction wherein the eutectic will undergo these transitions. For a eutectic composed of a square array of β rods in a α matrix, the system will undergo a rod-to-lamellar transition when β reaches above a critical volume fraction of $1/\pi \approx 0.32$ [\[64\]](#page-276-3). A hexagonal lattice rod array will undergo a transition above a critical volume fraction of $\sqrt{3}/2\pi \approx 0.28$ [\[64\]](#page-276-3). More recent extensions also account for regions in which lamellae and rods may coexist [\[55,](#page-276-4) [65\]](#page-277-0). Chao et al. observed the a lamerllar-to-rod transition in an Al-Al2Cu eutectic alloy initiated by thermo-solutal convection of impurities ahead of the growth front [\[17\]](#page-273-0). The impurities triggered local phase fraction changes which led to the formation of a long-wavelength instability (eutectic cells) as well as a co-planar lamellar-to-rod transition.

2.2 Growth of two-phase eutectics

2.2.1 Eutectic initiation

The initial stages of the eutectic reaction are controlled by heterogeneous nucleation on foreign particles in the liquid, on the mould wall, or of one eutectic phase on another [\[66\]](#page-277-1). Eutectic nucleation are generally understood to be a non-reciprocal heterogeneous process wherein one phase, α , is an efficient catalyst for the nucleation of a secondary phase, β , but not the converse, in a two-phase $\alpha - \beta$ eutectic [\[67\]](#page-277-2). The nucleating phase generally displays a more complex crystal structure, higher entropy of melting, and a higher melting point. Non-reciprocal nucleation has been observed in several different systems [\[68–](#page-277-3)[72\]](#page-277-4).

Within a hyper- or hypo-eutectic alloy compositions, the formation of primary phase dendrites or rods often act as heterogeneous nucleation sites from which eutectic grains originate. Lemaignan [\[4\]](#page-272-3) hypothesized that following the initial nucleation of the secondary eutectic phase on the primary phase substrate, the former would grow laterally across the primary surface. As shown in Fig [2.3](#page-41-0) A, eventually diffu-

Regular and irregular eutectic morphologies: Utilizing the volume fraction and dimensionless 'alpha factor' outlined by Jackson in Ref. [\[2\]](#page-272-1), different eutectic morphologies in a binary alloy can be categorized. Adapted from Ref. [\[3\]](#page-272-0).

Schematics of eutectic initiation: \bf{A}) shows Lemaignan's model [\[4\]](#page-272-3) for eutectic nucleation on a primary surface. B) shows the invasion process as described by Akamatsu et al [\[5\]](#page-272-4) in which a primary phase penetrates through the lamina of the secondary phase before spreading laterally across the surface. Both schematics were were retrieved from their original publications with permission.

sion field destabilize the flattened radial structure, transforming it into a pseudo-2D dendritic shape with branching primary and secondary arms. Upon reaching a critical undercooling, the secondary arm spacing is sufficient for coupled eutectic growth perpendicular to the primary surface. Here, the primary phase extends from the substrate to form an alternating, regular eutectic pattern.

More recently, Akamatsu *et al.* [\[5\]](#page-272-4), while studying a directionally solidified CBr_2 - C_2Cl_6 transparent eutectic, showed the initial stages of nucleation involved the secondary phase spreading along the primary phase surface. At distinct points, such as grain boundaries, the primary phase was seen penetrating through the outer layer before spreading across the outer most surface. This process, which they dubbed 'invasion', may repeat several times (see Fig [2.3](#page-41-0) B). Finally, coupled eutectic growth occurs when morphological instabilities form on the final invasive layer.

Serefoğlu et al. [\[73\]](#page-277-5) has since added to our understanding of the single layer

'invasion' model described above by evidencing heterogeneous nucleation of a coupled eutectic grain along a primary surface. The eutectic grains, which displayed a more radial spread than reported by Akamatsu *et al.* [\[5\]](#page-272-4), formed at grain boundaries through either seeded growth or nucleation along the grooves; they also appeared from morphological instability of the primary phase, and from random heterogeneous nucleation on the primary surface. Serefo $\breve{\text{gl}}$ u et al. hypothesized the absence of singlephase 'invasion' may be due to differences in sample geometry and initial conditions.

2.2.2 Regular eutectic growth and Jackson-Hunt model

In a steady-state thermal environment with fixed isotherms, featuring an isothermal, planar solid/liquid interface growing unidirectionally at a constant velocity where interface kinetics and thermal conductivity are fast (i.e., the growth velocity, V , and Peclet number, P_e , are small), eutectic undercooling is controlled by solute and capillary driving forces [\[3\]](#page-272-0). In this scenario, following eutectic nucleation, a two-phase lamellar structure, composed of α and β phases, can form (Fig. [2.4\)](#page-43-0). These phases cooperatively grow, establishing a symbiotic relationship where rejected material from one phase feeds the other and vice versa.

The lateral solute diffusion causes free energy gradients, creating a compressive force perpendicular to the α/β interface, reducing interlamellar spacing. As spacing decreases, the force to maintain mechanical equilibrium at the solid-solid-liquid trijunction (due to Young's law, see Fig. [2.4\)](#page-43-0) increases, leading to curvature changes in the solid-liquid interface. The specific interfacial free energy is defined as the reversible work required to create a new surface and is equal to the interfacial tension (*i.e.*, the force the system experiences to minimize surface energy) [\[3\]](#page-272-0). The forces that must be balanced at the trijunction include solid-solid interfacial free energy and solid-liquid interfacial free energies for both the α and β phases, determining the contact angles, $\theta_{\alpha,\beta}$, of the α-liquid and β-liquid interfaces. Capillarity drives the

Two-phase eutectic lamellar growth front: A) Depiction of coupled growth in the lamellar two-phase eutectic during directional solidification under an imposed undercooling ΔT , with highlighted solute fluxes in white. **B**) Illustration of Young's law at the solid-solid-liquid trijunction.

eutectic to increase interlamellar spacing, thus reducing curvature [\[3\]](#page-272-0).

The competing forces of diffusion and capillary forces that determine the shape of the composite s/l interface was first descibed by Jackson and Hunt in their seminal 1966 paper [\[74\]](#page-277-6). They derived a master question that elucidated how these factors influence interlamellar spacing, growth velocity, and undercooling.

$$
\Delta T = \Delta T_r + \Delta T_c = \frac{K_r}{\lambda} + K_c V \lambda \tag{2.1}
$$

Here, ΔT_r represents capillary undercooling, ΔT_c the solute undercoolings, λ the interlamellar spacing, V the growth velocity, and K_r and K_c are material-specific parameters defined as:

$$
K_c = \frac{\overline{m}\Delta C}{2\pi D} \tag{2.2}
$$

$$
K_r = \frac{2(1-f)|m_\beta|\Gamma_\alpha \sin(\theta_\alpha) + 2f|m_\alpha|\Gamma_\beta \sin(\theta_\beta)}{f(1-f)(|m_\alpha| + |m_\beta|)}\tag{2.3}
$$

Here, $\overline{m} = \frac{|m_{\alpha}||m_{\beta}|}{|m_{\alpha}+|m_{\beta}|}$ $\frac{|m_{\alpha}| |m_{\beta}|}{|m_{\alpha}|+|m_{\beta}|}$, $|m_{\alpha}|$ and $|m_{\beta}|$ are the slopes of the liquidus lines for α and β , ΔC is the concentration difference between α and β (see Fig. [2.1\)](#page-38-0), D is the interdiffusivity, f is the volume fraction of the solid phases, Γ_{α} and Γ_{β} are the Gibbs-Thomson coefficients for the α and β phases, and θ_{α} and θ_{β} are the contact angles at the trijunction.

Looking at Eqn. [2.1,](#page-43-1) we see that ΔT is a function of the product, λV , and thus the one equation is insufficient to fully describe the eutectic growth behavior. Following the *maximum growth rate* model proposed by Zener [\[75\]](#page-277-7), Tiller [\[76\]](#page-277-8) applied it to directionally growth eutectics. In his proposal, the undercooling, which acts as the driving force, ΔG , for solidification (Sec. [2.1\)](#page-36-0), will be minimized at a constant growth rate when the system selects a specific interlamellar spacing. In addition, the eutectic spacing would not change so as to maintain this minimum undercooling extremum condition $(i.e., \left(\frac{\partial \Delta T}{\partial \lambda}\right)_V = 0 \rightarrow \left(\frac{\partial \Delta G}{\partial \lambda}\right)_V = 0)$. Tiller's model, though widely used in the literature, has been shown to be a slight oversimplification as it does not take into account fault motion through eutectic grains [\[74\]](#page-277-6). Instead, eutectic growth occurs near the minimum undercooling with slight fluctuations in spacing [\[77\]](#page-277-9). Nevertheless, Tiller's proposal still predicts eutectic growth with reasonable accuracy. In addition, the extremum condition reveals the additional relationship between the growth velocity and the interlamellar spacing,

$$
\lambda^2 V = \frac{K_r}{K_c} \tag{2.4}
$$

$$
\frac{\Delta T}{V^{1/2}} = 2(K_r K_c)^{1/2}
$$
\n(2.5)

$$
\Delta T \lambda = 2K_r \tag{2.6}
$$

Since the inception of the Jackson-Hunt (JH) theory of eutectic solidification, numerous researchers have contributed to its development [\[78–](#page-277-10)[81\]](#page-278-0). Noteworthy among these contributors are Magnin and Trivedi (MT), who extended the JH model for lamellar eutectic growth. Their work incorporated eutectic phase densities in the calculation of the diffusion field, leading to a more comprehensive understanding of the solidification process [\[79\]](#page-277-11). In addition to refining the model, they conducted an indepth analysis of the mechanical equilibrium at the three-phase triple junction during eutectic growth, which constrains the s/l interface. MT found that the triple junction movement controls the volume fractions and the solidifying phases, regulating their growth and providing a physical justification for the isothermal interface used by JH. MT also coupled the capillarity and solute undercoolings which provided a more general treatment than JH model. Another significant advancement was made by Trivedi, Magnin, and Kurz, who expanded the JH model to account for large undercooling associated with rapid solidification [\[78\]](#page-277-10).

It is important to note that not all eutectic show coupled growth. Some eutectics experience uncoupled or divorced growth wherein the eutectic phases evolve independently from one another. This can occur in nearly fully solidified systems where the fraction of remaining liquid is small enough that singular eutectic particles form between dendrites [\[82\]](#page-278-1). An additional example of uncoupled growth is found in spheroidal graphite-austenite eutectic $(i.e.,$ ductile iron). Here, primary austenite and/or primary graphite spheriods form in contact with the liquid. During solidification, the graphite may become encapsulated by an austenite shell prior to contact with primary austenite. Once the graphite is complete surrounded by solid austenite, growth continues through solid diffusion of carbon through the shell [\[32\]](#page-274-3).

2.2.3 Irregular eutectic growth and Kurz and Fisher model

In 1980, Kurz and Fisher expanded upon the Jackson-Hunt regular eutectic growth model to faceted/non-faceted irregular eutectic materials [\[83\]](#page-278-2). The faceted phase exhibits preferential anisotropic growth in low-energy directions determined by its solid/liquid equilibrium Wulff shape. While the minimum lamellar spacing extremum is thought to persist, the faceted phase hinders an easy decrease in interlamellar spacing as it is energetically unfavorable for atomic attachment along high-energy interfaces. This inherent stiffness results in diverging branches following set orientations. Consequently, the non-faceted solid-liquid interface becomes highly depressed due to solute build-up at its center. As the branches spread, growth undercooling ΔT_C increases because capillarity cannot compensate for extensive solute build-up, and the interface is no longer isothermal. Eventually, the solute build-up becomes catastrophic, causing faceted branches to form depressions and split into two. These newly formed branches usually diverge and undergo the same process. As branches reduce their distance, growth undercooling decreases toward the minimum extremum λ_e . However, the faceted nature of the phase impedes easy realignment, causing undercooling to increase again due to highly curved interfaces halting expansion and forming a termination. This phenomena is depicted in Fig. [2.5,](#page-47-0) demonstrating that irregular eutectic solidification permits a range of interphase spacings.

Kurz and Fisher also investigated the effect of thermal gradient during irregular eutectic growth which, along with the growth velocity, may be independently controlled in directional solidification [\[83\]](#page-278-2). When two branches diverge, it is assumed the intervening non-faceted matrix becomes depressed due to solute build up. Under high thermal gradients, the solid/liquid interface of the matrix phase becomes flattened. This leads to constitutional undercooling at the faceted interfaces, which in turn contribute to instability (i.e., branches are more susceptible to splitting) and results in an overall decrease in the maximum interlamellar spacing.

Figure 2.5: Two-phase irregular eutectic growth front: Schematic depicting the irregular growth of eutectic branches between a nonfaceted α phase and a faceted β phase. Crystalline anisotropy influences the preferential growth directions of β branches. A closer examination of each phase surface reveals the smoothness of β in contrast to the atomic-scale rough interface of α . This discrepancy arises from the higher attachment barrier required for specific planes in the β phase, limiting available sites. In contrast, attachment to α is largely independent of crystal orientation. Adapted with permission from Ref. [\[3\]](#page-272-0).

Recently, Shahani and colleagues [\[84\]](#page-278-3) used 4D X-ray tomography to study pattern formation in an irregular Al-Ge eutectic during solidification. They found that irregular eutectic growth exhibits a temporary 'decoupling' between faceted and non-faceted phases. Defects, such as twinning within the Ge plates, caused holes and branching events between them, disrupting steady-state growth. Slow lateral growth velocities resulted from sluggish interface kinetics of Ge. Consequently, the metallic phase could penetrate through gaps in Ge, engulfing the faceted phase. They observed that the Kurz and Fisher model for cooperative or 'coupled' growth was only applicable when two or more twin planes were parallel to the growth direction, aligning the higher mobility Ge interfaces.

Mohagheghi et al. [\[85\]](#page-278-4) built upon Shahani's [\[84\]](#page-278-3) research by examining how growth velocity impacts the transition from decoupled to coupled growth. During directional solidification of a transparent 2-amino-2-methyl-1,3-propanediol (AMPD) succinonitrile (SCN) eutectic, they observed a quasi-steady decoupled growth regime, where the faceted AMPD phase advanced ahead of a planar SCN front at low velocities. With increasing velocity, an unsteady regime featuring both coupled and decoupled growth emerged, accompanied by noncrystallographic branching and two-phased invasion events (see Sec [2.2.1\)](#page-39-0). As velocity further increased, nonfaceted/faceted two-phase fingers became prevalent in the solidification process, resulting in dendritic growth of SCN surrounded by a thin AMPD layer.

2.3 Three-phase eutectics

In recent years, the use of three- or multi-phase eutectic alloys in industrial applications has significantly increased [\[38\]](#page-274-4). Notable examples include the Sn-Ag-Cu three-phase eutectic alloy [\[36,](#page-274-5) [86,](#page-278-5) [87\]](#page-278-6), replacing Pb-based alloys for soldering, and the Al-Ni-Cr ternary system, offering improved yield strength and hardness compared to its binary Al-Ni and Al-Cr counterparts [\[88,](#page-278-7) [89\]](#page-278-8). A representative phase diagram for a three-phase eutectic forming system is shown in Fig. [2.6.](#page-50-0)

Within a system containing multiple components and phases, the chemical potential of each component must be identical in every phase at thermodynamic equilibrium. This fundamental principle gives rise to the Gibbs phase rule, which asserts that a system of C components and P phases in equilibrium has F degrees of freedom [\[30\]](#page-274-0). The relationship, assuming constant pressure and constant temperature, is

$$
F = C - P \tag{2.7}
$$

Thus, in order to solidify a three-phase eutectic microstructure, we need three components which would yield zero remaining degrees of freedom $(i.e.,$ nonvarient growth). If instead we considier one- or two-phase growth ina ternary system then $F > 0$.

While the nucleation and growth of two-phase eutectic systems are well understood, predicting the behavior of three-phase eutectics has proven more challenging. The primary obstacle is the additional degree of freedom imparted by the third chemical component. In addition, many thermophysical properties, such as the distribution coefficient (the ratio of solute in the solid compared to that in the liquid) and the liquidus slopes, treated as constant in the J-H model, now vary as a function of two compositional variables [\[90–](#page-278-9)[92\]](#page-278-10). Two-phase eutectic growth, formerly a nonvariant process, now becomes univariant, allowing for the formation of eutectic cells $(i.e.,$ the eutectic-liquid front is destabilized by the third component). Meanwhile, nonvariant solidification now involves three discrete solid phases that may (or may not) cooperatively grow. In this section, we provide background on three-phase eutectic solidification as well as two-phase eutectic solidification in a ternary alloy system. For an in depth review of multi-phase materials in multicomponent systems, see Ref. [\[38\]](#page-274-4).

Figure 2.6: Ternary eutectic phase diagram: Representative schematic of a ternary alloy composed of A, B, and C, which displays a three-phase eutectic of α , β , and γ .

2.3.1 Selection of growth forms

McCartney et al. were the first to attempt an expansion of Jackson and Hunt's model [\[74\]](#page-277-6) for regular two-phase eutectic growth and Burden and Hunt's model [\[93\]](#page-278-11) for dendrite formation to a three-phase eutectic system [\[6\]](#page-272-5). They began by categorizing the different possible morphologies that may form in a ternary alloy: single-phase planar and dendritic growth; two-phase planar, cellular, and dendritic structures; and a three-phase planar eutectic front. Through competitive growth theory (see also Sec. [2.4\)](#page-58-0), they determined the predominant microstructure as a function of the local composition C and the solidification parameters $(e.g.,$ velocity V and thermal gradient G). McCartney *et al.* developed a map that lays out the regions around the three-phase eutectic point where each morphology is stable (Fig. [2.7\)](#page-52-0), based on which has the minimum undercooling given $\{C, V, G\}$. The predicted growth interfaces are shown schematically in Fig. [2.8.](#page-53-0) They also tested their hypothesis against directional solidification experiments [\[20\]](#page-273-1).

2.3.2 Three-phase eutectic and its morphology

The exploration of wholly three-phase eutectic systems initially centered on characterizing their morphologies [\[7,](#page-272-6) [94–](#page-279-0)[97\]](#page-279-1). Researchers extensively investigated in directional solidification the impact of velocity [\[7,](#page-272-6) [20,](#page-273-1) [95,](#page-279-2) [98](#page-279-3)[–100\]](#page-279-4), thermal gradient [\[98,](#page-279-3) [100\]](#page-279-4), volume fraction [\[95,](#page-279-2) [101,](#page-279-5) [102\]](#page-279-6), interfacial anisotropy [\[102](#page-279-6)[–105\]](#page-280-0), and compositions [\[20,](#page-273-1) [95\]](#page-279-2). Himemiya and Umeda developed scaling laws (akin to JH equations, Eqn. [2.1\)](#page-43-1) to characterize three-phase eutectic growth assuming regular, rod+hexagonal, and semi-regular geometries [\[106\]](#page-280-1). They identified consistent scaling behavior in all three morphologies, aligning with the JH model: $\Delta T \propto$ √ V and $V \propto \lambda^{-2}$ (cf. Eqns. [2.4\)](#page-44-0). Data on the Sn-Pb-Cd and Al-Ag-Cu ternary systems revealed substantial agreement in their findings [\[106\]](#page-280-1).

In more recent studies, Steinmetz *et al.* utilized 3D phase field simulations to

Figure 2.8: Stable growth interfaces in ternary system: Microstructures as suggested by McCartney et al. [\[6\]](#page-272-5) based on minimum undercooling criterion. Each interface corresponds to a region labeled in Fig. [2.7.](#page-52-0) A) Two-phase eutectic columnar growth ahead of a planar three-phase eutectic (region 3); B). Planar interface of a three-phase eutectic (region 4); C). Planar interface of a two-phase eutectic (region 2); D). Single phase columnar growth ahead of a three-phase eutectic planer interface (region 5c); \bf{E}) Single phase column growing ahead of two-phase eutectic columns followed by planar three-phase eutectic (region 5b); and \bf{F}) Single phase columner growth ahead of a two-phase eutectic planar front (region 5a). Adapted with permission from Fig. 3 of [\[6\]](#page-272-5).

reproduce the emergence of three distinct morphologies present in the $A1-Ag_2A1$ $\rm Al_2Cu$ three-phase eutectic: chain-like, paw-structure with parallel Ag₂Al rods, and paw-structure with displaced Ag_2Al rods [\[103\]](#page-279-7). Their phase field model successfully captured all three morphologies. Notably, each pattern exhibited a distinct stability range linked to the lamellar spacing, again aligning with observations in the JH model.

Hötzer *et al.* [\[107\]](#page-280-2) investigated the effects of growth velocity on pattern formation in directionally solidified $Al-Ag_2Al-Al_2Cu$ using a combination of phase field simulations and experimental results. They found that phase fraction was heavily influenced by velocity, changing nearly immediately upon velocity change followed by subsequent pattern realignment. The regular chain-like pattern was very stable, despite phase fraction and velocity changes. Similar stability regimes were thought to exist for other patterns over a range of different growth velocities. The evolution of individual rods, through coalecence, splitting, overgrowth, and nucleation persisted despite the stability of the overall microstructural pattern.

Through further large-scale phase field simulations, Steinmetz *et al.* [\[108\]](#page-280-3) examined the effects of lamellar spacing on pattern morphology and stability in the $A1-Ag_2A1-A1_2Cu$ eutectic. They found that the undercooling-spacing relationship followed the JH model for all arrangements of phase in the microstructure. Additionally, all three patterns they investigated (chain-like and two different paw-structures) had stability regimes characterized by different initial lamellar spacings in which the initial pattern remained throughout directional solidification. Depending on the lamellar spacings, the pattern with the minimum undercooling changes $(i.e., a$ morphological transformation would occur upon changing spacing). By considering both the local phase arrangements and the changing minimum undercoolings, the presence of multiple patterns in a single simulated micrograph is understandable.

Experimental work further enriches our understanding of three-phase eutectic morphology, with a primary focus on the Al-Ag-Cu [\[7,](#page-272-6) [20,](#page-273-1) [97,](#page-279-1) [98,](#page-279-3) [107\]](#page-280-2), In-Bi-Sn

[\[109–](#page-280-4)[111\]](#page-280-5), and Sn-Ag-Cu [\[86,](#page-278-5) [87,](#page-278-6) [112\]](#page-280-6) systems. Within Al-Ag-Cu, Dennstedt and Ratke conducted a comprehensive characterization of morphologies, ranging from regular brick-like (chain-like) structures to more irregular formations [\[7\]](#page-272-6). Fig. [2.9](#page-56-0) shows some of the morphologies they reported. Their analysis involved computing shape factors (indicating the degree of circularity) for the $Ag₂Al$ and $Al₂Cu$ phases across varying growth velocities. Notably, they observed opposing tendencies to velocity changes, with Ag₂Al appearing more circular at lower growth velocities, while Al2Cu exhibited increased faceting. Additionally, Dennstedt and Ratke verified that high thermal gradients played a crucial role in stabilizing the growth front, facilitating the favorable alignment of phases in the eutectic.

Various morphologies within the Al-Ag-Cu ternary system exhibit distinct and, at times, significantly different crystallographic orientation relationships. Steinmetz et al. identified common low-index planes and directions across different orientation relationships (OR) involving Al, Ag₂Al, and Al₂Cu [\[22\]](#page-273-2). This observation suggests that, under slow directional solidification, the three-phase eutectic tends to adopt a straightforward periodic stacking sequence, such as ABAC where A, B, and C are different phases. Moreover, the morphologies predominantly hinge on the behavior of the two intermetallics, with Al adjusting to align along a series of low-index common planes, as documented elsewhere. Lastly, a recurring finding in Refs. [\[22,](#page-273-2) [113\]](#page-280-7) is that $\rm Al_2Cu$ takes the lead during growth, aligning with the $\langle 001 \rangle$ direction irrespective of the specific morphology.

2.3.3 Two-phase growth in multicomponent alloys

As mentioned in the previous section, in ternary alloy systems, such as Al-Ag-Cu, two-phase eutectic growth is univariant can may occur along a valley of temperatures and compositions (see Fig. [2.3\)](#page-48-0). The additional component allows for the formation of Mullins-Serkerka-type instabilities [\[114\]](#page-280-8) along the eutectic front which give rise to

Figure 2.9: Three-phase eutectic morphologies in $Al-Ag_2Al-Al_2Cu$: Five microstructures reported by Dennstedt and Ratke in directionally solidified Al- $Ag₂Al-Al₂Cu$ [\[7\]](#page-272-6). The reported morphologies are **A**) regular brick-like (or chain-like), B) half-lamellar, C) H-structure, D) irregular (or paw structure), and E) H-structure with higher fractions of the intermetallic phases (*i.e.*, Ag₂Al and Al₂Cu) and a reduction in the fraction of Al compared to panel C). The growth conditions in directional solidification are shown in the bottom left corner of each micrograph. Adapted with permission from Ref. [\[7\]](#page-272-6).

eutectic cells. There are several explanations for the formation of these cells including a constitutional undercooling criterion [\[115\]](#page-280-9), negative thermal gradients in the liquid ahead of the eutectic front [\[116\]](#page-280-10), and thermal convection effects [\[117\]](#page-281-0). While observing the solidification of a Zn-Al alloy, Wang *et al.* [\[58\]](#page-276-5) tracked univarient solidification of a two-phase eutectic, showing the formation of cellular instabilities at the eutectic front. They found that the pile up of Cd impurities at the interface led to constitutional undercooling in the liquid. The Cd both slowed the eutectic growth velocities and triggered Mullins-Sekerka-type instabilities. Wang and colleagues also determined the eutectic cell diameter d decayed with solidification velocity according to the relation $d \sim V^{-n}$ where $n \approx 0.3$. This result agreed reasonably well with the primary spacing model in single-phase growth $(n = 0.25)$ [\[118\]](#page-281-1), demonstrating the importance of long-range diffusion.

Another area of research has focused on the microstructure on a more local scale, concerning the interphase spacing within the eutectic cells. Senninger and Voorhees [\[91,](#page-278-12) [92\]](#page-278-10) proposed a generalized model akin to the JH theory that accounted for multiple elements and hence, multivariant solidification. Using thermodynamic parameters acquired through CALPHAD tools, they computed the Gibbs free energy functions of each phase as a function of composition. They also expanded their model to remove all assumptions regarding thermodynamic properties for a ternary alloy system, resulting in distribution coefficient matrices to account for compositions of the solid phases. In addition to confirming the generality of the JH theory, namely the scaling relations given in Eqns. [2.4,](#page-44-0) Senninger and Voorhees found that small additions of tertiary elements, especially slow diffusers, can have a large influence on the microstructure. They tested their model on a binary $AIA₂Cu$ eutectic with Ag additions [\[92\]](#page-278-10). They found that Ag additions had significant effects on the thermodynamic properties of the α -Al phase, but whose influence on Al₂Cu was negligible. The curvature and solute interface undercoolings both lowered with additions of Ag, but the variation

was similar enough that the eutectic length scale was insensitive to the composition change.

2.4 The coupled zone

Most cast eutectic compositions do not undergo solidification under (global) equilibrium conditions [\[119\]](#page-281-2). Additionally, the composition at the solid-liquid interface or within the bulk may deviate from the eutectic composition, C_e . In such cases, the microstructure is determined by the kinetics of competitive growth, prioritizing phase(s) with the lowest total undercooling. This competitive growth can result in the formation of primary phases with eutectic filling only the interdendritic or intercellular spaces.

Attaining wholly eutectic microstructures is possible in directionally solidified alloys, even when the composition is off-eutectic under specific growth conditions. Tammann and Botschwar, in their investigation of an organic eutectic material, observed a range where the undercooling of the eutectic front exceeded that of the primary phase [\[120\]](#page-281-3). This led to the development of a purely eutectic microstructure within a stability domain known as the coupled zone.

The configuration of the coupled zone is not determined by the thermodynamics (it has nothing to do with the metastable extensions of the liquidus lines in the phase diagram) and relies on the kinetics of growth, including the interface structure of different eutectic phases [\[119\]](#page-281-2). In metallic systems, two types of coupled zones can emerge: regular and skewed, as seen in Fig. [2.10.](#page-60-0) Regular coupled zones (Fig. [2.10A](#page-60-0)) exhibit an approximately symmetrical shape that fans out with increased undercooling (particularly at low thermal gradients G). Mollard and Flemings uncovered that the width of the coupled zone may also expand at very low growth rates under a positive thermal gradient (i.e., a high G/V ratio), imparting an anvil-like structure beneath the solidus line [\[121\]](#page-281-4). The upper part of the anvil-shaped coupled zone only

forms when $G > 0$. This is due to the formation of cells at low velocities whose undercooling scales with G. As $G \to 0$, the coupled zone converges to the eutectic point, fanning out with increasing ΔT [\[12\]](#page-273-3).

Phase stability for any given composition is determined through competitive growth. As shown in Fig. [2.10](#page-60-0) A ii, for a composition of C_0 , there are regimes of different growth velocities V (correlated with undercooling ΔT through Eqns. [5.1](#page-122-0) and [5.2\)](#page-122-1) which result in different stable phases. We see that there are two V_{cut} regions, at low and high V. At intermediate V, primary β has a lower undercooling than the eutectic and thus will form first. Therefore, over the V_β velocity regime the front is outside the coupled zone.

As noted above, eutectic alloys featuring a faceted/non-faceted pairing of phases often show a skewed coupled zone that curves toward the faceted phase (Fig. [2.10](#page-60-0) B). The faceted phase presents growth difficulties, even at higher undercoolings, resulting in larger average interlamellar spacings [\[119\]](#page-281-2) (Ref. to Sec. [2.2.3\)](#page-46-0). This means that the undercooling-velocity curve for the faceted phase is not parallel to that of the nonfaceted phase, see Fig. [2.10](#page-60-0) B ii. That is, defects, such as twins (not considered here) [\[122\]](#page-281-5), can enable the faceted phase to overcome the kinetic barrier of atom attachment. Thus an alloy of composition C_0 can form eutectic, primary β , and primary α during solidification at velocities V_{euc} , V_{β} , and V_{α} , respectively.

A solid-liquid interface situated outside the eutectic coupled zone experiences instability formation of one or both phases. In binary systems, when a phase within the eutectic growth front destabilizes, it gives rise to needles, plates, or dendrites, influenced by the solute field and the interface kinetics of the primary phase [\[119\]](#page-281-2). The emergence of the primary phase depletes the excess solute in the liquid, leading to a shift in the liquid composition into the coupled zone. Consequently, the final microstructure shows a dispersion of the primary phase surrounded by a two-phase eutectic. This stands in contrast to instabilities within ternary or two-phase eutectic

Schematic of two-phase coupled zone: A) illustrates the symmetric coupled zone of a nonfaceted-nonfaceted regular eutectic, while B) depicts the skewed coupled zone of a faceted-nonfaceted irregular eutectic. i and ii show temperature versus composition and temperature versus growth velocity diagrams for an alloy of composition C_0 , respectively.

(discussed above in Sec. [2.3.3\)](#page-55-0), which may yield columnar cells. In such a scenario, both phases reject the third component into the liquid, creating a long-range diffusion boundary layer. At a critical G/V , the planar interface can destabilize into even eutectic dendrites.

In theory, competitive growth governs the coupled zone structure, determining that, for a given growth velocity, thermal gradient, and alloy composition, the phase(s) with the lowest undercooling will prevail. Jackson and Hunt's [\[74\]](#page-277-6) eutectic growth model (Eqn. [2.8\)](#page-61-0) provides a fundamental basis for predicting eutectic undercooling. Additionally, Burden and Hunt's [\[93\]](#page-278-11) model for primary dendritic undercooling (Eqn. [2.9\)](#page-61-1) helps identify its growth behavior.

$$
\Delta T_E = 2(K_r K_c)^{(1/2)} V^{1/2} \tag{2.8}
$$

$$
\Delta T_D = \frac{GD}{V} + 2 \left[-\frac{2aV}{D} \left(m(1-k)C_\infty + \frac{kGD}{V} \right) \right]^{1/2} \tag{2.9}
$$

In these equations, ΔT_E and ΔT_D represent the undercoolings of eutectic and primary dendrites, respectively. Key parameters include a (Gibbs-Thomson coefficient), k (distribution coefficient), m (liquidus slope), C_{∞} (alloy composition), and D (interdiffusion coefficient). The coupled zone for any eutectic can be semi-quantitatively determined by systematically adjusting composition, thermal gradient, and growth velocity within the scope of Eqns. [2.9](#page-61-1) and [2.8.](#page-61-0)

While the coupled zones of two-phase eutectics have been reasonably well investigated, predicting coupled zones in three-phase eutectic systems has proven more challenging [\[38\]](#page-274-4). This complexity arises from factors discussed in Section [2.3,](#page-48-0) such as non-constant thermophysical properties like liquidus slope and distribution coefficients. McCartney et al. developed a theoretical model, adapted from two-phase eutectic systems, to forecast the stability range for cellular primary growth in a threephase system [\[6,](#page-272-5) [20\]](#page-273-1). Drawing inspiration from Burden and Hunt's model (Eqn. [2.9\)](#page-61-1)

for cell and dendrite formation, McCartney's model incorporates a third component. Fig. [2.7](#page-52-0) depicts the stability map for a ternary alloy at a given isotherm below the three-phase eutectic point. Himemiya et al. further expanded McCartney's model to predict interface temperatures for three-phase cellular [\[123\]](#page-281-6) and three-phase planar [\[106\]](#page-280-1) growth in a three-phase system. Another extensively researched area is twophase cellular growth within three-phase systems [\[91,](#page-278-12) [124,](#page-281-7) [125\]](#page-281-8). Importantly, most models converge on the $\Delta T \propto V^{1/2}$ relationship observed in two-phase systems (see Sec [2.3.3\)](#page-55-0).

Although robust, the coupled zone theory breaks down under rapid solidification conditions. Wang and Trivedi [\[126\]](#page-281-9) investigated the significance of activation energy for diffusion and eutectic temperature. Typically, coupled growth regions are computed assuming a constant diffusivity, D. However, in rapid solidification, high undercooling leads to a low interface temperature, resulting in a significant reduction in the diffusion coefficient. Beyond a critical undercooling, steady-state lamellar eutectic growth becomes unfeasible. Diffusivity typically follows an Arrhenius relation: $D = D_0 e^{-Q/RT}$, where Q represents the activation energy for diffusion. Wang and Trivedi established a correlation between Q and the limiting undercooling ΔT_{le} , indicating that alloys with higher activation energies will exhibit smaller ΔT_{le} [\[126\]](#page-281-9). This intuitively aligns with the idea that atoms requiring more energy for diffusion necessitate a higher interface temperature.

For a comprehensive review of the coupled zone, refer to Ref. [\[119\]](#page-281-2).

2.5 Coarsening of eutectics

Beyond solidification, understanding the subsequent evolution of eutectic microstructures under annealing is an area of research. This is because eutectics, like other composite materials, often operate at elevated temperatures. Eutectics are intrinsically stable at high temperatures due to their near-equilibrium solidification and

low energy interphase boundaries [\[31\]](#page-274-1). Nevertheless, the microstructures, and hence properties may degrade over time while operating near the eutectic temperature due to interphase boundary migration.

During coarsening, capillarity facilitates the disappearance or realignment of highly energetic interfaces into more favorable morphologies [\[127\]](#page-281-10). In 1961, Lifshitz and Slyozov [\[128\]](#page-281-11) and Wagner [\[129\]](#page-281-12) introduced the LSW theory, a comprehensive model for diffusion-limited Ostwald ripening. This theory describes the evolution of selfsimilar, spherical precipitates distributed throughout a matrix. This is depicted in Fig. [2.11](#page-64-0) A. Assuming an initial distribution where the equilibrium volume fraction of the precipitates, f_e , approaches 0 (*i.e.*, the limit of infinite dilution), they derived the relationship:

$$
\langle r \rangle^3 - \langle r_o \rangle^3 = kt \tag{2.10}
$$

Here, $\langle r \rangle$ is the average radius, $\langle r_o \rangle$ is the initial radius at the onset of steady-state coarsening, k is the phenomenological rate constant, and t is the time. The LSW theory posits that the volume fraction, f, and particle density, N_v , are asymptotically proportional to time.

Numerous researchers have endeavored to extend the LSW theory since its inception by incorporating volume fraction [\[130–](#page-281-13)[136\]](#page-282-0). Despite these efforts, a universally accepted ripening model remains elusive. The challenge lies in accurately predicting solute diffusion, which is highly dependent on factors like particle size distribution, surface energy anisotropy, and spatial correlations [\[127,](#page-281-10) [137\]](#page-282-1). Nevertheless, a wealth of experimental and analytical studies has affirmed the robustness of the scaling relation in the LSW theory (Eqn. [2.10\)](#page-63-0) for a broad spectrum of materials undergoing bulk diffusion. This law not only explains particle coarsening but also characterizes solid-state evolution in eutectic alloys, encompassing rod and lamellae morphologies [\[86,](#page-278-5) [138\]](#page-282-2), particles dispersed in thin films [\[139,](#page-282-3) [140\]](#page-282-4), and dendrite arm evolution during solidification [\[141,](#page-282-5) [142\]](#page-282-6). Furthermore, interestingly, the cube root law applies to

Mechanisms of eutectic coarsening: A) shows Ostwald ripening in which material diffuses through the bulk between particles. **B**) depicts Rayleigh instabilities forming on a eutectic rod which undergoes spheroidization. C) shows fault migration/annihilation on a branched eutectic. The two eutectic phases α (matrix phase) and β (secondary phase) are shown in orange and blue, respectively. Time flows from left to right as indicated by the arrow.

two-phase mixtures exhibiting non-self-similar evolution of the two-phase morphology, primarily for dendrites or particles [\[142,](#page-282-6) [143\]](#page-282-7).

In eutectics in particular, the microstructure may also undergo fault migration or annihilation. Faults can arise from the branching or coalescence of eutectic rods or lamellae (as in Fig. [2.5\)](#page-47-0) or when growth stops to form a termination. Faults, characterized by highly curved interfaces and often an elevated surface energy, can evolve through the mechanisms of fault migration and annihilation initially described by Graham and Kraft [\[144\]](#page-282-8). In this process, faults diffuse material to adjacent rods, causing their shrinkage or disappearance (see Fig. [2.11](#page-64-0) C). Faults with higher curvature induce a concentration gradient between two rods, driven by the Gibbs-Thomson effect [\[145\]](#page-283-0). Energetically favorable saddle points along the branches lead to the recession of terminations, allowing the branches to grow in the opposite direction until both faults annihilate each other [\[146\]](#page-283-1). At sufficiently low fault densities, 2D Ostwald ripening or spheroidization becomes the dominant coarsening mechanism while fault migration comes into play subsequently [\[147\]](#page-283-2). The formation of terminations during 2D Ostwald ripening can lead to an increase in fault density, promoting termination migration and increasing the coarsening rate. Fault migration stands out as the primary mechanism of coarsening of lamellar eutectic structures [\[148\]](#page-283-3).

Alongside Ostwald ripening and fault migration, Rayleigh instabilities may also play a role in the evolution of rod-type eutectic alloys and fibrous materials [\[149\]](#page-283-4). During solidification, rods exhibit small variations in their diameter along the solidification direction. Capillarity drives material diffusion to and from these surface irregularities. For a eutectic rod with sinusoidal interface perturbations, Cline derived a relationship predicting the impact of capillary forces based on the wavelength of the perturbations and the rod's volume fraction [\[150\]](#page-283-5). When the wavelength is large and the rod volume fraction is small, the perturbations dampen over time, smoothing out the interface. Conversely, if the opposite holds true, the perturbation

amplitude grows, eventually causing the rod to deteriorate into a row of spherical particles (spheroidization). A schematic of spheroidization is shown in Fig [2.11](#page-64-0) B. Unlike rod-like structures, lamellar eutectic microstructures are inherently stable (due to presumably low energy or epitaxial hetero-interfaces), preventing the formation of the small shape variations necessary for Rayleigh instabilities.

2.6 Peritectic solidification

A peritectic reaction involves the transformation of a mixture of liquid and a primary solid phase into a secondary solid phase, described by the reaction $L+\alpha \rightarrow$ β during cooling [\[3,](#page-272-0) [30\]](#page-274-0). A representative phase diagram is given in Fig. [2.12.](#page-67-0) This reaction occurs at the 'peritectic point,' where the peritectic β phase has a composition C_p at a temperature T_p . Peritectic reactions are prevalent in alloy systems across various industries, including steel [\[41\]](#page-275-1), aluminum- [\[151](#page-283-6)[–153\]](#page-283-7), copper- [\[8,](#page-272-7) [154\]](#page-283-8), titanium- [\[155–](#page-283-9)[157\]](#page-283-10), and zinc-based [\[158](#page-284-0)[–160\]](#page-284-1) materials. In proximity to the peritectic point, a hypo- or hyper-peritectic regime often exists, allowing both primary and peritectic phases to coexist (see two-phase fields in the phase diagram, Fig. [2.12\)](#page-67-0). Microstructures formed in off-peritectic alloys exhibit diverse patterns, akin to those in two-phase eutectic systems [\[40\]](#page-275-2), such as rod or lamellar structures. Additional morphologies, including banded and cellular/dendritic microstructures (vide infra), may form depending on nucleation and growth kinetics.

Coupled growth within peritectic alloys differs from eutectic coupled growth in how solute diffuses away from the growth front. In peritectic alloys, flux from both the primary and peritectic phases are parallel to the growth direction producing a long-range solute boundary layer [\[12\]](#page-273-3). This differs from eutectic coupled growth which relies on lateral solute diffusion from one phase to the other (see Sec. [2.2.2\)](#page-42-0). This difference is shown in Fig. [2.13](#page-69-0) where a composition profile (along the growth direction) is present in the peritectic alloy (\mathbf{B}) , but absent in the eutectic alloy (\mathbf{A}) .

Peritectic phase diagram: Schematic of a peritectic phase diagram showing compositions at different interfaces at temperature T_i when a primary α phase and liquid undergo a peritectic reaction to form β under an undercooling ΔT below the peritectic temperature T_p .

As a result, coupled growth in peritectics is difficult to sustain, even with high $G \, |12|$. It was thought to be impossible for many years as compared to eutectics [\[12\]](#page-273-3).

Chalmers initially theorized the possibility of achieving peritectic coupled growth (PCG) in compositions between the primary and peritectic phase [\[161\]](#page-284-2). In 1975, Fisher and Kurz provided experimental support for PCG in directionally solidified Sn-SnSb alloys [\[162\]](#page-284-3). Boettinger could not identify isothermal PCG while investigating hypo- and hyper-peritectic compositions of Sn-Cd alloys [\[163\]](#page-284-4). He used the Jackson-Hunt [\[74\]](#page-277-6) model for lamellar eutectic growth to determine the conditions in which PCG is favorable. Boettinger concluded that a negative undercooling is critical for PCG. Several years later, Vandyoussefi et al. discovered isothermal PCG in Fe-Ni alloys, presenting a microstructure selection map that considered nucleation of the solid peritectic phase from the constitutionally undercooled liquid ahead of the primary solid [\[164\]](#page-284-5). PCG in Fe-Ni alloys is shown in Fig. [2.14](#page-70-0) A and B. More recently, Ludwig observed in situ PCG in an organically solidified system under diffusive conditions [\[52\]](#page-275-3). Peritectic initiation occurred between the primary phase and the glass observation window, taking the form of lateral bands. Following peritectic formation, a coupled growth relationship developed between the primary and peritectic phases. Initial solute pile-up led to weak diffusion coupling, hindering the transition to steadystate PCG. Eventually, the primary phase gradually disappeared, resulting in a final transient composed solely of the peritectic phase. The possibility of a steady-state PCG has yet to be ascertained.

In directionally solidified off-peritectic alloys, banded microstructures are more prevalent than PCG [\[9,](#page-272-8) [165](#page-284-6)[–167\]](#page-284-7), sparking renewed scientific interest in understanding their formation. Banded microstructures manifest as a series of layers with alternating phases parallel to the growth interface, i.e., the phase interfaces are perpendicular to the growth direction, as seen in Fig. [2.14](#page-70-0) C. When the volume fraction of the peritectic phase is small, microstructures may form partial or 'island' bands [\[9\]](#page-272-8) (see

Figure 2.13:

Isothermal coupled growth for a two-phase \bf{A}) eutectic and \bf{B}) peritectic alloy. In the eutectic alloy, the composition at the α -liquid interface $C_l^{*\alpha}$ is higher than the eutectic composition C_{eut} , while the composition at the β -liquid interface $C_l^{*\beta}$ $\ell_l^{*{\beta}}$ is lower than C_{euc} . This leads to a strong lateral diffusion coupling as solute diffuses from α to β . In the peritectic alloy with an initial composition C_p and at a temperature above T_p , the α-liquid composition C_l^* is greater than the composition at the β-liquid interface $C_l^{*\beta}$ $\ell_l^{*{\beta}}$. There exists a composition profile in the liquid phase ahead of both lamellae. λ and δ_c correspond to the lamellar spacing and diffusion boundary layer, respectively, for both A and B. Taken with permission from [\[8\]](#page-272-7).

Micrographs of peritectic morphologies: A) is a cross-section of a directionally solidified Fe-Ni alloy that has formed a mixture of island banding, coupled peritectic growth, and planar peritectic (taken with permission from Ref. [\[9\]](#page-272-8)). B) shows a closer look at cellular coupled peritectic growth in an Fe-Ni alloy (taken with permission from Ref. $[10]$). C) depicts multi-layered banding which formed in a directionally solidified Pb-Bi alloy (taken with permission from Ref. [\[11\]](#page-272-10)).

Fig. [2.14](#page-70-0) A). This morphology has been observed in various systems (e.g., Ag-Zn, Sn-Cd, Zn-Cu, Sn-Sb, etc.). Boettinger noted that layered structures exclusively formed in two-phase regions directionally grown under high G/V growth conditions such that the primary-liquid and peritectic-liquid interfaces are planar [\[163\]](#page-284-4). Furthermore, banded morphologies emerge over a limited compositional range where the nucleation undercoolings of the two phases are both small [\[165\]](#page-284-6). Finally, if solute is rapidly mixed into the liquid rather than accumulating at the interface (under condition of large diffusion length D/V , only a single band transition will appear as the peritectic.

Recently, Lo et al. explored the relationship between island band formation and PCG, ultimately concluding that island banding will either be sustained or lead to the initiation of PCG [\[9,](#page-272-8) [167\]](#page-284-7). This outcome depends on the stability range for coupled growth spacing and the mean distance between islands.

To synthesize all of the above morphologies, Hunziker et al. formulated a microstructural selection map for directionally solidified peritectic alloys, employing the concept of constitutional undercooling [\[168\]](#page-284-8),

$$
\frac{G}{V} \le \frac{m\Delta C}{D} \tag{2.11}
$$

Here, G represents the thermal gradient, V is the velocity, m is the liquidus slope, ΔC is the concentration difference between the liquid and solid at the interface, and D is the solute diffusivity in the liquid. Under low G/V , the velocity limit for constitution undercooling is overcome and cellular or dendritic morphologies are observed. In regions where neither the primary or peritectic phase are preferred, two-phase growth may occur. Under high G/V , planar banded structures appeared. At high velocities, constitutional undercooling destabilizes the one of the phases resulting in cellular formation (here we will assume the primary phase). In this regime, alternating layers of cellular primary and planar peritectic form 'mixed bands' [\[168\]](#page-284-8). PCG is predicted
to form at even lower G/V values as both the primary and peritectic form along a cellular interface. This model allows the prediction of stability regimes for various morphological patterns in a given binary system, as a function of typical variables such as G, V , and alloy composition. The researchers applied this approach to the Fe-Ni alloy system, achieving reasonable agreement with experimental findings.

A comprehensive review of peritectic solidification may be found in Ref. [\[40\]](#page-275-0).

2.7 Open questions

While we have reviewed much about the dynamic behavior of multi-phase eutectics and peritectics, there remain many open questions that have yet to be answered:

- Can we map the stability fields for a three-phase eutectic on the basis of the competitive growth principle, as a function of the alloy compositions and growth parameters? How might we incorporate in this model the interface kinetics of a faceted phase?
- In an off-eutectic alloy, how do primary phase(s) impact the nucleation and growth of a three-phase eutectic? Related to this question, how do primary phases influence the crystal orientations and morphologies of the eutectic solids?
- What mechanism(s) drive solid-state evolution in multi-phase eutectic systems, and do multiple rate-limiting mechanisms coexist? Which is dominant: the influence of curvature reduction or that of the solid-solid interfacial energy anisotropy?
- How do the peritectic and primary phases interact during solidification of twophase peritectic alloys? Can coupled growth be attained under modest thermal gradients in directional solidification?

• What prompts the formation of, and transition between, different growth patterns in off peritectic alloys?

The focus of this dissertation is to address these questions through the application of recent advancements in X-ray imaging and machine learning.

CHAPTER III

Experimental Methods

This chapter offers an overview of the experimental techniques employed in the work presented in this dissertation. Specific experimental procedures are provided within the respective chapters for each project.

3.1 Directional Solidification

Directional solidification (DS) is a commonly employed technique in materials science, offering precise control over specific parameters such as thermal gradient (G) and growth velocity (V) . The Bridgman-Stockbarger model serves as the standard method, utilizing two or three furnace zones set at different temperatures $(i.e.,$ a hot and cold zone) separated by an adiabatic zone to create a thermal gradient [\[169\]](#page-284-0). The sample stage or furnaces move at a preset velocity, enabling control over G and the isotherm velocity V_T . Under steady-state conditions, V_T is equivalent to the solidification front velocity V . This dictates the movement of the solid-liquid front. DS finds extensive use in manufacturing highly aligned and/or single crystal materials, particularly semiconductors [\[170,](#page-284-1) [171\]](#page-284-2), and shape-memory alloys [\[172,](#page-285-0) [173\]](#page-285-1). One of the most prominent achievements in DS is turbine blade production, originate by Versnyder and Shank [\[174\]](#page-285-2), which yielded columner grain and single crystal materials. Since then, advancements to DS such as high rate solidification have been developed for improved microstructures [\[175\]](#page-285-3).

For any given alloy, V and G are the main variables which control the microstructure [\[12\]](#page-273-0). Fig. [3.1](#page-76-0) summarises the columnar and equiaxed microstructures of a typical alloy as a function of V and G. Along with corresponding cooling rates \dot{T} , the plot shows the V and G ranges which are generally achievable during casting, DS, and through additive manufacturing (AM) . For most DS systems, G is far more limited than V, spanning only about one order-of-magnitude (OoM) around 10^4 - 10^5 K/m. By comparison, both casting and AM have access to a wider range of G values (although with these techniques it is impossible to decouple G and V). Where DS excels is the wide range of low V spanning three OoM about 10^{-4} - 10^{-7} m/s.

For most of our directional solidification experiments, we used a vertical three-zone Bridgman directional furnace (MTI Corporation EQ-SKJ-BG) (Fig. [3.2\)](#page-77-0). To operate a standard DS experiment in this furnace, a ∼20-30 mm long cylindrical sample with a 1 mm diameter is placed in an alumina crucible fitted to prevent sample tilt during solidification. This ensures that G is either parallel or anti-parallel with gravity within the sample. We then place the crucible on a flange which is centered with the furnaces to prevent any horizontal thermal gradients. Once the flange is raised into the furnace, the sample remains stationary for the duration of the growth process. We then move the furnaces so the sample is aligned with the center of the hot zone. The furnaces, as shown in Fig. [3.2,](#page-77-0) are each ∼100 mm in height. Each furnace is placed with a set temperature so that a preset G forms between them. The maximum G feasible is dependent on the specific machine (ours was 3000 K/m). Before a V is imposed, we allow the sample to fully melt within the hot zone. Finally, a preset V is chosen (our V ranged between 0.014-1.4 μ m/s) so that the furnace moves at V and the sample shifts from the hot zone to the cold zone, solidifying while it cools.

There do exist situations where furnace movement or sample pulling (another means of DS where the furnaces remain stationary and the sample is moved $[5, 52]$ $[5, 52]$

Figure 3.1: Schematic of columnar and equiaxied microstructures as a function of V and G . The plot, reprinted from Ref. [\[12\]](#page-273-0), shows general V and G ranges achievable in casting, DS, and AM. The red line shows the columner to equiaxed transition. The lines running a 45° angle correspond to cooling rates $\dot{T} = VG$.

Figure 3.2: Vertical three-zone Bridgman directional furnace: Picture on the left shows the MTI Corporation EQ-SKJ-BG model we used for most DS experiments. The schematics of the three furnaces (red box) zones are on the right.

is insufficient to achieve high V or is inaccessible, such at synchrotron beam-lines. In such scenarios, an alternative mechanism for achieving DS is through a process known as '*qradient freeze*,' where a G is established along a stationary sample with an imposed \dot{T} on all furnace zones (where $\dot{T} = V_T G$). These procedures grant users precise control over the solidification process and, consequently, the pattern formation in the sample.

3.2 Synchrotron full-field X-ray imaging

To understanding microstructural formation and evolution, researchers have relied upon numerous materials characterization techniques including optical microscopy, thin sample directional solidification of transparent compounds, and scanning electron microscopy (SEM), among others. While these techniques are useful, they have a limited scope of applicability in studying metal solidification. Many require the destruction of the sample to obtain a picture of the internal structure, resulting in the loss of potential information out of view. 2D imaging may also obscure features observable only in 3D. In situ solidification of transparent organic eutectics also has limited translation to metals $(e.q.,\,$ the Prandtl number or the ratio of thermal and solute diffusion is higher in organics). Furthermore, there is the question of the effect of the spatial confinement of the few-nm-thick sample between two quartz slides on the solidification dynamics. That is, solidifying materials experience sample-boundary effects which can alter the interface behavior when compared to bulk solidification. We need an imaging technique which is 4D (three spatial and time), non-destructive, and can capture dynamic changes in a metal eutectic.

Full-field X-ray imaging is a non-destructive method for capturing the interior structure of a focal object that overcomes many of these limitations. X-rays penetrate the region of interest (ROI), interacting with the atoms within (as described below). Transmitted photons are captured by a scintillator, which converts high-energy X-rays into visible light, projected onto a CCD camera. This imaging technique is widely used in both medical [\[176,](#page-285-4) [177\]](#page-285-5) and materials science fields [\[178,](#page-285-6) [179\]](#page-285-7). While laboratoryscale X-ray instruments have seen significant improvements in recent years, achieving comparable spatial resolutions to synchrotron sources, they may not be suitable for time-dependent experiments [\[180\]](#page-285-8). Laboratory-scale X-ray instruments employ tube sources which emit a broad spectrum of energies in a cone where the maximum energy is determined by the accelerating voltage [\[13\]](#page-273-1). This range of beam energies, paired with less beam flux compared to synchrotrons, increases the scan times, preventing in situ experimentation. In addition, laboratory-scale X-ray tomography reconstructions are susceptible to beam hardening effects $(i.e.,$ low energy photons are absorbed more than the high energy photons in the material) which lead to artifacts. In contrast, the abundance of photons produced at synchrotron sources allows for monochromatic beams to be used, avoiding beam hardening altogether.

Synchrotron radiation sources offer high-brightness, high-flux X-ray beams with tunable, low-energy photon beams. These sources utilize an accelerator ring larger than a kilometer in circumference, employing magnets to propel electrons to nearly the speed of light. At tangential connection points, beam-lines tap into the ring path to access the emitted X-rays [\[181\]](#page-285-9). In our work, we use in particular the 2-BM and 32-ID beam-lines at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL).

3.2.1 Basic principle

Full-field transmission-based X-ray imaging at synchrotrons may take advantage of a monochromatic beam (in other cases, a polychromatic beam is used, in order to provide a higher flux). This beam originates as a 'white' X-ray beam with a broad range of X-ray energies, which is then tuned and filtered until only photons of a desired wavelength (or bandwidth) interact with the imaged object. As the beam passes through the object, its intensity exponentially decreases as photons interact with the matter [\[182\]](#page-285-10). This interaction results in three possible outcomes: transmission, absorption, and scattering. The former two processes together form the dominant interaction mechanism, known as *attenuation*. When a photon is absorbed by an atom, its energy is transferred to the electron cloud, leading to excitation and/or ionization. Larger atoms, such as those of lead, with more subatomic particles, are more likely to absorb X-rays. This is why lead is used in the medical practice to shield patients' reproductive organs during routine imaging exams.

The total attenuation reflects five contributions: coherent scatter, Compton scatter, photoelectric effect, pair production, and photonuclear interactions [\[183\]](#page-285-11) (see Fig. [3.3\)](#page-81-0). Coherent scattering, or Rayleigh scattering, occurs when a low-energy photon (below 30 keV) interacts with the atom as a whole, preserving its energy and wavelength in a different direction. This phenomenon is particularly valuable in X-ray crystallography, where the regular arrangements of atoms within the lattice lead to constructive interference of scattered X-rays. Incoherent scattering, or Compton scattering, becomes dominant at higher energies, where photons transfer some of their energy to the atom, altering their direction. The photoelectric effect occurs when a photon strikes an atom, resulting in the emission of an electron. A characteristic photon may also be emitted when an outer electron drops to a lower orbital state. The final two interactions, pair production and photonuclear interactions, occur exclusively with high-energy gamma-rays and are not discussed further. Coherent scattering and photoelectric absorption are the primary sources of X-ray attenuation in the experimental energy range (8-30 keV). For an in-depth exploration of all interactions, additional readings are available [\[182,](#page-285-10) [183\]](#page-285-11).

The intensity loss from attenuation is derived from the Beer-Lambert law. The law, originally discovered by Pierre Bouguer and later attributed to Johann Lambert who cited Bouguer's work, relates the attenuation of light to the material properties

X-ray interaction with a solid material: X-ray attenuation of intermetallic Ag2Al divided into different component interactions as a function of photon energy. Data sourced from the photon cross-sections database XCOM.

of the medium and the path length. Beer later expanded the law to include the concentration of the solutions [\[184\]](#page-285-12). For simplicity, if we assume that a monochromatic beam transmits through a material, the X-ray attenuation can be expressed by the relationship,

$$
\frac{dI}{I(x)} = -\mu dx\tag{3.1}
$$

where I is the beam intensity (in units of photons/unit time), dx is the distance traveled in the medium (in units of cm), and μ is that material's attenuation coefficient, which describes the reduction in radiant flux per unit thickness of material $(i.e., expressed in cm⁻¹)$. Integrating both sides of Eqn. [3.1,](#page-82-0) we find an equation that characterizes the decay of X-ray intensity, known as the Beer-Lambert law:

$$
I(x) = I_0 e^{-\mu x}
$$
 (3.2)

where I_0 is the intensity of the incident beam. The attenuation coefficient is proportional to the atomic number of the material, Z , to the $4th$ power [\[180\]](#page-285-8). Thus, heavier materials absorb more photons and appear darker compared to less dense phases in the X-ray projection image [\[182\]](#page-285-10). 'Absorption contrast' describes the difference in absorption between multiple phases/mediums in the path of the X-ray beam, wherein high contrast is preferred for imaging [\[180,](#page-285-8) [182,](#page-285-10) [185\]](#page-286-0). Multi-phase materials with low absorption contrast, resulting from either comparable attenuation coefficients or $\mu \times x$ values, cannot be differentiated and require alterations in beam optics to be studied [\[13,](#page-273-1) [182\]](#page-285-10). Such is the case for phase-contrast tomography [\[186\]](#page-286-1). Fig. [3.4](#page-83-0) gives the attenuation lengths (i.e., the distance a photon of a given energy can travel in a material before the X-ray intensity decays to 1/e of the surface value) of all solid phase discussed in this dissertation. Fortunately, for the two multi-phase systems examined, $Al-Ag₂Al-Al₂Cu$ and $Zn-AgZn₃$, there are ranges of photon energies which display an adequate attenuation contrast between the different phases, namely for

Figure 3.4: X-ray attenuation lengths of solid phases studied in this dissertation: Variation in X-ray attenuation lengths versus photon energy. Data sourced from The Center for X-ray Optics (CXRO).

energies above 9 keV for Al-Ag₂Al-Al₂Cu and below 9 keV for Zn-AgZn₃. It is worth noting these attenuation lengths are tabulated at room temperature and do not take into account solubility changes under elevated temperatures (see Sec. [7.2\)](#page-178-0).

3.2.2 In situ X-ray radiography

X-radiography (also known as projection microscopy or videomicroscopy) is an imaging technique that employs X-ray transmission through a targeted, stationary object to capture a snapshot of its internal structure in the plane orthogonal to the incident beam [\[185\]](#page-286-0). As noted previously, attenuating X-rays interact with a detector

containing scintillators, which then convert them into visible light. This light is subsequently captured by a CCD camera and transformed into a digital image. The image represents a projected view of the structure inside the material, hence we often call it a projection image. Post-processing of the images are detailed in Sec. [4.1.](#page-108-0) Temporal resolution in sequentially captured images depends on the frame rate of the camera, on the order of 100-175 fps. In situ X-radiography leverages this high frame rate for studying dynamic phenomena like melting, solidification, and phase changes, which also require a high-temperature furnace with in situ viewing. In our experiments, we calibrate resistance heaters at the synchrotron using a K-type thermocouple, and we verify the calibration by comparing with known eutectic and/or peritectic liquidus temperatures. In some cases, we use for DS a two-zoned furnace with a natural thermal a gradient of $\sim 20K/mm$. Systematic control of cooling rates (0.3-2.0 K/min) manages growth velocity through the gradient freeze method (Sec. [3.1\)](#page-74-0).

3.2.3 X-ray computed tomography (CT)

X-ray computed tomography (CT) is an advanced imaging technique that captures the internal structure of a three-dimensional object by combining X-ray imaging (now during sample rotation) and computational processing [\[13,](#page-273-1) [179,](#page-285-7) [180,](#page-285-8) [182,](#page-285-10) [187\]](#page-286-2).That is, the object is rotated continuously within a 0-180° angular range, capturing its internal structure from various perspectives. Reconstruction algorithms, such as the filtered backprojection (FBP) method, are then employed to mathematically reconstruct the 3D structure from the projection images.

Slices, representing two-dimensional cross-sections at specific heights along the sample, are created using FBP. If we consider a single slice of an object, recorded by a row of pixels on the detector, we can represent the cumulative attenuation as a line plot. This is shown in Fig. [3.5](#page-86-0) a and b. For a given projection angle, θ , each point on the line plot corresponds to the sum total (line integral) of photons passing through the object along the beam path. Over 180° of rotation, attenuation line plots for the same slice are recorded and trace out a sinogram (Fig. [3.5](#page-86-0) c). A back projection reconstruction algorithm then takes each line within the sinogram and mathematically projects them back along the angle it was captured at (Fig [3.5](#page-86-0) d). With each angle, 'mass' build up of intensities where projections intersect eventually yields a reconstructed image slice, as seen in Fig. $3.5 e$ [\[13\]](#page-273-1).

The reconstructed slice still lacks crisp boundaries and is blurry. This is caused by 'mass' spreading where no 'mass' exists. To account for this blurring, we use FBP. Here a filter is applied which suppresses the low frequencies, adjusting for absent high frequencies in Fourier space from insufficient sampling. This results in a sharper final image (Fig. [3.5](#page-86-0) f) [\[13\]](#page-273-1).

The tomopy package [\[23\]](#page-273-2) is commonly used for reconstructions for the experiments detailed in this dissertation. Additional details on tomographic reconstruction are found in Sec. [4.2.](#page-111-0) CT reconstructions generate a stack of grayscale slices, which may need to be registered (spatially aligned) and segmented (categorized into designated phases) to visualize the 3D structure and obtain qualitative and quantitative information about the microstructure-of-interest.

A major challenge that we face when working with CT is the inherent trade-off between the image quality and the temporal resolution accessible in CT [\[13\]](#page-273-1). Efforts in the past decade have greatly improved our capability to meet the need for both extreme space and time-scales [\[180\]](#page-285-8). In general, however, higher spatial resolution require longer scan times. This reflects the need to balance the signal-to-noise ratio (SNR). SNR can be described by

$$
SNR \propto \sqrt{N_p * t_{exp} * I_0} \tag{3.3}
$$

Figure 3.5: $Backprojection$ reconstruction method for single slice obtained by parallel beam computed tomography. a is the original $\frac{1}{100}$ slice in which the highly attenuating features are brightest. b shows projections being taken at different angles. c depicts the creation of the sinogram from many projections. d is the process of backprojecting the sinogram. e is the final backprojection image without filters. f Filtered backprojection image of sample slice. Figure taken from Figure 3.5: $\,$ Backprojection reconstruction method for single slice obtained by parallel beam computed tomography. $\,$ a is the original $\,$ slice in which the highly attenuating features are brightest. b shows projections being taken at different angles. c depicts the creation of the sinogram from many projections. d is the process of backprojecting the sinogram. e is the final backprojection image without filters. f Filtered backprojection image of sample slice. Figure taken from Ref. [13] with permission. Ref. [\[13\]](#page-273-1) with permission. where N_p is the number of X-ray projections, t_{exp} is the exposure time, and I_0 is the mean photon count per second assuming we use FBP to reconstruct [\[180,](#page-285-8) [188\]](#page-286-3). We can see that lowering N_p or t_{exp} will diminish the SNR. To acquire the same resolution in a smaller sample as a larger one, we need a higher dose of photons (i.e., a higher beam flux).

The trade-off between temporal and spatial resolution also contextualizes our need for X-radiography (see Sec. [3.2.2\)](#page-83-1) to capture in situ solidification whose temporal resolution is limited only by the frame-rate of the the camera. Furthermore, postmortem 3D analysis through either CT or focused ion beam (FIB) tomography (see Sec. [3.4\)](#page-105-0) allows us to maximize spatial resolution as scan times are no longer a limiting requirement. Furthermore, by limiting the sample thickness in the direction of the beam, such as for X-radiography, to less than 100 μ m, we can correlate our *postmortem* CT scans with in situ X-radiography scan results to produce a pseudo-4D reconstruction of our solidifying sample (see Sec. [4.3](#page-112-0) for more details).

There are two types of CT which we employed during our research: microcomputed tomography, μ -CT, and nano-computed tomography, n-CT. Both function through the same general approach as described above, wherein projections are taken of a rotating sample which are then reconstructed into slices of the interior microstructure. However, n-CT, through the use of X-ray optics (*vide infra*), achieves 10 nm resolution OoM with a 55 \times 45 μ m² FOV. μ -CT generally will have ∼1 micrometer spatial resolution with a 2.5 \times 1.5 mm² FOV. This makes n-CT more effective at capturing the microstructural connectivity and eutectic interphase boundaries, which is necessary for the Al-Ag₂Al-Al₂Cu eutectic with its ∼5 μ m interlamellar spacing, λ . μ -CT, on the other hand, is more effective at capturing larger dynamic behavior such as the formation of primary dendrites and/or the macroscopic eutectic growth front. Fig. [3.6](#page-88-0) shows a chart of various energies and spatial resolutions available in different X-ray imaging techniques. The location of the n-CT and μ -CT conditions

Figure 3.6: Schematic summarizing the capabilities of various X-ray imaging modes. Current capabilities are marked by points, and potential future developments are indicated by the colored regions. Square points correspond to lab source while circle are from synchrotron imaging. Filled points are based on measured values, and open points are calculated. The spatial resolutions and energies used for n-CT and μ -CT experiments used in the dissertation are indicated by the red and green circles, respectively. Figure taken with permission from Ref. [\[14\]](#page-273-3).

we work in are marked.

3.2.3.1 Micro-computed tomography

CT is a versatile tool for capturing 3D structures across various size scales. For investigating large-scale phenomena like primary phase solidification, we employed micro-computed tomography $(\mu$ -CT). [\[13,](#page-273-1) [180,](#page-285-8) [187\]](#page-286-2). We conducted experiments at the advanced photon source (APS) beam-line 2-BM at Argonne National Laboratory (ANL) in Lemont, Illinois, USA. A 30 keV monochromatic X-ray beam provided sufficient flux (for comparison, a source energy of 19.5 keV maximized the flux to \sim 1.12 \times 10¹³ photons/s) and absorption contrast (Fig. [3.4\)](#page-83-0). A Eu-doped Gd–Ga–Garnet

Figure 3.7: Schematic of X-ray micro-tomography: Setup at beam-line 2-BM of Argonne National Laboratory's Advanced Photon Source. A parallel, monochromatic X-ray beam is focused on a sample in a 2-zone directional furnace. Attenuated X-rays are transformed by a scintillator into visible light which is then redirected into a camera. The sample is mounted on a kinematic mount; it rotates to acquire multiple projections of the internal structure at various angles

(GGG) scintillator detected transmitted X-rays and converted them into visible light. A FLIR Oryx camera with a 1.632×2.422 mm² field of view and magnifying capabilities of a $5\times$ objective lens captured each projection. The pixel size was 1 μ m. Typical scan times for CT were on the order of 9.5 min. A schematic of μ -CT is shown in Fig. [3.7.](#page-89-0)

We conducted additional μ -CT at the Michigan Center for Materials Characterization (MC²) in Ann Arbor, Michigan, USA, utilizing their Zeiss Xradia Versa 520 3D X-ray Microscope [\[189\]](#page-286-4). The X-ray beam in this system is divergent and polychromatic compared to the parallel and monochromatic beam used at 2-BM, due in part to the absence of beam-focusing optics. To compensate for photon loss, a relatively high beam voltage and longer scan times were on the order of 4-12 hours necessary to achieve sufficient absorption contrast. Voltage settings between 60-150 kV were employed, and a total of 1601 tomographs were captured over a 360° rotation, using a $4\times$ objective lens for magnification. This resulted in a pixel size of 1-4 μ m. The built-in scintillators converted transmitted X-rays into visible light, captured by a 2000×2000 pixel, noise-suppressing charge-coupled detector. The desired FOV was achieved through the Zeiss Resolution at a Distance (RaaD) two-stage magnification technique. Projections are initially enlarged through geometric magnification before a scintillator converts X-ray into visible light, which are then optically magnified [\[189\]](#page-286-4).

3.2.3.2 Nano-computed tomography

To capture minute sub-micrometer features, such as the solid-solid interphase boundaries in a three-phase eutectic (where the typical lamellar spacing is on the order of \sim 5 μ m), absorption-based nano-computed tomography (n-CT) was employed. n-CT utilizes additional focusing optics compared to conventional CT (Fig. [3.8\)](#page-91-0), including a capillary condenser and pinhole apparatus, to concentrate the incident beam into a small field-of-view (FOV) [\[13,](#page-273-1) [14,](#page-273-3) [180\]](#page-285-8). Transmitted X-rays pass through a Fresnel zone plate (FZP) to project a magnified perspective of the sample onto the detector. This gives rise to a pixel size in the tens of nm, on the detector [\[14,](#page-273-3) [190\]](#page-286-5). We harnessed the n-CT capabilities at APS's beam-line 32-ID at ANL. A monochromatic X-ray beam of 8.4 keV optimized absorption contrast between the captured phases and beam flux. For context, at an energy of 13 keV, the X-ray source achieves a flux of 1×10^{13} photons/s (comparable to conventional CT, see above Sec. [3.2.3.1\)](#page-88-1). We selected the beam energy of 8.4 keV to slightly exceed the absorption edge of Al_2Cu at which point the attenuation length decreases compared to Al (Fig. [3.4\)](#page-83-0). Attenuated X-rays struck a 50 nm FZP objective lens, focusing the beam onto a Eu-doped GGG

Figure 3.8: Schematic of X-ray nano-tomography: Setup at beam-line 32-ID of Argonne National Laboratory's Advanced Photon Source. The n-CT system integrates a capillary condenser and pinhole to focus the incident beam, and a Fresnel zone plate projects attenuated X-rays onto a detector. The sample is mounted on a kinematic mount; it rotates to acquire multiple projections of the internal structure at various angles.

scintillator. A Grasshopper3 GS3-U3-51S5M camera with a 2448×2048 FOV and voxel resolution of 22.5 nm³ recorded each projection.

3.2.4 Sample preparation

3.2.4.1 X-radiography

Samples intended for X-radiography must be $\leq 100 \mu m$ thick for adequate X-ray attenuation. Uniform thickness is crucial to ensure homogeneous attenuation across the field-of-view, preventing mischaracterization of features due to thickness variations (refer to Eqn. [3.2.](#page-82-1) Two methods were employed to achieve uniform thickness. Firstly, we cut $\sim 0.5 \times 10 \times 10 \text{ mm}^3$ pieces from an as-cast ingot using a SBT model 650 low-speed diamond wheel saw. Subsequently, we polished the sample surface with SiC metallurgical paper and diamond lapping film to achieve a uniform thickness of no more than 100 μ m. For the second approach, 4 \times 10 \times 2 mm³ pieces were sectioned from the as-cast ingot and cold-rolled into $\leq 100 \mu m$ thick ribbons. To provide structural support during solidification, both sets of samples were sandwiched between 200 μ m quartz slides, using boron nitride spray as adhesive (following the procedures described in [\[17,](#page-273-4) [58,](#page-276-0) [59\]](#page-276-1)). At the beam-line, each sample was mounted atop an alumina or boron nitride rod attached to a kinematic mount at its base. Stage controls for rotation and translation provided the necessary maneuverability to align samples within the path of the incident X-ray beam.

3.2.4.2 n-CT

To prepare samples for n-CT, considerable time and effort was invested due to their small size and delicacy. N-CT samples must have a maximum thickness of ≤ 50 μ m to allow for sufficient X-ray attenuation and also to fit within the FOV of the detector (if ant part of the sample is out of the FOV, this may lead to reconstruction artifacts [\[13,](#page-273-1) [191\]](#page-286-6)). This study employed three distinct procedures to produce such samples, each with its own set of advantages and drawbacks. These procedures were designed to address the limitations of the previous ones, progressively optimizing the overall process. Regardless of the approach, the process began with an ingot of cast material produced through vacuum arc remelting. Electrical discharge milling (EDM) was then utilized to cut out 1 mm diameter cylindrical rods, each measuring 1-5 cm in length (Fig. [3.9\)](#page-93-0). In general, a longer rod ensured that the steady-state regime was attained in DS. We subjected these rods to DS under the desired conditions, as detailed in Sec. [3.1.](#page-74-0)

In the first approach, we extracted samples using a focused ion beam (FIB) lift-out technique (see Fig. [3.10\)](#page-95-0). We cut a DS sample at approximately its midpoint along the growth direction to ensure that we did not obtain the imaged microstructure during the initial or final transients of DS. We polished the sample surface using

Figure 3.9: Sample production for DS at University of Michigan: Image depicting an as cast material (top right) produced via vacuum arc remelting, with 1 mm diameter rods obtained through electrical discharge milling (bottom).

SiC metallurgical paper and diamond fluid. To prevent tapering, we affixed the rods to a steel base using crystal bond. After observing the microstructure in SEM, we chose a region-of-interest (ROI) depending on the experimental objectives, and cut a cylinder with a diameter of approximately $45 \mu m$ from the surrounding sample. We milled away an adjacent wedge-shaped region to access the bottom of the cylinder. Simultaneously, we connected the sample to an omniprobe manipulator by depositing a platinum joint through gas injection. Once securely fastened, we cut away the connecting base of the sample, and the manipulator lifts it out. The lift-out was then attached to the tip of a tungsten needle by depositing layers of platinum joints. Finally, we cut the sample away from the manipulator, resulting in the final nano-CT sample. While this process is laborious, somewhat inefficient (it takes ∼3-5 hours to produce one sample in this manner), and fragile samples are prone to loss during transport, it offers benefits such as the ability to extract precise microstructural features with minimal distortion.

The second approach we used to produce micropillars for n-CT closely resembles a lift-out but employs the fast milling capabilities of the Thermo Fisher Helios G4 PFIB UXe at MC². With an ion current of up to 2.5 μ A, this instrument enables rapid milling, allowing substantial material removal around a selected ROI in the microstructure. The key advantage of this method, aside from extracting a desired initial microstructure, is that the pillar base remains attached to the bulk sample, providing increased support. The samples we produced using this method were more likely to survive transport to the beam-line. However, it is important to note that this process is more time-consuming (on the order of ∼10-15 hours to yield one sample) and costly compared to lift-outs.

The third method for n-CT sample preparation we used is notably more efficient and faster than the previous two and hence particularly advantageous when multiple micropillar samples (of difference compositions or solidification conditions, etc.) are

Figure 3.10: Schematic of FIB lift-out Depicted on top, with an inset showcasing the milling processes. Images on the bottom-right provide snapshots of this technique applied to an $AI-Ag₂AI-Al₂Cu$ three-phase eutectic sample, demonstrating the extraction of the sample and its attachment to a tungsten needle.

warranted. In this approach, we mechanically polished the 1 mm diameter DS sample to create a fine tip, accomplished by grinding with high grit SiC metallurgical paper while the sample was spun in a Dremel $\mathcal{O}(Fig. 3.11)$ $\mathcal{O}(Fig. 3.11)$. This technique can generate a dozen finely tipped samples within four hours, with tips as fine as 100 μ m in diameter at their point. we used FIB milling to further reduce and refine the tips to a desired shape. This entire process can yield up to $25\times$ the number of samples compared to the previous two approaches in a single week. However, it is important to note that this procedure results in substantial mechanical deformation and produces randomly selected initial microstructures. As a result, it is unsuitable for studies of a specific initial microstructure nor is it viable for diffraction-contrast tomography (since deformation can compromise the diffraction spots).

In addition to the three sample preparation techniques, we explored electropolishing as a method to thin samples before employing the Focused Ion Beam (FIB). During electropolishing, we connected the metal sample to the positive terminal of a DC power rectifier, functioning as the anode. Simultaneously, we attached a copper bar to the negative terminal of the DC power rectifier, acting as the cathode. Both the cathode and anode were immersed in a temperature-controlled bath of electrolyte solution, using $HNO₃$ solutions with concentrations ranging from 50-70 wt%. Applying an electrical current caused metal ions from the sample surface to dissolve into the electrolyte and oxidize. This process allowed us to reduce the diameter of the sample tip to approximately 100 μ m. Electropolishing proved to be a rapid method, taking around 20-30 minutes to yield one sample. However, after preliminary testing, we opted against electropolishing due to varying rates of ion removal among elemental components. Aluminum and copper demonstrated greater resilience than silver, resulting in substantial and unpredictable composition changes, the concentration of Ag reducing by 30 wt%. Due to the shift in composition during electropolishing, we do not pursue this route further.

Figure 3.11: Sample preparation steps for transmission X-ray nano-tomography $(n-CT)$ through the abrasion route: A) Image of the workstation with the Dremel[©] mounted parallel to the table. The magnified view in **B**) displays a cylindrical rod clamped in the Dremel©, where the sample tip is machined to a point as small as $100 \ \mu m$ in diameter using grinding paper as the sample spins. C) depicts the final product of this process. Finally, in D) the sample tip (purple box) may undergo further FIB milling for subsequent thinning.

3.2.5 In situ beam-line furnace

The objective of our work was to investigate the solidification and solid-state evolution of eutectic and peritectic alloys. Therefore, X-radiography, μ -CT, and n-CT all required established high temperature environments which simultaneously allowed in situ observation of the evolving microstructures. Both beam-lines 2-BM and 32-ID at APS had in-house furnaces which allowed us to complete our studies. The single zone furnace at 32-ID (suitable for annealing studies) was composed of a MicroFiber Heater FibHeat200-THM-XRD encased in a Cu cooling socket (Fig. [3.12A](#page-99-0)) which was fitted with an X-ray port aligned orthogonal to the incident beam. At 2-BM, we used two-zone induction furnace with a similar Cu casing and X-ray viewing window aligned with the incident beam (Fig. [3.12B](#page-99-0)).

Metal alloys, like the ones discussed in this thesis, typically have a thin oxide layer covering the bulk material (a reference Ellingham diagram is given in Fig. [3.13\)](#page-100-0). This oxide layer remains solid during melting, offering some structural support for observing the solidification process. However, there is a risk of samples buckling or collapsing, especially since the oxide may be only a few nanometers thick. To address this potential issue, we applied an additional layer of boron nitride using an aerosol spray and/or a paste (Fig. [3.14\)](#page-101-0). Boron nitride is chosen for its high melting point and small attenuation coefficient, making it nearly transparent during absorptionbased X-ray imaging. Likewise, boron nitride or alumina rods are also utilized to mount the sample onto the kinematic mount, again for their structural stability and chemical inertness at high temperatures.

3.3 Electron backscatter diffraction (EBSD)

Texture analysis provides complementary information on the crystallographic alignment of grains within a material, thus offering insights into the impact of kinetic

Figure 3.12: Synchrotron beam-line furnaces at the APS: Single-zone furnace at beam-line 32-ID at the APS. i presents a photograph of the furnace, with red arrows highlighting the X-ray port and the direction of the Xray beam. ii provides a schematic of the furnace, demonstrating various perspectives. B) Two-zone furnace at beam-line 2-BM at APS. i features an image of the furnace with the indicated X-ray port. *ii* displays a schematic of the furnace, showcasing the sample centered along the path of the incident beam. The temperature gradient within the furnace is illustrated on the left, along the direction of gravity.

Figure 3.13: Ellingham diagram in which the metals relevent to this dissertation (i.e., Ag, Cu, Zn, and Al) are circled in red. Figure adapted from Ref. [\[15\]](#page-273-5).

Figure 3.14: *Mounting samples for X-ray tomography:* Boron nitride spray and paste are employed to coat and affix samples onto a boron nitride or alumina rod (purple inset). The spray provides a thin coating around the sample transparent in absorption-based X-ray imaging. The paste is used as a high temperature adhesive to secure the sample on the boron nitride or alumina rod. These materials offer structural support, mitigating the risk of sample buckling or collapse during the melting process.

processes such as DS or isothermal annealing on grain formation and growth [\[192\]](#page-286-7). It also reveals the interfacial bi-crystallography of a multi-phase system, the orientation relationships between different phases, and the anisotropic growth directions influencing the as-cast microstructure. None of this information can be determined with the attenuation signal from full-field X-ray imaging. Instead, diffraction is necessary. To this end, electron backscatter diffraction (EBSD), commonly performed in a scanning electron microscope (SEM), is a widely used method for capturing the texture of materials [\[192,](#page-286-7) [193\]](#page-286-8).

To conduct EBSD, the sample undergoes fine polishing, achieved either through FIB milling of the surface layer or traditional hand polishing using alumina and/or diamond fluid. Polishing removes deformation, scratches, and other crystal damage. This improves the diffraction bands and ensures a representative surface lattice. The polished sample is then placed in the SEM chamber and tilted to 70° with respect to the sample stage; this is used to maximize the sample tilt, thus improving the diffraction pattern, while maintaining sufficient image resolution. $\frac{1}{1}$ $\frac{1}{1}$ $\frac{1}{1}$ Focusing the beam onto an ROI, electrons scatter off the crystalline surface, with some satisfying the condition for Bragg diffraction as defined by the equation

$$
n\lambda = 2d\sin\theta\tag{3.4}
$$

where *n* is an integer, λ is the electron wavelength, *d* is the lattice spacing of the crystal, and θ is the incident angle. The Bragg condition displays cylindrical symmetry with respect to the lattice plane normal and therefore Kossel diffraction cones form. The Kossel cone than spreads out at the incident angle (also known as the Bragg angle), getting wider. The edge of the cone will eventually intersect with the phosphor screen of the detector forming a hyperbolic edge known as a Kikuchi line

¹Historically, 70.5° was originally used for the tilt angle because the ⟨114⟩ direction for a silicon (001) crystal would be positioned at the pattern center, making calibration simple. While modern EBSD calibration is automated, the 70° tilt angle is still used today [\[192\]](#page-286-7).

[\[194\]](#page-286-9). Kikuchi lines are a series of bands displaying the unique symmetry and orientation of the crystalline surface interacting with the electrons [\[192\]](#page-286-7) (Fig. [3.15\)](#page-104-0). Due to the angling of the sample, the Kossel cone is shallow (∼1°) and the Kikuchi lines are nearly straight.

In our research, we employed two approaches to index crystal orientations from Kikuchi patterns: Hough transform [\[193\]](#page-286-8) and dictionary indexing [\[195\]](#page-286-10). The former is a prevalent analysis technique in commercial EBSD systems and involves remapping Kikuchi bands into Hough space, where straight lines in image space become single points. In this manner, the problem of identifying bands in a diffraction pattern is reduced to finding a peak of high intensity in Hough space. Peaks are then converted back into Kikuchi bands with enhanced contrast. The resulting pattern is compared with a built-in library to identify the crystal orientation of the mapped phase.

Obtaining clear Kikuchi bands for multiple phases within the same FOV proves challenging for some materials due to their mechanical properties. Specifically, we faced difficulties polishing the $\text{Al-Ag}_2\text{Al-Al}_2\text{Cu}$ eutectic as the Al_2Cu phase has a microhardness nearly $8\times$ that of other two phases [\[196,](#page-286-11) [197\]](#page-286-12). Traditional indexing via Hough transform did not effectively characterize the crystal orientations. In contrast, dictionary indexing emerged as a robust approach for characterizing noisy datasets [\[195\]](#page-286-10). In essence, the backscatter electron yield is forward-simulated for a hypothetical single crystal of a specific phase, considering the geometrical model of our sample-detector configuration. The simulated and experimental patterns are then transformed into Rodrigues-Frank vectors within the fundamental zone. Finally, a dot product of the two vectors is computed as a measure of similarity with the simulated pattern most similar to the actual one identified as the crystal orientation [\[195\]](#page-286-10).

Figure 3.15: *EBSD* characterizes the crystallographic textures of material: A polished surface is subjected to an electron beam, and the back-scattered electrons are captured by a detector, forming diffraction patterns known as Kikuchi patterns. The provided image gives an example of the orientation of a solid $Ag₂Al$ crystal.

3.4 Focused ion beam (FIB) tomography

In addition to X-ray tomography, we utilized focused ion beam (FIB) tomography to obtain a three-dimensional view of internal microstructures. This technique is a destructive approach which functions by milling away slices in a ROI by a known amount (e.g., 50 nm) and capturing an SEM image of the newly exposed microstructure [\[16\]](#page-273-6). A key advantage of this technique is the high spatial resolution it offers compared to X-ray tomography. As shown in Fig. [3.16,](#page-106-0) FIB tomography can achieve voxel resolutions as low as 10 nm [\[16\]](#page-273-6). Additionally, the size of the ROI can be ordersof-magnitude smaller than accessible through X-ray tomography. The typical depth of milling is hundreds of nanometers [\[16\]](#page-273-6). The minimum reliable depth which may be achieves is 10-15 nm using a 50 pA beam current [\[198\]](#page-286-13). One major disadvantage of this technique is the long acquisition times, which can range from a few hours up to a few days depending on volume, step size, and beam current [\[198\]](#page-286-13). This can lead to beam drifting during the milling that must be accounted for throughout the procedure. One common means in which this may be automated is by introducing a fiduciary mark which the system can use to remain centered. These drifts can lead to distortions during reconstruction which may require image registration to compensate for.

FIB tomography was necessary for one sample in particular during our work. We needed to examine the 3D connectivity of $\text{Al-Ag}_2\text{Al-Al}_2\text{Cu}$ eutectic adjacent to a primary Al₂Cu rod. The eutectic displayed an interlamellar spacing of \sim 5 µm compared to the primary rod which was $\sim 60 \mu m$ wide. Such a substantial size difference made in situ μ -CT insufficient to capture both features with sub-micrometer resolution (more details in chapter [VI\)](#page-150-0). Likewise, the FOV in n-CT would not accommodate the full extent of the primary phase. During our experiment, to safeguard the microstructure's integrity, we deposited a layer of platinum over the ROI, shielding it from stray ions during the cutting process. Additionally, we employed a low ion beam current

Figure 3.16: Comparison of 3D tomography techniques including electron tomography, X-ray tomography, and FIB tomography. The figure only considers μ -CT, not n-CT. Chart taken from Ref. [\[16\]](#page-273-6) with permission.

(15 nA) for sectioning to ensure a smooth surface for imaging. While effective for capturing the postmortem microstructure of as-solidified or as-processed materials not easily observed through X-ray imaging, we caution that this technique is destructive in nature and should thus only be used as a last step in materials characterization.
CHAPTER IV

Data Analysis Procedures

Much of the data collected through CT, X-radiography, and FIB tomography is in a large, unprocessed format, usually as a folder including thousands of images. The volume of collected data can range from tens of GB to hundreds of TB in size. For this reason, manual processing is impractical. Furthermore, much of this data requires substantial work to extract any quantitative results. This includes image registration (*i.e.*, alignment), segmentation (*i.e.*, partition of features), and threedimensional reconstruction. For this reason, much of this dissertation focuses on various techniques which we used to process our data.

4.1 Processing procedure for X-radiography

The high temporal resolution offered by X-ray radiography enables us to observe the evolution of the solid-liquid interfaces during solidification. We employed MAT-LAB [\[199\]](#page-287-0) to process the projection images, with the aim of enhancing contrast between solids and liquids, thereby enabling us to measure reliably the morphology of the solid/liquid interface and its propagation over time. This involves normalizing each image to eliminate detector artifacts, achieved through a pixel-by-pixel division between a image of interest and a 'background' image [\[200\]](#page-287-1). Two forms of normalization are used: so-called constant division and sequential division [\[58,](#page-276-0) [59,](#page-276-1) [200,](#page-287-1) [201\]](#page-287-2). In

constant division, each image is divided by the same background image of an entirely liquid sample to illuminate the solidified products. Meanwhile, sequential division is used to capture an area of the image swept by the solid-liquid interface by dividing each image N by a previous image $(e.g.N - 10th$ one). Provided that the temporal increment between the two images is small, sequential division allows us to visualize the solid-liquid interfaces. These two procedures are shown in Figs. [4.1](#page-110-0) A. Additionally, we constrain the pixel intensity values to within four standard deviations of the mean, thereby addressing random dead pixels on the detector.

To further enhance contrast we implemented two additional operations. First, we applied a non-local means filter [\[202\]](#page-287-3) to the normalized frame, effectively eliminating speckle noise while preserving edges. Additionally, we created a 'stacked' image by combining a set number of normalized and filtered images into a single image. Each pixel in the stacked image represents the sum of the corresponding pixels in the same spatial location within each image in the stack. An image processed by these two supplemental procedures is shown in Fig. [4.1](#page-110-0) B. Finally, we segmented or partitioned the phases in the stacked image using Otsu's method [\[203\]](#page-287-4). Otsu's method determines ideal image-intensity-based threshold limits by maximizing the inter-class variance, σ , described by the equation

$$
\sigma^2 = W_0 W_1 (\mu_0 - \mu_1)^2 \tag{4.1}
$$

where W_0 and W_1 are the class probabilities, and μ_0 and μ_1 are the class means. For the image shown in Fig. [4.1](#page-110-0) B, we used a threshold of 130 on a scale of 1-255 to segregate the eutectic phase, as indicated by the red line on the histogram. Otsu's method by itself is often insufficient for a crisp segmentation. Following segmentation, we employed a variety of morphological operations such as image dilation, erosion, masking, and/or the application of filters to clean up the image. A segmented image

which has undergone this process is shown in Fig. [4.1](#page-110-0) C.

For certain materials, Otsu's method proved insufficient for segmentation of projection images and/or reconstructed ones. To address this limitation, we employed pixel-based CNN method for image segmentation (refer to Section [4.4.2\)](#page-116-0).

4.2 Processing procedure for X-ray tomography

X-ray tomography data sets consist of projections captured over a 180° rotation. We use Tomopy, a Python-based open-source tool, to process this data into a stack of reconstructed, cross-sectional slices [\[23\]](#page-273-0). The process involves normalizing the data using flat-field (no object/sample) and dark-field (no X-ray beam) images, attempting to eliminate 'ring' artifacts caused by issues like dead pixels or X-ray beam instability. Various algorithms are applied for artifact correction, such as the Nghia Vo approach for stripe removal in the sinogram space due to dead pixels [\[204\]](#page-287-5). Subsequently, we used reconstruction algorithms like Gridrec [\[205\]](#page-287-6), which employs Fourier-based remapping. Detailed information can be found in Ref. [\[23\]](#page-273-0) and reference therein. To improve the low signal-to-noise ratios, we applied the Parzen-filtered back projection (FBP) algorithm. Like many other smoothing filters, the Parzen filter works by reducing high frequency noise through a cut-off frequency in Fourier space [\[206\]](#page-287-7). The Parzen filter is a low-pass filter, reducing noise, but degrading image resolution [\[207\]](#page-287-8). The resulting grayscale slices depict the reconstructed X-ray attenuation coefficients through the material. Common steps for registration and segmentation, discussed in Sec. [4.1,](#page-108-0) follow. Finally, the fully segmented image stack can be converted into 3D using techniques like the marching cubes algorithm [\[208\]](#page-287-9).

Figure 4.2: Psuedo-4D approach performed on an Al-Al₂Cu eutectic: wherein an (a) in situ X-ray projection radiograph captures the moving solid-liquid interface (red line) and an (b) ex situ tomograph to resolves the microstructure evolution. Al is shown in blue and Al_2Cu in yellow. (c) shows the interpolated solid-liquid interface within the tomographic volume to create a psuedo-4D dataset. Figure taken with permission from Ref. [\[17\]](#page-273-1).

4.3 Pseudo-4D data fusion procedure

Dynamic processes, like solidification, often unfold too rapidly for true fourdimensional X-ray tomography, which involves three spatial dimensions and time. To address this, we combine the high temporal resolution of X-radiography with the enhanced 3D spatial resolution of postmortem X-ray tomography. Imaging samples with a thickness of $\leq 100 \ \mu m$ allows us to assume negligible microstructural changes in that spatial dimension. Consequently, the solid/liquid interface tracked with Xradiography can be interpolated onto a postmortem X-ray tomography reconstruction, providing a pseudo-4D perspective of the solidification process. This process is shown in Fig. [4.2.](#page-112-0) By doing so, we assume no tilt of the solidification front with respect to the X-ray beam, and also no pronounced evolution of the microstructure between the X-radiography and tomography scans (done in series). In this approach, temporal resolution is only limited by the camera's framerate. Additionally, this technique eliminates convection induced by sample rotation, a challenge in true 4D X-ray tomography. More details can be found in Ref. [\[17\]](#page-273-1).

4.4 Machine learning

Machine learning (ML) is a blanket term for an area of computer science that aims to emulate human learning in a computer by leveraging provided data and algorithms [\[209\]](#page-287-10). The objective is for the computer to iteratively enhance its ability to develop potential solutions to a given problem. In recent years, the application of ML has expanded into various fields [\[210\]](#page-287-11), including biology [\[211\]](#page-287-12) and genetics [\[212\]](#page-288-0). In our studies, we leverage the capabilities of two ML approaches—genetic algorithms (GA) [\[213\]](#page-288-1) and neural networks [\[60\]](#page-276-2) with application to solidification and materials science more broadly. This section provides background information on both techniques and their utilization in this dissertation.

4.4.1 Genetic algorithms

Genetic algorithms (GA) represent a class of problem-solving models inspired by evolution [\[19,](#page-273-2) [213\]](#page-288-1). Solutions are encoded as chromosome-like attributes, which evolve to enhance their accuracy based on a designated fitness function. The execution of a GA involves introducing an initial population of potential solution candidates into the system's search space as genotypes—a binary representation of search elements used for future reproduction stages. Through genotype-phenotype mapping (GPM), this population is transformed into phenotypes (elements in solution space), which are tested against the developed objective function to assess their fitness value. In essence, genotypes and phenotypes represent the same potential solution differently. The GA employs genotypes for internal processing and gene manipulation (limiting user interaction), while phenotypes serve the user's understanding and interpretation of the solution.

Parents of subsequent generations are selected through a weighted method favoring genotype-phenotype pairs with better fitness values, while still allowing the possibility for less favorable solutions to be chosen. In our work, a universal stochas-

Figure 4.3:

Aspects of the genetic algorithm illustrating A) parent selection utilizing *universal stochastic sampling*, and \bf{B}) reproduction involving random mixing and mutation.

tic sampling method [\[19,](#page-273-2) [213,](#page-288-1) [214\]](#page-288-2) was employed to select parents. The line plot provides a useful illustration of this procedure: the length of the line for each parent is proportional to its fitness score (Fig. [4.3A](#page-114-0)). The line plot is subdivided into n segments, each delineated by uniformly spaced increments corresponding to the population size (n) . These segments serve as the basis for determining the configuration of the next generation. This sampling approach reduces the likelihood of converging to local minima.

Paired parent solutions generate offspring through a system-specific mixing algorithm, replacing a select percentage of the worst solutions from the current generation. A universal crossover approach is utilized (Fig. [4.3B](#page-114-0)), randomly mixing various components from the selected parents' genotypes [\[214\]](#page-288-2). The produced children undergo varying degrees of mutation before finalizing the next generation (Fig. [4.3B](#page-114-0)). The cycle repeats until a tolerance threshold is met, such as failing to leave a minima for a set number of iterations or reaching the maximum number of iterations.

The selected approach for incorporates a weighted Gaussian centered at zero, reducing in scale with each subsequent iteration to prevent mutations outside a global minima and encourage convergence [\[215\]](#page-288-3). In this manner, GA explores the solution space to find a global minima, providing the best answer to the unknown problem with minimal initial information.

In one application of GA, we employed it to predict the three-phase coupled zone of the Al-Ag-Cu ternary system in composition-velocity space by solving a set of unknown kinetic constants (i.e., the proportionality factors between veloicty and undercooling, see Eqns. [2.8](#page-61-0) and [2.9\)](#page-61-1). In this context, the genotypes and phenotypes both correspond to the kinetic constants. The former employs a binary structure, hidden from the user, allowing for crossover and mutation operations. Meanwhile, the latter takes the form of numerical values, used to compute undercooling. Further details of this approach are elaborated in Chapter [V.](#page-120-0)

A second application of GA was in the registration of X-ray tomography reconstructions. Samples often exhibit inherent tilt, misalignment, or bending along their height, stemming from various sources such as residual mechanical strain, nonorthogonal FIB milling, tilt of the alumina rod within the kinematic mount, and more. Registration is a crucial post-processing step [\[182\]](#page-285-0) to investigate microstructural connectivity, distinguish real and artificially tilted features, reduce data size for ease of analysis, and/or investigate evolution of microstructure over time (in *in situstudies*). However, samples may not uniformly shift throughout the entire field-of-view, making manual registration slow and laborious. GA-based registration offers a robust approach to overcome these challenges [\[216,](#page-288-4) [217\]](#page-288-5). In our work, our GA-based registration algorithm shifts each image to maximize its fitness function. In this context, the genotypes and phenotypes represent the shifts along the coordinate axes used to minimize their difference with a reference image.

4.4.2 Neural networks

Neural networks (NN) function as interconnected layers of nodes, akin to neurons in the brain [\[209\]](#page-287-10). These layers, including input, hidden, and output layers, organize the network's nodes. Within this realm, Convolutional Neural Networks (CNNs) stand out as a specialized subclass adept at image analysis and segmentation [\[60,](#page-276-2) [218,](#page-288-6) [219\]](#page-288-7). In a CNN, the input image undergoes examination through convolutional layers, where convolutional filters or kernels scour the image for distinct features such as edges and textures. The gathered insights are then pooled, facilitating the network in emphasizing significant features while downplaying less relevant ones. Activation functions introduce non-linearity, helping the network learn intricate mappings. Pooling layers contribute by reducing dimensionality, optimizing computational efficiency. Finally, fully connected layers interconnect the network's insights, enabling it to categorize findings across the entire image. Like genetic algorithms, CNNs necessitate training data to assess input images [\[60\]](#page-276-2).

In our work, CNNs play a vital role in segmenting complex datasets with varying pixel values for the same phase, such that conventional segmentation techniques fall short. We use the Zeiss Zen Blue 3.1 with the Intellesis deep learning module developed by Carl Zeiss AG [\[220\]](#page-288-8). The software develops an operational recipe from approximately 15 manually segmented images used as training data. Subsequently, the system can segment an entire dataset based on the learned model, albeit with some residual noise. It employs a *random forest classifier* to classify each pixel in the image. In a random forest classifier, decision trees try to identify accurate predictions based on various qualifiers $(e.g.,$ pixel thresholds). While single decision tree can easily impose bias and given incorrect results, by combining several decision trees into a forest and making a selection based on the majority outcome, the random forest model can improve overall accuracy [\[221\]](#page-288-9). A schematic of the random forest model the Intellesis module uses is given in Fig. [4.4.](#page-117-0) In addition to segmented images, the

Figure 4.4: Random forest workflow used by the Zeiss Zen Blue 3.1 software. A collection of decision trees classify the chosen pixel. The final pixel classification and the confidence index is determined by majority rule. Image adapted from Ref. [\[18\]](#page-273-3).

software also produces a confidence map which displays the degree of certainty the CNN has for each pixel classification. The lack of clarity of the phase-interfaces may be subsequently improved by applying a median or average filter [\[222\]](#page-288-10) in MATLAB. Further information can be found in Sec [7.2.3.](#page-182-0) The complete workflow for segmentation is shown in Fig. [4.5.](#page-118-0) For more details on the Intellisus software, we refer the reader to Ref. [\[18\]](#page-273-3).

Figure 4.5: Complete workflow for image segmentation in the Zeiss Zen Blue 3.1 software. The left column shows the procedure for training segmentation recipes. The right column describes the segmentation procedure using the trained recipe. Image adapted from Ref. [\[18\]](#page-273-3)

Part II

Experimental Results and Discussion

CHAPTER V

Accelerated Discovery of the $Al-Ag_2Al-Al_2Cu$ Eutectic Coupled Zone Through Genetic Optimization

This chapter is based on the article published in Journal of Alloys and Compounds [\[223\]](#page-288-11).

Abstract: Microstructure control in multi-component alloy systems is made complicated by the multiplicity of phases as well as the non-equilibrium nature of solidification. In particular, primary phases in a eutectic matrix may have a detrimental effect on the properties of the cast state. Instead of searching for wholly eutectic microstructures within a vast combinatorial space, we harness genetic algorithms (GA) to identify the stability field (coupled zone) of the three-phase $\text{Al-Ag}_2\text{Al-Al}_2\text{Cu}$ eutectic, using previously reported observations as input. The output maps of the coupled zone have an accuracy of greater than 85% when compared against experimental data. In parallel, we conducted our own directional solidification (DS) experiments in order to assess the validity of our models. GA predictions of the eutectic coupled zone were further refined by incorporating our experimental observations into the constitutive growth laws. Our iterative approach of GA and DS not only improves the accuracy of the shape of the eutectic coupled zone in composition-velocity space,

but also provides predictions on the microstructures of Al-Ag-Cu alloys where no such observations exist.

5.1 Introduction

Recent need for complex materials in engineering, such as in the areas of metamaterials and semiconductors, has increased our interest in multi-phase systems and especially that of eutectics [\[38\]](#page-274-0). The properties and microstructures within these selfassembled composited are greatly influenced by their solidification and processing pathways [\[49,](#page-275-0) [62\]](#page-276-3). When investigating such materials, knowledge of phase stability is critical to manufacture a desired microstructure, e.g., fully eutectic or a combination of primary phases plus eutectic. In eutectic systems, one such aspect is its coupled zone that lies beneath the eutectic point. This region of the phase diagram indicates the range of compositions that form wholly eutectic microstructures under predetermined growth conditions [\[119\]](#page-281-0). These growth conditions strongly influence the microstructure selection due to the non-equilibrium nature of alloy solidification. Systems grown outside of the coupled zone develop single phase dendrites whose undercooling is less than that of pure eutectic.

Through the use of directional solidification (DS) experiments, under which the interfacial velocity and thermal gradient are controlled, the coupled zone for a variety of binary alloys containing Al, Fe, and Ni, have been determined [\[224,](#page-288-12) [225\]](#page-288-13). Results from DS experiments have been justified on the basis of constitutive models derived by Jackson and Hunt (hereafter abbreviated as J-H) and Bruden and Hunt (B-H) to find eutectic and primary dendritic undercooling as a function of interlamellar spacing and inferface velocity [\[74,](#page-277-0) [79,](#page-277-1) [93\]](#page-278-0). A complete knowledge of how all structures grow within the system allows for a determination of the coupled zone. The J-H and B-H models thus provide fundamental starting points to predict eutectic growth (Eqn. [\(5.1\)](#page-122-0)) and primary dendritic growth (Eqn. [\(5.2\)](#page-122-1)), respectively,

$$
\Delta T_E = 2\sqrt{K_1 K_2} \sqrt{V} \tag{5.1}
$$

$$
\Delta T_D = \frac{G\tilde{D}}{V} + 2[-\frac{2aV}{\tilde{D}}(m(1-k)C_{\infty} + \frac{kG\tilde{D}}{V}]^{1/2}
$$
(5.2)

where ΔT_E is the undercooling of the eutectic (itself composed of solutal and capillarity contributions), V is the interface velocity (controlled *via* DS), K_1 and K_2 are constants, ΔT_D is the undercooling of primary dendrites, G is the thermal gradient, a is the Gibbs-Thomson coefficient, k is the distribution coefficient, m is the liquidus slope, and \tilde{D} is the interdiffusion coefficient. Both growth laws assume low Péclet numbers.

While the coupled zones of two-phase eutectics have been reasonably well investigated, three-phase eutectic systems have proven to be far more challenging to predict [\[38\]](#page-274-0). This is attributed to the higher degree of freedom resulting from additional elemental components. Thermodynamic factors such as distribution coefficients and liquidus slopes, which are considered constant within binary systems, now vary with composition throughout the coupled zone. Increased variety in growth morphologies and stable phases also affect the microstructural complexity. The multiplicity of components, phases, and morphologies results in computational challenges down the line when attempting to predict microstructural stability fields. Therefore, extensive experimental work is required to accurately interpret the coupled zones of three-phase eutectics.

McCartney *et. al.* [\[6\]](#page-272-0) developed a theoretical model based on the phenomenology two-phase eutectic systems, to predict phase stability of cellular primary growth in three-component systems. This model for eutectic growth mirrors that which was derived by Burden and Hunt for binary cellular or dendritic growth, now with the

addition of a third component. Recent models expanded on these ideas to predict the interface temperatures associated with three-phase cellular growth [\[123\]](#page-281-1), three-phase planar growth [\[106\]](#page-280-0), and two-phase cellular growth within a three-phase system [\[91,](#page-278-1) [125\]](#page-281-2). Others have expanded upon the J-H model to model directional solidification of a generic multi-component, multi-phase eutectic alloy [\[226\]](#page-289-0). Despite their differences, all models generally agree on the $\Delta T \propto V^{1/2}$ relationship for not only the single and two-phase growth modes, but also three-phase planar and cellular eutectic growth modes.

Though theoretical expansions or re-imagined models for multi-phase eutectic growth have been developed, limited work has been done to experimentally determine the coupled zone for three-phase eutectic systems, likely due to the exponential increase in data points needed to accurately map competitive growth at a single growth velocity. One of the few systems in which microstructural data has been measured *via* DS experiments is the Al-Ag-Cu ternary system, which forms a three-phase eutectic of α -Al, Ag₂Al, and Al₂Cu below the eutetic temperature of 500.45 °C. The eutectic point is also surrounded by large single-phase fields. In particular, McCartney and Hunt considered interface velocities, V, of 0.64, 0.063, and 0.0056 mm/s and a constant thermal gradient, G, of approximately $12\degree C/\text{mm}$ [\[20\]](#page-273-4) when investigating the Al-Ag-Cu system. On the basis of their experimental observations, the team predicted a three-phase eutectic coupled zone that expanded with increasing V [\[6\]](#page-272-0).

In this manuscript, experiment, theory, and computation are unified into a cohesive framework that delivers a model of coupled three-phase eutectic growth in the Al-Ag-Cu alloy system. A key strength of our approach is the use of genetic optimization, a machine learning approach that enables the calculation of various growth coefficients from existing experimental data and ultimately the full extent of the eutectic coupled zone in processing-composition space. That is, we succeed in predicting the boundaries of the three-phase eutectic coupled zone under solidification conditions where no experimental observations exist, to the best of out knowledge. The boundary positions are further refined by incorporating our experimental observations into constitutive models. This paper highlights the resulting calculations and examines the potential of machine learning in exploring the stability fields within non-equilibrium microstructures.

The article is divided in a number of sections. First, we present a brief background of genetic optimization. Second, we demonstrate our use of genetic optimization to calculate the three-phase coupled zone within the Al-Ag-Cu system. Third, we discuss the experiments conducted in order to compare with the produced model of the coupled zone. Last, we integrate the computed and experimental results before drawing final conclusions.

5.2 Genetic Optimization

5.2.1 Introduction

In recent years, machine learning (ML) techniques have branched into many fields of scientific study. Due to the flood of data on the structure of cast metals, we believe solidification science is an ideal field to apply such computational tools. The ability of ML to find patterns in observed data makes it possible to model kinetic relationships and coefficients that are as yet unknown $(e.g., K_1 \text{ and } K_2 \text{ in Eqn (5.1)})$ $(e.g., K_1 \text{ and } K_2 \text{ in Eqn (5.1)})$ $(e.g., K_1 \text{ and } K_2 \text{ in Eqn (5.1)})$. To derive the three-phase coupled zone (here-on only referred to as the coupled zone) for the Al-Ag-Cu system, the ML method of genetic algorithms (GA) was selected as the technique of choice. As will be explained below, GA is one class of evolutionary ML algorithms that use ideas inspired by natural evolution in order to evolve a population of possible solutions to a given problem. GA was chosen for a variety of reasons including its simplicity, ability to work with limited information/parameters, and potential to mutate out of local minima (*vide infra*) unlike some other contemporary techniques

Figure 5.1: Genetic algorithm (GA) logic path: General schematic of the GA logic path, adapted from Ref. [\[19\]](#page-273-2). Solid arrows indicate the path in which the machine follows directly. The system starts with an initial population of random solutions represented by binary strings called genotypes. These genotypes are mapped on to the solution space and converted into phenotypes which are subsequently appraised/ranked through a fitness function. A select percentage of highly ranked genotype-phenotype pairs go through various crossover and mutations to generate a new population. The cycle is repeated until the system cannot mutate out of a minima or no global minima is found in a select number of iterations.

such as simple hill climbing. The latter technique is computationally more efficient but can often reach undesirable or incorrect solutions [\[19\]](#page-273-2). Other global optimization techniques, including simulated annealing, were also considered with produced results being comparatively less accurate than GA.

GA operates through the evolutionary selection of solutions based on derived fitness values which rate candidates on their likelihood to best solve the proposed problem. The problem, in our case, can be stated as, "Where lie the boundaries of the three-phase eutectic, two-phase eutectic, and primary dendrite stability fields in composition-processing space, given a limited set of experimental measurements?" To solve this problem, we follow the GA flowchart in Fig. [\(5.1\)](#page-125-0), adapted from Ref. [\[19\]](#page-273-2). Populations are read in to the system's search space as *genotypes*, a binary representation of the search element that is used for future reproduction stages. Through genotype-phenotype mapping (GPM), the population is converted to phenotypes (elements in solution space) which are tested against the developed objective function to identify their fitness value. Parents of subsequent generations are chosen through a weighted selection method that favors *genotypes* with better fitness values, while still allowing the possibility for unfavorable solutions to be picked. It is this feature that reduces the likelihood of a final solution being found within local minima. Paired parent solutions generate offspring through a system-specific mixing algorithm that in turn replaces a select percentage of the worst solutions from the current generation. Finally, produced children undergo varying amounts of mutation before the next generation is finalized and the cycle can repeat until a tolerance threshold is attained, e.g. the system fails to leave a minima for a set number of iterations or the maximum number of iterations is exhausted. In this manner, GA can "explore" a solution space to find a global minima resulting in the best answer to the unknown problem with minimal initial information. Below, we translate our problem into the vernacular of GA. Of particular importance is the representation of individuals and their fitness. Details on our implementation of GA, including methods used for sampling, crossover, and mutation, are given in Appendix A.

5.2.2 Individuals and their Fitness

The fitness function measures the accuracy of a generation's phenotypes and ranks them next to other potential solutions. In our proposed system, the individual phenotypes of each generation are specific growth coefficients that are used to calculate the interface temperature of each possible growth form (vide infra). To construct the most accurate stability field map of the Al-Ag-Cu system, the phenotypes with the least error (highest fitness) need to be computed.

The fitness function for the coupled zone calculation is based upon the determined interface temperature of each phase at a given V and G . According to the competitive growth principle of metastable thermodynamics, the phase with the highest interface temperature should dominate the microstructure and thus indicate where about the coupled zone the sample is located [\[120\]](#page-281-3). In order to determine the interface temperature (T^*) , we require expressions for the liquidus temperature (T_L) and undercooling $(\Delta T = T_L - T^*)$. The former can be expressed as a second-order polynomial whose quadratic terms help resolve non-linear dependencies along the single-phase liquidus plane. Applying values determined from Thermo-Calc by Witusiewucz et. al. [\[21\]](#page-273-5), equations were developed for the three liquidus planes and three phase boundary lines (Table [5.1\)](#page-128-0). These were used to map the liquidus temperatures of the Al, $Ag₂Al$, and $\rm Al₂Cu$ primary phases at varying compositions (Fig. [5.2\)](#page-129-0) along with each two-phase eutectic boundary line. The calculated three-phase eutectic point was found to be located at a temperature of 509.8 °C and a composition of Al-40.3 wt%Ag-21.8 wt%Cu.

As for the interface undercooling, we are faced with a challenge: thermodynamic parameters such as the distribution coefficient, k, which are only mildly dependent upon composition in binary systems, are now heavily impacted with the introduction of a third component. To utilize genetic algorithms in the determination of the coupled zone, a number of specific assumptions were made to work around this compositional dependency. First, there was no planar growth observed in the vicinity of the eutectic point [\[6\]](#page-272-0) and thus the $k\tilde{G}D/V$ term can be dropped without any loss of generality; second, the undercooling is assumed dependent solely on the interface velocity, temperature gradient, interdiffusivity, and a yet unknown growth coefficient; and lastly the interdiffusivity was assumed constant (due to the lack of diffusion data). By invoking these three assumptions, the underlying models for eutectic (E) and dendritic (D) growth in a ternary system reduce to the aforementioned J-H and B-H models for binary eutectic systems, respectively (see Eqns. [5.1](#page-122-0) and [5.2](#page-122-1) and Ta-ble [5.1\)](#page-128-0). Here the set of growth coefficients $(A_1, A_2, A_3, A_4, A_5, A_6, \text{ and } A_7)$ represent the phenotype. Despite these obvious simplifications, we hypothesize that the general layout of the formulated coupled zone will provide a good approximation of the true

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Figure 5.2:

Eutectic valley in Al-Ag-Cu: Liquidus planes (T_L) for Al (green), Ag₂Al (red), and $Al₂Cu$ (blue) phases as found by the equations shown in Table [5.1.](#page-128-0) The black point identifies the location of the predicted three-phase eutectic point while the gray plane shows the eutectic temperature.

coupled zone with higher accuracy near experimental interface velocities used in the calculation.

By integrating the liquidus plane/line and undercooling equations, we were able to perform the GPM and develop a fitness function to score each generation's phenotype. At a given interface velocity and thermal gradient, the stable phase would be determined by simply identifying the maximum interface temperature and determining to which phase it belonged. A graphical representation of this idea can be seen in Fig. [5.3](#page-131-0) for V of 0.64 mm/s and 0.063 mm/s and a G of 12 $°C/mm$. In practice, an interdiffusion coefficient, \tilde{D} , of 5.0 x 10⁻³ mm²/s was taken from work done by Himimaya and Umeda [\[106\]](#page-280-0). These calculations would be determined for each of compositions for which experimental data is given by McCartney et. al. [\[20\]](#page-273-4) and compared to the actual phase observed. Fitness is then computed as the percentage of accurately determined data points such that the most accurate phenotype is the one with the highest fitness.

5.2.3 Results

When the developed GA was used for a V of 0.64 mm/s and G of $12\degree\text{C/mm}$, sixteen separate combinations of growth coefficients were found to accurately predict 92.5% of the 41 experimental data points from Ref. [\[20\]](#page-273-4) (see Fig, [5.9a](#page-147-0)). One such combination of coefficients is shown in Table [5.2.](#page-133-0) Using this particular set of coefficients, we are now positioned to map the coupled zone (see Fig. [5.4a](#page-132-0)). The results suggest that, under these DS conditions, a three-phase eutectic is stable within \pm 0.03 wt% of the eutectic point.

Points of error within the model were found to all lie along boundary edges with the correct phase. Upon closer inspection, the interface temperature of the correct (actual) phase was less than $10\,^{\circ}\text{C}$ below that of the GA-predicted phase. A box-andwhisker plot comparing the values of the 16 sets of growth coefficients is shown in

Figure 5.3: Stable phase determination through minimum undercooling: Genetically optimized interface velocities vs. interface temperatures for Al-41.6 wt%Ag-23.6 wt%Cu at $G = 12 °C/mm$. Thick lines identify the structures that exhibit the highest freezing temperature at $V = 0.64$ mm/s and 0.063 mm/s (see dashed lines). Above a critical velocity of 0.175 mm/s (where the blue curve crosses the purple), the stable growth for transitions from Ag_2Al-Al_2Cu (purple) to Al_2Cu (blue). This particular velocity delineates the boundary of the three-phase coupled zone.

Figure 5.4: Computed coupled zone for $Al-Ag_2Al-Al_2Cu$: GA calculated maps of coupled zone for $G = 12 \degree C/\text{mm}$ and (a) $V = 0.64 \text{ mm/s}$ and (b) 0.063 mm/s. (c) Three-phase eutectic coupled zone constructed through parameters calculated pertaining to V of 0.64 mm/s and G of $12\degree\text{C/mm}$, rendered in 3D composition-velocity space. The model has been centered vertically at the same velocity. (d) Top-down view of the coupled zone to highlight anisotropic expansions of three-phase stability field into different regions. (e) Three-phase coupled zone constructed through parameters calculated for V of 0.64 mm/s and G of $12\degree C/\text{mm}$ with the inclusion of a kinetic undercooling term, rendered in 3D composition-velocity space. The model has been centered vertically at the same velocity. (f) Topdown view of the coupled zone. Notable increase can be seen in the width of Al-Al₂Cu (cyan) and Ag₂Al-Al₂Cu (purple) boundaries and further outward expansion of the Al_2Cu primary phase (blue) with the introduction of a kinetic term in the expression for the undercooling of primary $Al₂Cu$. See Discussion for details.

Interface Velocity, V (mm/s)	0.64	0.063
Fitness Value (Fraction Correct)	38/41	20/23
A ₁ , Al-Ag ₂ Al-Al ₂ Cu (°C $s^{1/2}$ mm ^{-1/2})	4.17(6)	1.69(2)
A_2 , Al (°C $s^{1/2}$ mm ^{-1/2})	25.7(7)	61.2(6)
A ₃ , Ag ₂ Al (°C $s^{1/2}$ mm ^{-1/2})	47.1(6)	95.3(8)
A_4 , Al ₂ Cu (°C $s^{1/2}$ mm ^{-1/2})	10.8(8)	7.76(7)
A ₅ , Al-Ag ₂ Al (°C $s^{1/2}$ mm ^{-1/2})	14.32	13.9(0)
A ₆ , Al-Al ₂ Cu (°C $s^{1/2}$ mm ^{-1/2})	7.66(1)	8.93(0)
A ₇ , Ag ₂ Al-Al ₂ Cu (°C $s^{1/2}$ mm ^{-1/2})	32.4(0)	60.3(9)

Table 5.2: Example growth coefficients and fitness values

Fig. [5.5.](#page-134-0) Despite the large diversity of predicted solutions and the stochastic nature of genetic optimization [\[213\]](#page-288-1), the consistency in scale between the various growth coefficients and their relative magnitudes (e.g. the higher value corresponding to $Ag₂Al$ and lower value of $Al₂Cu$) was ever present within our results. That is, our approach is robust under repeated application of GA.

We also preformed calculations of the growth coefficients for V of 0.063 mm/s and G of 12° C/mm and found a solution with 87.0% accuracy (Table [5.2\)](#page-133-0) for 23 experimential data points from Ref. [\[20\]](#page-273-4) (see Fig. [5.9b](#page-147-0)). A coupled zone with the listed parameters was also generated (Fig. [5.4b](#page-132-0)). While the specific values of the growth coefficients are quite varied from those found for V of 0.64 mm/s, similar trends are seen between the phases. This further suggests some statistically significant correlation between the thermophysicial parameters hidden within the growth coefficients (see Discussion).

To further investigate the coupled zone, a three-dimensional interpolation of the derived equations with the vertical axis corresponding to interface velocity centered about $V = 0.64$ mm/s was constructed. The smallest calculated growth coefficients were chosen from the best fit solutions for said V . Calculations for the nearby velocities also used these parameters as it was hypothesized that constants for velocities of similar orders-of-magnitude would be similar in scale/value. The resulting construc-

Figure 5.5: Computed growth coefficients: Box-and-whisker plot of determined growth coefficients for $V = 0.64$ mm/s with single-phase (red), two-phase (green), and three-phase (blue) values grouped together.

tion, as seen in Fig. [5.4c](#page-132-0) (side view) and [5.4d](#page-132-0) (top view), shows the boundaries of the three-phase coupled zone going from a V of 0.4 mm/s to 0.9 mm/s . The inner locus of the colored planes/boundaries represents the velocities and compositions for which a wholly three-phase $Al-Ag_2Al-Al_2Cu$ eutectic is predicted. Colors represent the growth forms that are stable on the other side of the coupled zone as V increases. The size of the three-phase coupled zone with increased velocity indicates the expansion of the three-phase eutectic stability field into the off-eutectic phases, similar to that typically observed in DS experiments [\[20\]](#page-273-4). Anisotropic behavior can be seen in the Al, Ag₂Al, and Ag₂Al-Al₂Cu boundaries expanding outward while the Al-Al₂Cu and $\rm Al-Ag_2Al$ boundaries are relatively stationary with increased V. Again, these trends mirror that which are seen when comparing the experimental work with the sole exception of the $Al₂Cu$ phase. The predicted $Al₂Cu$ stability field fails to expand outward (see Fig. [\(5.4\)](#page-132-0)), while simultaneously over-stretching the coupled zone boundary length compared to the experimental expectations [\[20\]](#page-273-4) (see Fig. [5.9\)](#page-147-0). The predicted 3D stability zone becomes notably less accurate the farther away from the centered interface velocity of 0.64 mm/s (e.g. the Ag₂Al primary phase disappears at low V). Nevertheless, the shape of the coupled zone agrees well with theoretical predictions [\[3,](#page-272-1) [63\]](#page-276-4).

5.3 Experimental

5.3.1 Sample Preparation

To verify the trends seen in the GA produced model, high purity samples (99.999% Al, 99.999% Ag, and 99.999% Cu) were aquired from the Materials Preparation Center at Ames Laboratory (Ames, IA, USA), which is supported by the US DOE Basic Energy Sciences, with a composition of Al-42.2 wt%Ag-17.6 wt%Cu through vacuum arc remelting. Cylindrical rods of 0.5 mm diameter and 5 mm length were cut from the

cast ingot and solidified in a vertical three-zone Bridgeman furnace (MTI Corporation EQ-SKJ-BG). In such thin samples, the effects of radial convection have been shown to be negligible [\[227\]](#page-289-1). The molten samples were held within a boron nitride crucible. The thermal gradient, G, was imposed onto the fully molten sample by independently fixing the temperatures of the three-zones. A cooling rate, \dot{T} , was directly applied to impose a growth velocity V based on the relation $\dot{T} = GV$ in a process known as *gradient freeze.* Samples were solidified at G of \pm 0.4 °C/mm for V of 0.063 mm/s and 0.64 mm/s. Here, positive G indicates the thermal gradient is antiparallel to gravity, q , while negative G is the converse.

Following DS, samples were cut and polished along the longitudinal plane for subsequent microstructural examination (*i.e.*, G and q run along the field-of-view). Analysis of the developed microstructure was performed through scanning electron microscopy (SEM). Electron backscatter diffraction (EBSD) was done on a few notable single phase dendrites found within the samples to investigate their crystallographic orientations.

5.3.2 Results

Composite SEM images of the samples were constructed so as to investigate the progression of growth along the direction of the thermal gradient. Figs. [5.6a](#page-138-0) and [5.6b](#page-138-0) show the effects of positive and negative thermal gradient on eutectic stability within the $V = 0.063$ mm/s grown samples, respectively. Under the positive thermal gradient, the sample displayed some primary $\rm Al_2Cu$ dendritic phases (light gray) at initial and terminal stages of DS $(i.e.,$ near the bottom and top of the cylinder sample, respectfully) (Fig. [5.6a](#page-138-0) (ii)), but generally appeared to be constructed of a fine, three-phase eutectic microstructure composed of α -Al (dark gray), Al₂Cu, and Ag₂Al (white) (Fig. [5.6](#page-138-0) a, (i)). The primary Al_2Cu dendrites grew along the direction of the thermal gradient in the form of faceted and rectangular shards. Examining the sample solidified under a negative thermal gradient (Fig. [5.6](#page-138-0) b (iii - vi)), a plethora of single, two, and three-phase regions are visible across the microstructure, despite the alloy composition being within the expected three-phase coupled zone. Numerous A_2 Cu primary phase dendrites along with two-phase eutectic A_1 - A_2 A_1 can be seen throughout the sample $(\alpha$ -Al and Ag₂Al primary dendrites were also observed in similarly grown samples, refer to Supplementary Information (SI) redin Appendix B (Fig. [5.10\)](#page-147-1)). Surrounding these regions is a thick web of three-phase eutectic with a wide range of morphologies across the entire surface including 'chain-like' regular, crossed, and irregular structures $[22]$. Unlike the case with positive G, we do not detect any stabilization of the three-phase eutectic morphology as DS progressed. In other words, steady-state three-phase eutectic growth cannot be maintained when $g \parallel G$. Similar trends were noted for samples solidified with positive and negative G and a higher V of 0.64 mm/s (see Appendix B).

The faceted and directional nature of the primary $Al₂Cu$ dendrites motivated us to examine their crystal structures in greater detail. EBSD results on an $\text{Al}_2\text{Cu primary}$ dendrite (Pearson symbol: $tl12$) formed under $G = +0.4 °C/mm$ and $V = 0.64$ mm/s revealed that the crystals grew along [001] and are bounded by {110} habit planes (Fig. [5.7](#page-139-0) (a)).

The anisotropic morphology of the $Al₂Cu$ phase might arise due to cusps on its equilibrium or kinetic Wulff shapes [\[228\]](#page-289-2). To examine the two possibilities, we compute kinetic and equilibrium crystal morphologies in BIOVIA Materials Studio (Cambridge, UK), using a PCFF force field $(i.e.,$ Lennard-Jones potential in the 9-6 form) [\[229\]](#page-289-3). Following Hartman and Perdok [\[230,](#page-289-4) [231\]](#page-289-5), the kinetic shape assumes the growth rate of the crystal face is proportional to its attachment energy, which is itself calculated from the Donnay-Harker prediction [\[232\]](#page-289-6). That is, faces with the lowest attachment energies are the slowest growing, and therefore, have the most morphological importance. Ultimately, we find that while both equilibrium and ki-

Figure 5.6: Micrographs of directionally solidified Al-Ag-Cu alloy: Overview of sample with V of 0.063 mm/s and G of (a) $0.4\degree\text{C/mm}$ and (b) $-0.4\degree\text{C/mm}$. Magnified sections of sample (a) can be seen in $(i-ii)$ which highlight the three-phase eutectic microstructure and Al_2Cu dendrites (see arrow) found within the final transient. Similarly, magnified sections of sample (b) can be seen in (iii-vi), highlighting the wide range of eutectic morphologies and off-eutectic phases found within the sample.

 Al_2Cu crystal morphology: (a) EBSD IPF image of Al_2Cu dendrite sample solidified at $V = 0.64$ mm/s and $G = 0.4$ °C/mm showing (110) habit plane (see fundamental zone as inset). Direction of positive G is labeled. Simulations of crystal morphology, assuming a (b) growth shape and (c) Equilibrium shape of $Al₂Cu$. Both (b) and (c) were calculated using a 9-6 LJ potential.

netic shapes are highly faceted (Figs. [5.7b](#page-139-0) and [5.7c](#page-139-0), respectfully), our results agree more with predictions of the kinetic Wulff shape, which shows large-area {110} habit planes and a tendency for columnar growth along <100> (Fig. [5.7a](#page-139-0)). This result indicates that the strong faceting of the $Al₂Cu$ dendrites is determined by kinetic limitations at the solid-liquid interface, an insight that can be used to further refine the growth law of the primary Al₂Cu phase (*vide infra*). Despite the fact that the shapes were calculated at 0 K and neglected chemical effects, the simulations showed good agreement with both the literature [\[233–](#page-289-7)[235\]](#page-289-8) and our experimental results.

5.4 Discussion

The GA-calculated model for the coupled zone revealed some notable features regarding phase stability with changing growth velocity. One such characteristic was the size of the primary phase stability fields which grew larger as velocity decreased. For example, as seen in Figs. [5.4a](#page-132-0) and [5.4b](#page-132-0), the region where the Ag_2Al primary phase is dominant (red) expanded in size while the surrounding two-phase (yellow and purple) and three-phase (black) coupled zones receded. This mirrors that of coupled zones determined for binary systems, where the total undercooling required for eutectic solidification is large at lower interface velocities due to the influence of capillarity; thus, the primary phases are instead preferred by the system, in accordance with the competitive growth principle. A notable exception to this trend is the stability field of the Al_2Cu primary phase which changes little in size over the considered velocity range (Fig. [5.4c](#page-132-0) and [5.4d](#page-132-0) (blue)). Given the faceted nature of Al_2Cu , the coupled zone should be skewed in the direction of the Cu constituent. That is, the sluggish kinetics of the faceted $\rm Al_2Cu$ phase should increase the total undercooling of primary $\rm Al_2Cu$ with respect to the other phases so considered.

There are a number of ways to incorporate kinetic limitations on facet planes in the expressions for total undercooling [\[236](#page-289-9)[–239\]](#page-289-10). One route is to add a term representing the kinetic undercooling $(\Delta T_k = V/\mu)$, where μ is the kinetic coefficient of the {110} solid-liquid interfaces in our case). To determine the effect of this term, the model was recomputed whilst utilizing the following equation for the A_2Cu primary phase:

$$
\Delta T_D(V) = \frac{\tilde{D}G}{V} + A_4 \sqrt{V} + \frac{V}{\mu} \tag{5.3}
$$

This growth law thus accounts for capillarity, constitution, and interface kinetics. As a purely qualitative exercise, GA was done using the other coefficients (as retrieved from our first-order predictions), except for coefficients A_4 and μ pertaining to the Al₂Cu primary phase. We obtained nine combinations of A_4 and μ ranging from 1.06-9.18 °C $s^{1/2}$ mm^{-1/2} and 0.062-1.81 mm °C⁻¹ s^{-1} , respectively. These coincide well with those found in Ref. [\[240\]](#page-290-0), who found for FeSi and CoSi binary alloys μ on the order of 0.14-0.21 $mm \text{°C}^{-1} \text{ s}^{-1}$. The resulting second-order predictions of the coupled zone (Figs. [5.4e](#page-132-0) and [5.4f](#page-132-0)) from GA revealed that the two-phase and threephase stability fields opened more at lower interface velocities towards the $\rm Al_2Cu$ constituent, as predicted. The effect of kinetic undercooling, given further investigation, may yield more accurate models of complex, three-phase eutectic growth (as a nonfaceted-nonfaceted-faceted eutectic) and could potentially impact the eutectic morphology in yet unknown ways.

When comparing the calculated values for the growth coefficients, notable trends were found within their magnitudes (see Fig. [5.5\)](#page-134-0). These growth coefficients are directly related to a number of parameters, including the Gibbs-Thomson (a) and distribution coefficients (k) . For instance, both a and k are lower for Al₂Cu compared to Al, and this may account for the corresponding differences in their growth coefficients [\[22,](#page-273-6) [241\]](#page-290-1). However, and in general, one should exercise caution when interpreting the growth coefficients presented in Fig. [5.5.](#page-134-0) This is because the interfacial energies (hence a) and thermodynamic properties (thus liquidus slopes, k , etc.) vary

with alloy composition. That is, in reality, the growth coefficients are compositiondependent. The values that we determine *via* genetic optimization therefore represent compositional averages along the boundaries of the three-phase eutectic coupled zone. Remarkably, despite these simplifications, by using our optimized set of growth coefficients we can achieve a description of the coupled zone that is consistent with experimental observations.

From our proofs-of-concept, we observe that the sample solidified under a negative thermal gradient was unable to achieve steady-state growth. This is likely attributed to the denser solute (Ag) segregating above the hotter liquid. Convection currents are generated continuously as the liquid rises up towards the interface and gravity pulls the solute to the base of the melt (when solidified from the top). This thermal instability is reinforced by the solute boundary layer since the rejected solute is denser than the solvent [\[63\]](#page-276-4). Thus we expect macrosegregation and hence the formation of Ag-rich phases like Ag_2 Al throughout the sample despite the alloy composition being located within the coupled zone and far away from its boundaries. Of note is that Mathiesen and Arnberg similarly observed that directionally solidified Al-Cu alloys grown under a negative thermal gradient were unable to achieve steady-state for these reasons [\[242\]](#page-290-2). Ultimately, the concept of a coupled zone is only valid after establishment of a steady-state in a directional solidification process.

Given that the evidence that steady-state cannot be reached under a negative thermal gradient, the next natural step is to consider its effect on the morphology of the system. While samples solidified under a positive thermal gradient showed a variety of eutectic morphologies, a single eutectic morphology became dominant once steady-state DS was achieved. On the other hand, samples solidified with a negative thermal gradient produced a wide diversity of morphologies. This variation could indicate that morphological selection is sensitive to compositional fluctuations at the growth front, such that the enrichment of Ag changes the solid-liquid interfacial

energy due to increased solubility of Ag in the α -Al phase [\[243\]](#page-290-3). Investigation on the morphological selection of three-phase eutectics is left for separate treatment.

Moving forward, we are faced with two complementary choices. Our genetic optimization method of calculating the coupled zone provides a sufficiently reliable, yet still imperfect, approximation for the Al-Ag-Cu coupled zone. One avenue of further research is to improve upon the constitutive models that are used to formulate the fitness function in GA. Chief among our pursuits will be to remove the independence of composition in the undercooling equations. As stated previously, the growth coefficient is determined from the liquidus slopes and the distribution coefficients, all of which depend on composition. Predictions of the curvatures of the liquidus planes could be used to solve for liquidus slopes for each phase as a function of composition. Furthermore, binary distribution functions (those independent of the third elemental composition) could be used to predict the solidification within a ternary system (successful approximations of Scheil-Gulliver solidification paths have been performed an Al-Fe-Cu using this method [\[90\]](#page-278-2)). A second avenue is to perform a wide range of DS experiments (through, e.g., high-throughput characterization [\[244\]](#page-290-4)), particularly at the borders of the three-phase coupled zone. This would not only improve the prediction accuracy of the GA model but also allow us to solve for any additional, composition-dependent parameters that are seen in the higher-order growth laws [\[6,](#page-272-0) [91,](#page-278-1) [106,](#page-280-0) [123,](#page-281-1) [125\]](#page-281-2). Advances in both modelling and experiment would enable the prediction of non-equilibrium microstructures in Ag-Al-Cu as well as other multi-component and multi-phase alloy systems.

5.5 Conclusion

Genetic optimization was utilized to approximate a set of growth coefficients in order to identify the three-phase eutectic coupled zone within the Al-Ag-Cu alloy system. Subsequently, DS experiments were done so as to validate and refine our pre-
dictions. Samples were solidified under both negative and positive thermal gradient. A number of conclusions can be drawn from out experiments and computations:

- Our predictions of the coupled zone had an accuracy of 92.5% for the growth velocity of 0.64 mm/s and 87% for 0.063 mm/s. Incorrectly labeled points were found to be less than 10° C off from the experimental results. Broadly, our model agree with experimental expectations and also delivers a physically plausible set of growth coefficients. One can plug-and-play these coefficients in simulations of alloy solidification, e.g., phase field [\[245\]](#page-290-0).
- Improvements to the shape of the coupled zone in composition-velocity space were made on the basis our EBSD observations, namely, the faceted morphology of the Al2Cu primary phase. We introduced in our constitutive models a kinetic term that accounts for the sluggish growth kinetics of the faceted planes. As a result, the coupled zone skews towards the Cu constituents, matching our expectations for a system containing a faceted phase [\[119\]](#page-281-0). Our efforts suggest that the three-phase eutectic should be treated as a nonfaceted-nonfacetedfaceted eutectic in future analysis.
- A look at the effect of positive and negative thermal gradient provided clues on the system's ability to achieve steady-state as well as the morphological selection of the three-phase eutectic. Samples grown with negative G lacked stable growth patterns despite the composition falling into the coupled zone. This is attributed to the rejection of Ag into the melt and constant convection present beneath the solid-liquid interface when G is parallel to g . The wide diversity in three-phase eutectic morphology is likely due to the sensitivity of the solid-liquid interfacial energy to compositional variations ahead of the growth front, although this particular interpretation would require further confirmation. Samples grown with positive G (anti-parallel to g) resulted in the usual and uniform three-

phase eutectic microstructure.

5.6 Acknowledgements

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5.7 Appendix: Genetic Optimization Selection Parameters

Parameter selection for GA is critical to optimize its efficiency and effectiveness for a given problem. Based on the results of Ref. [\[214\]](#page-288-0), uniform crossover and universal stochastic sample selection were chosen as the crossover and parent selection methods, respectively. This was due to their higher degree of accuracy when compared to other conventional methods such as single and double point crossover or roulette and tournament selection methods. Universal stochastic sampling works in similar fashion to a line plot with each parent having a larger region depending on their fitness score (*i.e.*, better score $=$ larger area). Uniformly spaced increments are then used to select the following generation (Fig.([5.8a](#page-146-0))). Uniform crossover is a random mixing of various components from the selected parents' genotype (Fig.([5.8b](#page-146-0))). The final component for parameter selection is the mutation method. The selected approach was based upon a weighted Gaussian centered at zero that reduced in scale each subsequent iteration to prevent mutating outside a global minima and encourage convergence. The child would have a certain amount of mutation applied to it depending on where upon the Gaussian it was randomly placed and a specific scaling function. For further information on GA, please see Refs. [\[19,](#page-273-0) [213\]](#page-288-1).

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Figure 5.8:

Genetic algorithm parameters: Graphical representations of the (a) stochastic universal sampling method and (b) reproduction through random mixing.

5.8 Supplementary Information

Figure 5.9: Reference $Al-Ag_2Al-Al_2Cu$ coupled zone: Experimentally determined maps of the coupled zone for $G = 12 °C/mm$ and (a) $V = 0.64$ mm/s and (b) 0.063 mm/s [\[20\]](#page-273-1)

Figure 5.10: Directionally solidified microstructure: Micrographs of samples grown at V of 0.063 mm/s and G of $-0.4\degree\text{C/mm}$ that display (a) an Ag₂Al dendrite, and (b) α -Al dendrites, Ag₂Al dendrites, and Al-Ag₂Al twophase lamellar eutectic.

Figure 5.11: Directionally solidified microstructure: Microstructure of sample grown at V of 0.64 mm/s and G of 0.4 \degree C/mm. (a) Final transient (top of sample rod). (b) Large Al_2Cu dendrites seen Approximately 1 mm below the top of the sample highlighting a negative concentration gradient in Ag as one move up the sample. (c) Wide range of eutectic microstructures, including large regions of regular eutectic, are found approximately 1 mm from the base of the sample. (d) Initial transient (bottom of rod).

Figure 5.12: Directionally solidified microstructure: Microstructure of sample grown at V of 0.64 mm/s and G of $-0.4\degree\text{C/mm}$. (a) A large cluster of α -Al dendrites were found approximately 1 mm from top of sample rod. (b-c) Very fine three-phase eutectic can be seen throughout the base of the sample. (d) Region of largely indiscernible, stretched morphology surrounded by a small section of fine regular eutectic.

CHAPTER VI

Formation of Three-Phase Eutectic Grains on Primary Phases: Observations From Correlative Imaging

This chapter is based off the article published in Journal of Alloys and Compounds [\[201\]](#page-287-0).

Abstract: We investigate the interaction between three-phase eutectic and a primary phase during solidification of an off-eutectic Al-Ag-Cu alloy through correlative imaging. In situ synchrotron X-radiography reveals the locations and orientations of primary $Al₂Cu$ rods, with respect to the surrounding eutectic. We also identified an unusually high and anisotropic eutectic growth velocity, often exceeding $100 \mu m/s$ when the growth front was parallel to the surface of a primary Al_2Cu rod. By combining these results with three-dimensional (3D) focused ion beam tomography, scanning electron microscopy, and electron backscatter diffraction, we demonstrate that this anomaly results from two-dimensional $(2D)$ dendrites, or 'fingers', of Al and $Ag₂Al$ that spread along the primary Al_2Cu rod surfaces; meanwhile, protrusions of Al_2Cu grow in between pockets of the fingers and into the surrounding eutectic, preserving their crystallographic orientations and morphology in the process. We propose a competitive growth relationship between the three phases of the eutectic to explain these

features as well as the diversity of two- and three-phase microstructures obtained at the onset of eutectic solidification.

6.1 Introduction

Eutectic-forming alloys are of great importance due to their composite-like be-havior [\[61\]](#page-276-0). Several models describing the steady-state growth dynamics of eutectics have been proposed from the 1960s to present day [\[78,](#page-277-0) [79,](#page-277-1) [83,](#page-278-0) [246\]](#page-290-1), which define the relations between undercooling, lamellar spacing, and interfacial velocity. In comparison to their growth, the nucleation of eutectics is not as well understood. The latter is generally thought to be a non-reciprocal, heterogeneous process [\[48,](#page-275-0) [68,](#page-277-2) [72\]](#page-277-3), in which an initial solid phase (α) acts as a nucleant for a second phase (β), but not the converse, in a two-phase α - β eutectic; that is, α has a catalytic effect on the formation of nuclei of β , potentially brought on by a higher entropy of melting, a more complex crystallography, or a higher melting point [\[247\]](#page-290-2). While non-reciprocal nucleation theory is generally agreed upon, there exists still some ambiguity on the salient factors that promote it and the alloy systems that abide by it [\[248\]](#page-290-3).

A more contested topic concerns the formation of eutectic adjacent to a primary phase within a hypoeutectic or hypereutectic alloy [\[4,](#page-272-0) [71,](#page-277-4) [247,](#page-290-2) [249\]](#page-290-4). According to Lemaignan [\[4\]](#page-272-0), a solid droplet of a secondary phase nucleates on the surface of a primary phase. The secondary phase spreads out radially into the surrounding liquid before diffusion fields flatten the droplet into a short spherical cap. Growing out laterally, the structure begins to destabilize into a pseudo-2D, branched dendritic shape as secondary arms form. Upon reaching a critical undercooling, the secondary arm spacing becomes suitable for eutectic coupled growth in a direction perpendicular to the primary surfaces. The primary phase thereby grows from the "substrate" into the eutectic, forming an alternating, regular structure. More recently, while investigating the nucleation of the lamellar-eutectic $CBr_4-C_2Cl_6$, Akamatsu et al.

built upon Lemaignan's theory $|5|$. In a thin film, they showed in situ a single-phase layer growing laterally across the surface of the primary phase. At distinct junctures of the thin layer, such as grain boundaries, the primary phase grew outward through the lamina and eventually connected to the melt in a process dubbed "invasion." The primary phase then spread laterally $(i.e.,$ in a direction perpendicular to the macroscopic growth front) across the new surface, thereby repeating the process. An alloy may undergo "invasion" several times before instability on the outermost layer leads to coupled eutectic growth. This oscillatory behavior bears some semblance to that of halo formation [\[250\]](#page-290-5).

In contrast to the single-phase "invasion" process observed by Akamatsu *et al.*, Serefoğlu and coworkers reported the direct, heterogeneous nucleation of a eutectic grain on a primary surface [\[73\]](#page-277-5). Also under directional solidification, the eutectic grains (discrete cells of two or more phases separated from other such regions by a solid/liquid interface) nucleated at several locations including the liquid channels within the grain boundaries, sample edges, and points of morphological instabilities along the surface of the primary phase. Once nucleated, the eutectic grains showed a more radial enveloping shape, compared to those eutectic structures identified by Akamatsu *et al.* [\[5\]](#page-272-1). Serefoğlu theorized a difference in initial conditions and sample geometry may have contributed to their result [\[73\]](#page-277-5).

The aforementioned studies report on solidification in transparent organic compounds examined via in situ light microscopy [\[5,](#page-272-1) [73,](#page-277-5) [251\]](#page-290-6) or on fully-solidified eutectic microstructures analyzed *via postmortem* metallography [\[71,](#page-277-4) [247,](#page-290-2) [249\]](#page-290-4). While offering insight on the solidification dynamics, both approaches have some drawbacks: For one, the behavior of organic materials does not always translate to metallic systems, e.g., the Prandtl number is much higher for organic compounds compared to metals [\[252\]](#page-291-0). Furthermore, it is non-trivial to deduce the mechanism of eutectic nucleation from micrographs as the eutectic may detach from the seed location during solidifica-

tion. Multi-phase eutectics accentuate these challenges. The introduction of a ternary component and also a third eutectic phase leads to complex eutectic patterns not seen in binary alloys [\[38,](#page-274-0) [226\]](#page-289-0). Nevertheless, the demand of such materials in commercial applications [\[109,](#page-280-0) [253,](#page-291-1) [254\]](#page-291-2) has renewed interest to understand multi-phase eutectic nucleation in off-eutectic alloys. It remains to be determined how a primary phase influences the selection of multi-phase patterns in the early stages of eutectic solidification: How do two (or more) pseudo-2D dendrites on the surface of a primary phase compete with each other? Under what conditions is a locally two- and three-phase microstructure achieved?

With the above questions in mind, we characterize an Al-Ag-Cu alloy as a model system, which forms a three-phase eutectic of Al, Ag_2Al , and Al_2Cu at a eutectic temperature of 773.15 K. Due to its well-characterized thermophysical parameters [\[6,](#page-272-2) [7,](#page-272-3) [22,](#page-273-2) [223,](#page-288-2) [255,](#page-291-3) [256\]](#page-291-4), relatively low eutectic temperature, and established three-phase coupled zone [\[223\]](#page-288-2), the system is ideal for our investigation. Here, we probe solidification in an alloy enriched in Cu (∼1 wt% off the eutectic composition) with the aid of in situ X-radiography and ex situ 3D focused ion beam (FIB) tomography. The combination of the two techniques allows us to resolve in unprecedented detail and for the first time the onset of a three-phase eutectic microstructure. We find a highly anisotropic eutectic/liquid interfacial velocity perpetuated by the growth of 2D dendrites or 'fingers' of Al and Ag_2Al which spread rapidly along the primary $Al₂Cu$ phase (which exists as long, faceted rods). Driven by the local supersaturation, these fingers growing along the primary $Al₂C_u$ rod surface determine the microstructure of the surrounding material, in accordance with an "invasion" like process. Further characterization reveals a diversity of single-, two-, and three-phase patterns, the origins of which will be presented and discussed.

6.2 Methods

An alloy of composition Al-42.2 wt%Ag-17.6 wt%Cu was vacuum arc remelted at Materials Preparation Center at Ames Laboratory (Ames, IA, USA) using high purity elements (99.999% Al, 99.999% Ag, and 99.999% Cu). Note the eutectic composition c_E is Al-42.9 wt%Ag-17.0 wt%Cu according to a thermodynamic assessment in [\[21\]](#page-273-3), thus verifying an excess of Cu in our samples with respect to c_E . Note also that in the Al-Ag-Cu eutectic system, small variations (∼1 wt%) from the eutectic composition can lead to changes of up to 10 vol $\%$ in the phase fraction of the three solid phases [\[256\]](#page-291-4). Indeed, Scheil simulations for our alloy composition predict the existence of primary Al_2Cu (1.5 wt%, see Fig. [6.7\)](#page-171-0).

From the Al-Ag-Cu ingot, we prepared a film of $100 \pm 10 \mu$ m thickness for in situ synchrotron X-radiography. We performed the experiments at beamline 2-BM at the Advanced Photon Source of Argonne National Laboratory (Lemont, IL, USA). Following the same setup given in Ref. [\[58\]](#page-276-1), we coated the film in a boron-nitride spray and sandwiched it between two 100 μ m thick quartz plates while a copper wire held the assembly in place [\[257\]](#page-291-5). In the experiments, we heated the samples to 788 K, i.e., 15 K above the eutectic temperature, and allowed it to fully melt over a 10 min. period. We then cooled the sample at a rate of 9.5 K/min. to a final temperature of 770 K (undercooling of 3 K below the Al-Ag₂Al-Al₂Cu eutectic temperature). We used a K-type thermocouple to calibrate the furnace temperature at the sample location. An incident broad-bandwidth 'white' X-ray beam penetrated the film sample along the thinnest dimension during continuous cooling. A scintillator detected the transmitted X-rays and converted them into visible light. A FLIR Oryx detector with a field-of-view (FOV) of 1.868 \times 2.422 mm and pixel size of 1.73 μ m/pixel captured the illuminated area. We collect a total of 300 frames at an exposure of 0.15 s, which span the dynamic events within the FOV.

Subsequently, we processed the collected X-radiographs in MATLAB [\[199\]](#page-287-1) to en-

hance the attenuation contrast between the solids (primary $Al₂C_u$ rods and eutectic) and liquid and hence to delineate the solid/liquid interface.^{[1](#page-155-0)} To do so, we first normalize each frame to remove detector artifacts by using a pixel-by-pixel division operation between two successive images, namely, a frame of interest and a background frame [\[200\]](#page-287-2). Then, we limit the range of the pixel intensity values to four standard deviations from the mean to adjust for random dead pixels on the detector. Fig. [6.1\(](#page-157-0)a-f) shows the resulting X-radiographs.

To accurately define the solid eutectic/liquid interface within a specific frame, we performed two additional operations: we applied a non-local means filter [\[202\]](#page-287-3) to the normalized frame to remove speckle noise while preserving edges. Furthermore, we 'stacked' together 20 normalized and filtered images into a single image. Each pixel in the stacked image is the sum of the pixels in the same spatial location within each image in the stack. This step is crucial since it improves further the contrast between the solid and liquid phases. Lastly, we segment or partition the phases in the stacked image using Otsu's method [\[203\]](#page-287-4). Fig. $6.1(g)$ shows the resulting segmented isochrones of the eutectic growth front.

For a detailed understanding of the solidified microstructures, including crystallographic relations between various phases, we conducted scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) with a focus on the primary $Al₂Cu$ rods and the neighboring material. To mimic the same annealing schedule used in the above X-radiography studies, we heated metallic pucks of identical composition to the films (described above) to 823 K and subsequently cooled at 9.5 K/min. to 723 K. To investigate the 3D connectivity of eutectic phases surrounding the primary A_2 Cu rods, we performed FIB tomography on a sample cooled at 5 K/min. We used a Thermo Fisher Helios G4 Plasma FIB at the Michigan Center for Materials Characterization for all milling and imaging. The ion beam had an energy and cur-

¹We do not capture the phases Al, Ag₂Al, and Al₂Cu *within* the eutectic because the lamellar spacing is on the order of the pixel size. Instead, we detect the eutectic/liquid interfaces only.

rent of 30 keV and 15 nA, respectively; meanwhile, the electron beam had an energy and current of 3 keV and 0.4 nA, respectively. We collected 1050 images at 50 nm spatial intervals along the milling direction. The images were then registered *via* Matlab [\[199\]](#page-287-1) to reconstruct a total volume of $60,112 \ \mu \text{m}^3$. By integrating our data from X-radiography, EBSD, and FIB tomography, we provide a cohesive picture of the initiation process for a three-phase eutectic.

6.3 Results

6.3.1 In situ X-radiography

According to the image sequence presented in Fig. [6.1,](#page-157-0) primary Al_2Cu rods (dark bands) formed prior to the eutectic. These rods nucleate and grow in different directions as elongated, faceted plates. Many originate along the sample edge and extend toward the interior, as seen in Fig. $6.1(a)$. Facets on Al_2Cu are attributed to a relatively low interfacial mobility of {110} planes [\[223\]](#page-288-2).

At an undercooling of 2 K below the three-phase eutectic temperature (773 K), we identify a eutectic front with intermediate contrast. Fig. [6.1\(](#page-157-0)a-f) shows the progression of the eutectic front. Note that increased brightness of regions in the liquid may be the result of solidification shrinkage [\[258\]](#page-291-6). We take the 0 s mark to represent the frame right before the eutectic appears in the FOV (Fig. [6.1\(](#page-157-0)a)). Fig. 6.1(g) shows a superposition of isochrones of the eutectic front over the next 30 s. The eutectic/liquid interfacial velocity is clearly anisotropic, with a pronounced growth rate in a direction parallel to the major axis of the nearest primary Al_2Cu rod (e.g., between 7.5 and 9 s, the front grows \sim 200 µm along the exposed surfaces of the bottom-most rod while only expanding radially outward by \sim 30 µm). This behavior is not isolated, as the eutectic 'zips' along primary rods oriented in several directions rather than maintaining its initial path. Rapid outward or radial growth does oc-

Figure 6.1:

Progression of three-phase eutectic solidification front: $(a-f)$ X-radiographs showing solidification of $A1-Ag_2A1-Al_2Cu$ three-phase eutectic at a temperature of 771 K. The edge of the sample is visible along the right side of the images. Time since eutectic front first appeared is displayed in top-left corner. (g) Spatiotemporal diagram of eutectic front during solidification (over the same field-of-view), where the eutectic/liquid interfaces are colored according to time-step. Black arrows in (g) point to primary Al₂Cu rods.

cur at several locations (at \sim 24 s), most notably on the leftmost Al₂Cu rod. It is noteworthy that this bulbous region of solid eutectic appears in the same direction as that of the initial eutectic growth (Fig. $6.1(a)$). One potential explanation for it is that the eutectic front grows behind the leftmost primary rod, thus continuing its growth rather than nucleating along the rod surface. Even so, the bulbous region expands at a slower rate than the eutectic growing tangentially along the leftmost primary rod surface (50 vs. 100 μ m/s). This sets the macroscopic wetting angle to be $\theta = \tan (V_{\parallel}/V_{\perp})$ where V_{\perp} and V_{\parallel} are the interfacial velocities parallel and perpendicular to the primary surface, respectively. We find $\theta = 14^{\circ}$.

We may account for the discrepancy between $V_{||}$ and V_{\perp} if we assume that $V_{||}$ corresponds to that of the eutectic and V_{\perp} to that of the *pseudo-2D* dendrites that grow along the primary Al_2Cu phase surfaces. To lend credence to this idea, we first compare our measurements of V_{\parallel} with predictions from the Jackson-Hunt (JH) model of eutectic solidification. Assuming an undercooling of 2 K for an $Al-Ag₂Al-Al₂Cu$

eutectic, we would anticipate a growth velocity of \lesssim 20 μ m/s using the JH constants retrieved from Ref. [\[259\]](#page-291-7). This value falls in line with our findings from above. Next, we compare theoretical spreading velocities of Al and Ag_2Al phases modelled as *pseudo-2D* dendrites [\[260\]](#page-291-8) to our measured V_{\parallel} . Under the assumption of a constant diffusivity, and at high dimensionless supersaturation (in the range of $40-45 \text{ wt\% Al}$), we find the spreading velocities of Al and Ag_2Al equaled or exceeded those found *via* X-radiography (30-200 μ m/s). In what follows [\(6.3.2\)](#page-158-0), we reveal the microstructural signatures of these *pseudo-2D* dendrites along with their effect on the eutectic.

6.3.2 Ex situ Electron Microscopy

For a three-dimensional view of the connectivity of phases, we turn to FIB tomography. Fig. $6.2(a)$ displays a reconstructed volume of the three-phase Al-Ag₂Al-Al₂Cu eutectic microstructure (shaded dark gray, white, and light gray, respectively). The structure reveals a somewhat irregular morphology, identified by the unaligned and irregular contacts between the two intermetallic phases, Ag_2Al and Al_2Cu [\[7\]](#page-272-3). The appearance of an irregular eutectic morphology is unsurprising when we consider the disturbance of a primary phase on the solidification process of the eutectic. Here, the $\rm Al₂Cu$ preferentially aligns with the neighboring primary $\rm Al₂Cu$ rod, highlighted in green. Fig. [6.2\(](#page-160-0)b) shows a sectioned volume that displays the phases adjacent to the rod surface. We see several $pseudo-2D$ dendrites, or 'fingers,' of Al and Ag_2Al which grew along the primary $\rm Al_2Cu$ rod surface. These fingers encase the rod and appear to grip around the surface (see faceted juncture at $X = Y = 22 \mu m$ in Fig. [6.2\(](#page-160-0)b)). The morphology of the two types of fingers, however, differ greatly. The Al fingers appear to grow as large, uniform structures, upwards of $15-17 \mu m$ across, with large spacing between fingers (3-8 μ m). By comparison, the Ag₂Al fingers show a wide range of both width (3-12 μ m) and spacing (1-15 μ m). Protrusions of primary Al₂Cu appear to extend between the $Ag₂Al$ fingers along the entire length of the primary rod surface.

For a thorough analysis of the primary $\rm Al_2Cu$ rod interface, we extracted a 3D isosurface (Fig. $6.2(c)$). It displays large and smooth regions intermittently broken by bumpy protrusions (on the mesoscale). In one location a ring has formed where two Al2Cu protrusions have coalesced around anther solid phase along the rod surface. To shine light on the other phases, we mapped the solid-solid interface type in 3D (Fig. [6.2\(](#page-160-0)d)). This rendering confirms that these Al_2Cu protrusions occur primarily along the Ag_2Al-Al_2Cu solid-solid interface (as previously noted from Fig. [6.2\(](#page-160-0)b)). By comparison, the Al-Al₂Cu solid-solid interface is characteristically flat, only displaying significant roughness at the microscale near an $Al-Al_2Cu//Ag_2Al-Al_2Cu$ trijunction. Looking again at the ring structure (inset of Fig. $6.2(d)$), we find the cap or point of coalescence matches with a curved Al₂Cu interface located at $X = Y = 22 \mu m$ and $Z = 28 \ \mu m$ in Fig. [6.2\(](#page-160-0)b). Interestingly, the outward expansion of the ring is halted when an Ag_2Al-Al_2Cu interface is replaced by an $Al-Al_2Cu$ interface. We believe the formation of this ring and the large number of protrusions along the primary Al2Cu interface, together with the irregular eutectic morphology in the surrounding microstructure, all point to a cooperative relationship between the pseudo-2D dendrites and the primary phase that determines the eutectic pattern formation and its crystallography.

To explore this hypothesis further, we performed an EBSD scan of an elongated primary Al2Cu rod along with the surrounding three-phase eutectic microstructure. We generated a phase map and Al_2Cu misorientation map (with respect to the neighboring primary phase) using the open source toolbox MTEX [\[261\]](#page-291-9), see Fig. [6.3\(](#page-161-0)a-b). The orientation of the primary Al_2Cu rod is nearly identical to that of the eutectic $\text{Al}_2\text{Cu}\text{ lamella}$ (no $\text{Al}_2\text{Cu}\text{ lamella}$ is rotated more than 5^o from the primary rod). We see that the eutectic Al_2Cu lamellae adjacent to the primary Al_2Cu rod have nearly 0^o misorientation at the rod surface with a gradual increase the farther away from

Figure 6.2: Focused ion beam (FIB) tomography of $Al-Ag_2Al-Al_2Cu$: (a) Reconstructed volume from FIB tomography sample solidified at a cooling rate of 5 K/min. Primary Al_2Cu rod is shown in the upper right corner and is highlighted in green. (b) Extracted volume of the primary rod which shows the various phases along its surface. Within (a-b), the white, light grey, and dark grey regions represent the Ag_2Al , Al_2Cu , and Al phase, respectively. (c) Closer look at the Al_2Cu rod surface, showing the Al_2Cu phase interfaces in 3D. (d) Same Al_2Cu rod surface, now illuminated in 3D by interface boundary type (cyan: Ag_2Al-Al_2Cu and orange: Al-Al₂Cu). Inset of (d) shows a ring-shaped protrusion of Al_2Cu , bounded by Ag_2Al-Al_2Cu interfaces.

Figure 6.3:

Crystallography and morphology of Al_2Cu : (a) Phase map of a primary $Al₂Cu$ rod and the surrounding $Al₂Al₂Al₂Cu$ three-phase eutectic microstructure. (b) Misorientation map of eutectic Al_2Cu lamellae compared to the neighboring primary Al_2Cu phase. (c) Autocorrelation map of the Al2Cu eutectic lamellae. The lamellae are highly correlated and orientented at a nearly identical tilt (in the plane of the page) to the neighboring primary Al₂Cu phase (*cf.* (a)). (d) An inverse pole figure of the $\rm Al_2Cu$ habit planes on a per-grain basis, colored by the degree of misorientation to the primary phase. Size of data points is scaled by grain size. Orientation of the primary rod circled in red. A magnified view reveals the same trend as seen in (b).

the primary phase the lamellae are. A closer look at the crystal orientations of each individual lamella of Al_2Cu [\(6.3\(](#page-161-0)d)) confirms a clustering of nearly identical orientations that gradually rotate away from that of the primary rod. We find a crystal rotation rate ∼0.15 \degree/μ m across the FOV. For comparison, Wang *et al.* reported a misorientation evolution of ~1.4 \degree/μ m for Al₂Cu eutectic lamellae in an Al-Al₂Cu eutectic grain [\[262\]](#page-291-10) without any neighboring primary phase.

Turning to the morphological relation between the primary Al_2Cu rod and the surrounding eutectic, we generated an autocorrelation map of the Al_2Cu eutectic lamellae displayed in [6.3\(](#page-161-0)b). Autocorrelation relates the pixels in an image to each other and reports the likelihood that they belong to the same phase (here, Al_2Cu) as a function of separation distance and direction [\[263\]](#page-291-11). Analytically, we are taking the convolution of the image with itself [\[264\]](#page-292-0). Fig. [6.3\(](#page-161-0)c) shows that the $\rm Al_2Cu$ lamellae are highly correlated with a slight tilt (in the plane of the page) which matches that of the neighboring primary Al₂Cu rod (*cf.* Fig. [6.3\(](#page-161-0)c)). A strong, directional correlation such as this is indicative of an identical morphology for the eutectic structure across the FOV. The primary $Al₂Cu$ rod in our sample appears to restrain both the surrounding eutectic Al_2Cu orientation and morphology, preventing substantial misalignment of the eutectic lamellae.

6.4 Discussion

From X-radiography, FIB tomography, and corresponding EBSD analysis, we draw a link between eutectic initiation and crystallographic orientation of pre-existing primary $Al₂Cu$ rods. In short, we find that the eutectic $Al₂Cu$ phase originates from the primary rod during solidification from protrusions extending from the rod surface. Fig. [6.3\(](#page-161-0)b) support this claim as it indicates the eutectic Al_2Cu shares the same orientation as that of primary $Al₂Cu$, at least on local scales. It follows that the growth direction of the $Al₂Cu$ eutectic rods mirrors that of the primary rod, leading to nearly identical habit planes and morphology, see again Fig. [6.3.](#page-161-0) Paired with the evidence from FIB tomography, we also associate these $\rm Al₂Cu$ protrusions with the free space between $Ag₂Al$ fingers as they spread along the primary rod surface. This picture resembles the "invasion" theory for eutectic formation [\[5\]](#page-272-1). Even so, the diversity of neighboring phases along the primary surface is unique to multi-phase systems and is therefore worthy of comment.

From our results, we predict that the competitive growth between Al and $Ag₂Al$ pseudo-2D dendrites along the primary Al_2Cu rod controls the final microstructure of the surrounding material. We have thus identified four unique final structures that are most likely to appear around a primary $Al₂Cu$ in near-eutectic Al-Ag-Cu alloy, all of which may coexist along the primary rod surface due to the effect of chemical microsegregation. Put more quantitatively, we find the maximal driving force (DF) for phase transformation (computed through the parallel tangent construction [\[265\]](#page-292-1)) is *strongly* dependent on alloy composition: Over a range of $8wt\%$ of Ag and $4wt\%$ Cu about c_E for a fixed temperature of 771 K, the DF for Ag₂Al varies by 700 J/mol while aluminum varies by 450 J/mol , see Fig. [6.4.](#page-164-0) In general, DF represents the Gibbs free energy change per mole reacted when small amounts of material with composition c_r are transferred from the liquid phase at composition c_L to β phase at composition c_{β} ; graphically, it can be found by reading the vertical distance at c_r between the tangent lines drawn for β at c_{β} and liquid at c_L [\[266\]](#page-292-2). It follows that the maximal DF associated with forming β from a liquid of given composition c_L occurs when the two tangents are parallel. In summary, Fig. [6.4](#page-164-0) demonstrates the compositional sensitivity of the DF in the Al-Ag-Cu system. The diverse microstructures and coexistence of both Al and $Ag₂Al$ fingers are further indicative of a volatile local c_L . The range of c_L considered above is well within reason for the liquid surrounding an $\rm Al_2Cu$ rod. In a somewhat similar vein, phase-field simulations by Nestler et al. indicate that the pattern selection varied extensively within ± 1 at % of the eutectic melt composition

Figure 6.4: *Parallel tangent construction of driving forces*: The maximal solidification driving forces for the (a) aluminum and (b) $Ag₂Al$ phases as a function of composition at a fixed temperature of 771 K. Color bar shows the range of computed driving forces. A positive driving force indicates that formation of a solid phase is favored.

for the Al-Ag-Cu ternary system [\[103\]](#page-279-0).

In the first scenario (case I), the liquid has a higher local concentration of Al compared to Ag. Fingers of Al will nucleate and grow along primary rod and spread rapidly, encasing much of the rod surface, ultimately forming a halo-like structure.[2](#page-164-1) At elevated temperatures, the solid Al phase is supersaturated in Ag [\[256\]](#page-291-4), leading to the precipitation of Ag₂Al Widmanstätten plates upon cooling (Fig. [6.5\(](#page-165-0)a-b)). Several others have also reported Ag_2Al precipitates in their work [\[97,](#page-279-1) [256,](#page-291-4) [267\]](#page-292-3). As the Al phase grows, it rejects Ag into the melt thereby increasing its local concentration. This may lead to the formation of eutectic Ag_2Al along the exposed Al_2Cu rod surface (if Ag_2Al does not nucleate on Al), see Fig. [6.8\(](#page-172-0)a). The lower ratio of Al to Ag in the remnant liquid either causes these $Ag₂Al$ solids to halt the progression of the Al dendrite or else the Ag₂Al solids are completely encased by the Al dendrite.

The second scenario (case II) is when the liquid has a higher local concentration

 $2A$ halo envelopes the primary phase entirely whereas a *finger* covers only a small portion.

Figure 6.5:

Micrograph of primary Al_2Cu and surrounding microstructures: (a) Primary $\rm Al_2Cu$ rod which displays four possible structures along its surface. Panel (b) displays one ROI in blue and shows two extremes (cases I and II) where fingers of Al and $Ag₂Al$ have encased large regions of the primary $Al₂Cu$ rod surface. Within the Ag₂Al phase, there are veins of Al_2Cu , which lead to an Ag_2Al-Al_2Cu pattern on local scales. (c) shows another ROI in green and reveals a two-phase patterns of Al-Ag2Al along the primary surface (case III). This is shortly overtaken by a three-phase Al-Ag₂Al-Al₂Cu structure (namely, threads of Al_2Cu that are parallel to the primary phase). Several protrusions from the primary $Al₂Cu$ rod at the bottom right of the ROI are seen extending out into the three-phase eutectic structure. (d) depicts the last ROI in red and shows a *pseudo*-three-phase pattern along the primary $Al₂Cu$ rod surface (case IV). In all panels, the white, light grey, and dark grey regions represent the Ag_2Al , Al_2Cu , and Al phases, respectively. This sample underwent equiaxed solidification with a cooling rate of 5 K/min

of Ag compared to Al. In this case, fingers of Ag2Al form along the rod surface. The wetting angle of these fingers, as compared to that of the Al phase, is likely much larger (based on our metallographical and 3D observations), leading to a more radial growth of the $Ag₂Al$ fingers and a higher variability of spacing between fingers. If the fingers of Ag_2Al along the primary Al_2Cu rod surface coalesce or remain few in number, a halo-like structure of Ag_2Al may form (Fig. [6.8\(](#page-172-0)b)). Otherwise, protrusions of $\rm Al_2Cu$ may extend outward from the primary rod surface between fingers of $\rm Ag_2Al$, as show in both Fig. [6.5\(](#page-165-0)b) and Fig. [6.8\(](#page-172-0)b), giving the appearance of a two-phase Ag_2Al-Al_2Cu pattern. Two neighboring protrusions of Al_2Cu can even encase part of an Ag2Al finger (see also inset of Fig. [6.2\)](#page-160-0), leading to the appearance of a broken eutectic rod of Ag_2Al . The Al_2Cu protrusions may also grow far enough outward to escape the confined space between fingers and extend laterally, tangential to the primary rod surface, to form the $Al₂Cu$ phase within the irregular three-phase eutectic microstructure (Fig. $6.5(c)$ and Fig. $6.8(b)$). Generally speaking, our explanation for broad regions of Al and $Ag₂Al$ surrounding primary $Al₂Cu$ aligns with Sundquist's early studies, which suggested that halo formation is highly dependent on the local liquid composition [\[69\]](#page-277-6).

The third and fourth scenarios are a combination of the first two: Here, the two types of fingers will compete with each other in solidification leading to a mixture of two-phase Al-Ag₂Al and three-phase Al-Ag₂Al-Al₂Cu patterns, depending on the spatial distribution of both Al and $Ag₂Al$ fingers. If the *pseudo-2D* dendrites of both Al and Ag_2Al form along the surface of a primary Al_2Cu rod, they may grow into one another, interweaving their fingers. Indeed, the liquid between the Al and Ag₂Al fingers is enriched with rejected Ag and Al, respectively, promoting growth of the reciprocal phase in these regions. This would lead to the third pattern (case III), an alternating arrangement of Al and Ag_2Al bordering the primary Al_2Cu surface (Fig. $6.5(c)$). However, if the Al and Ag₂Al dendrites do not interweave com-

pletely, the $\rm Al_2Cu$ phase may extend outward between $\rm Ag_2Al$ fingers, leading to fourth and final microstructure (case IV), a Al-Ag₂Al-Al₂Cu pattern (Fig. [6.5\(](#page-165-0)d)). Fig. [6.6](#page-168-0) schematically illustrates this final scenario. We note that two-phase $Al-Al_2Cu$ patterns do not appear in the vicinity of the primary $Al₂Cu$ rod. This may be due to the presumably rapid spreading of Al on $\mathrm{Al}_2\mathrm{Cu}$ (*i.e.*, small contact angle) and thus a difficulty of A_2Cu in growing past a solid metal layer. Furthermore, during studies of coupled eutectic growth within the Al-Ag-Cu system [\[22,](#page-273-2) [268\]](#page-292-4), there is evidence of a strong growth association between Ag_2A and Al_2Cu believed to be caused by a low interfacial energy boundary. This strong epitaxy likely links the two phases together in these scenarios as well, where protrusions of Al_2Cu extend into the melt near or between regions of $Ag₂Al$ on the primary phase surface.

Our explanation for the appearance of local regions of two-phase microstructure in a three-phase eutectic differs from previous theories. Ruggiero [\[109\]](#page-280-0), concluded that at high growth rates, a three-phase eutectic may decompose into a double binary eutectic (separate regions of two-phase eutectic structures, e.g., ABABAB and ACA-CAC). This occurs because the standard three phases cannot subdivide before freezing to form the classical ABCABCABC structure, due to topological constraints. Our results indicate that, at least near existing primary phases and during an equiaxed solidification process in which the liquid composition is continually changing, the formation of two-phase regions may originate not from eutectic growth but instead eutectic initiation. There are differences between both the alloy system and experimental condition (ours being equiaxed solidification and theirs being unidirectional). However, these differences only demonstrate that the more dynamic and complex nature of equiaxed solidification may give rise to similar microstructures as those obtained via directional solidification. Our previous study [\[223\]](#page-288-2) confirms that Cu-rich, hypereutectic samples that produced primary Al_2Cu in directional solidification show a similar morphology and orientation as in this work.

Figure 6.6: Proposed growth mechanism for $Al-Ag_2Al-Al_2Cu$ formation on primary Al_2Cu : Schematic illustration of mechanism by which protrusions along primary $Al₂Cu$ extend between fingers of Ag₂Al, thereby contributing to a three-phase eutectic structure (top layer) adjacent to the primary rod (bottom layer). This case corresponds to the fourth scenario discussed in the main text. Time progresses from the top to the bottom image. The two protrusions may merge, creating a ring structure of $Al₂Cu$ around $Ag₂Al$, similar to that seen in Fig. [6.2.](#page-160-0) This process gives rise to the appearance of (broken) rods of Ag₂Al that are surrounded by Al_2Cu .

We reserve for future work the direct confirmation of this formation mechanism. To this end, X-ray nano-tomography would be the most suitable technique to capture the solidification process in 3D and in real-time at the relevant length- (nm) and timescales (s), respectively.

6.5 Conclusion

In this study, we investigated the initiation process of a three-phase eutectic within an off-eutectic Al-Ag-Cu alloy. Through in situ synchrotron X-radiography, we identified a highly anisotropic interfacial velocity which often surpassed 100 μ m/s when the front was tangential and adjacent to a neighboring rod of primary $Al₂Cu$ phase. We reason that this anomalously high velocity (for only a modest undercooling of $2 K$) is due to the spreading of *pseudo-2D* dendrites of Al and $Ag₂Al$ on the surfaces of the primary Al_2Cu rod. Ex situ SEM, EBSD, and 3D FIB tomography revealed numerous protrusions that extend from the exposed surface of the primary rod and grow between the dendrite arms, and into the neighboring eutectic. In the same specimen, we see large, single-phase regions of Al and Ag_2Al bordering primary Al_2Cu ; two-phase patterns of Ag_2Al-Al_2Cu and $Al-Ag_2Al$ (the latter resulting from two interwoven fingers); and three-phase patterns of $Al-Ag_2Al-Al_2Cu$. The existence of the different patterns arises from variations in the local supersaturation and the spacing between the dendritic fingers. The Al_2Cu phase protrudes into the eutectic provided that its propagation rate (into open spaces between fingers) exceeds the spreading velocity of the fingers, particularly those of Ag_2Al due to the relatively higher contact angle and lower interfacial energy between $Ag₂Al$ and $Al₂Cu$.

6.6 Acknowledgements

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6.7 Supplementary figures

Figure 6.7: Theoretical solidification of alloy composition: Scheil simulation of Al-42.2 Ag-17.6 Cu wt% solidification progression computed using TCAL7 database [\[21\]](#page-273-3).

Figure 6.8:

Micrographs of additional observe microstructures: (a) Primary $Al₂Cu$ rod surrounded by Al, which encases much of the structure (case I in the main text). Within the Al, eutectic $Ag₂Al$ appears to jut from the Al_2Cu surface at several points. (b) Primary Al_2Cu rod surrounded by Ag₂Al with several protrusions of Al_2Cu extending from the rod surface (case II). In (a-b), the white, light grey, and dark grey regions represent the Ag₂Al, Al₂Cu, and Al phase, respectively. Both samples shown in $(a-b)$ underwent equiaxed solidification with a cooling rate of 1 K/min and 0.5 K/min, respectively.

CHAPTER VII

Complexity and Evolution of a Three-Phase Eutectic During Coarsening Uncovered by 4D Nano-Imaging

This chapter is based on the article published in Acta Materialia [\[269\]](#page-292-5).

Abstract: We investigate the coarsening dynamics of the three-phase eutectic $\text{Al-Ag}_2\text{Al-Al}_2\text{Cu}$ at 723 K *via in situ* transmission X-ray nano-tomography. Unlike previous investigations that compared observations between different samples annealed for different times, our three-dimensional measurement shows at nanoscale resolution the microstructural changes occurring in the same field-of-view, enabling new insight on the capillary-driven evolution of a ladder-like pattern. With the aid of a new reconstruction algorithm and machine learning segmentation, we trace the interfaces of the eutectic and observe significant structural changes within 4 hr of aging. Even though the average length-scales of the eutectic solids follow a temporal power law, the microstructure is not self-similar. Instead, it evolves (in part) through the coalescence of neighboring $Ag₂Al$ solids at the expense of the intervening $Al₂Cu$. By combining our X-ray data with electron diffraction to identify the common planes at the interphase boundaries, we show that coalescence leads to a decrease in lattice misfit, and hence, interfacial energy. At longer times, the interphase boundaries with low misfit compete for surface area, resulting in a 'locking' of the interfacial shape.

7.1 Introduction

Naturally occurring, multi-phase eutectic alloys have composite-like properties [\[61,](#page-276-0) [270\]](#page-292-6), beneficial for many technological applications. This has sparked renewed scientific interest in understanding how they nucleate and grow [\[17,](#page-273-4) [38,](#page-274-0) [57,](#page-276-2) [105\]](#page-280-1). However, we currently have limited knowledge on how the increased number of solid phases in these multi-phase alloys influences the coarsening process after eutectic solidification. Many of these materials operate at elevated temperatures wherein their microstructures and properties change over time, often to the detriment of reliability [\[86,](#page-278-1) [87,](#page-278-2) [136,](#page-282-0) [148,](#page-283-0) [271](#page-292-7)[–273\]](#page-292-8). Likewise, in additive manufacturing, the transient thermal gradients in the heat-affected zone may lead to a microstructural evolution *via* coarsening that may influence the load transfer between phases [\[274–](#page-292-9)[277\]](#page-293-0). Therefore, it is crucial to have a thorough understanding of the coarsening process in these materials to predict how they might evolve during their life-cycle.

In the absence of a chemical driving force for precipitation, solid-state microstructural evolution is driven purely by a reduction of interfacial free energy. Depending on the material system and characteristic coarsening length, this process can cause changes in both morphology and bicrystallography, resulting in different features at different stages. When annealed below the eutectic temperature, eutectic microstructures coarsen continuously in the solid-state *via* Ostwald ripening, Rayleigh instabilities, and fault migration [\[31\]](#page-274-1). The eutectic may also undergo discontinuous coarsening, in which the original eutectic cells or grains are replaced by new ones with larger interphase spacing [\[145\]](#page-283-1).

Elementary mechanisms of coarsening in two-phase systems. The mechanism of continuous coarsening depends on the interfacial structure. If the Wulff shape is isotropic, the interfaces are curved and the eutectic coarsens *via* curvature reduction,

as depicted in Fig. [7.1\(](#page-176-0)a). In contrast, some eutectic alloys have faceted rods or plates due to their anisotropic solid-solid interfacial free energy [\[3,](#page-272-4) [63\]](#page-276-3). Examples of such alloys include Bi-In-Sn [\[109,](#page-280-0) [278\]](#page-293-1), Zn-Mg-Al [\[59\]](#page-276-4), and Al-Ag-Cu [\[201,](#page-287-0) [223\]](#page-288-2). Facets on rods may form to reduce their interfacial surface energy by aligning with a low energy crystallographic plane during annealing [\[150,](#page-283-2) [271\]](#page-292-7), see Fig. [7.1\(](#page-176-0)b). In such a scenario, we may also expect that the faceted rods are resistant to Rayleigh instabilities since any perturbation would require the creation of surfaces with higher interfacial energies. As such, faceted phases tend to coarsen through 2D Ostwald ripening or through fault migration [\[150\]](#page-283-2). It is also possible for faceted eutectic rods to reduce their interfacial energy by coalescing along relatively high energy planes (Fig. $7.1(c)$) [\[279,](#page-293-2) [280\]](#page-293-3) or rotating to align with a low energy orientation (Fig. [7.1\(](#page-176-0)d)) [\[273,](#page-292-8) [281\]](#page-293-4).

Role of multiple solid phases on the coarsening dynamics. Beyond the interfacial structure, we must also account for the effect of other dispersed solid phases in a multi-phase system. For example, consider a material consisting of β and γ phase "particles" embedded in an α phase matrix. The growth of each particle depends on the solute sources and sinks. Holmes [\[282,](#page-293-5) [283\]](#page-293-6) describes three possible scenarios for particle interaction based on their so-called cross coupling coefficients, $\Gamma_{n,p}$, defined as

$$
\Gamma_{n,p} = \frac{D_j \Delta c_i^{m,n} \Delta c_i^{m,p} + D_i \Delta c_j^{m,n} \Delta c_j^{m,p}}{D_j (\Delta c_i^{m,n})^2 + D_i (\Delta c_j^{m,n})^2}
$$
(7.1)

where D_i and $\Delta c_i^{m,n}$ $\binom{m,n}{i}$ are the diffusivities and equilibrium concentration differences of component i, respectively, in which the subscript indicates the solute, m is the matrix phase, and n and p are the dispersed solid precipitates. If $\Gamma_{n,p} \to 0$, the particles experience a weak coupling. This means that the β and γ produce small or non-existent solute depletion zones, leading to a spatial correlation of β and γ particles. When $\Gamma_{n,p} \geq 1$, the particles display a strong positive coupling. In this case, β particles have greater interaction with neighboring γ particles than with other β particles. This leads to a highly segregated microstructure, wherein large regions of β are broken up by veins of γ . Finally, strong negative coupling occurs when $\Gamma_{n,p} \ll 0$. In this scenario, β and γ particles act as solute sources, resulting in growing β particles neighboring growing γ particles, and large regions devoid of precipitates appear within the material as particles of both phases are consumed through bulk diffusion.

Allen *et al.* conducted a study on the time-evolution of a Sn-Ag-Cu eutectic alloy that consisted of three phases: Sn (matrix), Cu_6Sn_5 (rods), and Ag₃Sn (plates) [\[86,](#page-278-1) 87. The overall eutectic coarsened according to an $r^3 \propto t$ relationship, which they attributed to bulk Cu diffusion. That said, the two intermetallic phases, $Cu₆Sn₅$

Figure 7.1: Four elementary mechanisms of solid-state coarsening, as depicted in the schematics. a Curvature reduction dissipates surface energy by removing regions of high curvature (see arrows). b Interfacial energy anisotropy drives a particle or grain to align along low energy crystal orientations (oftentimes producing facets). c Coalescence enables two particles/grains to fuse into a single entity, thereby removing the high misfit boundaries in the channel between them. d Grain rotation reconfigures grains to a lower energy state with their surrounding neighbors by aligning to lower misfit planes. The two phases are α and β throughout; the black color gives the initial state, while the red shows the final state.

and Ag₃Sn, coarsened at different rates and independently from one another (*i.e.*, $\Gamma_{n,p} \rightarrow 0$, such that the rate-controlling mechanism is the same in ternary and binary systems: Ostwald ripening for $Cu₆Sn₅$ and spheroidization for Ag₃Sn, mediated by interface diffusion of Ag along the Ag3Sn/Sn interphase boundary. This study provided support for the above model, which predicted weak coupling between $Cu₆Sn₅$ and Ag3Sn phases due to the low mutual solubilities.

The above results suggest that, in order to predict how the microstructure in multiphase and multi-component eutectic alloys will coarsen, we must follow the evolution of three or more solid-solid interfaces and map an even more complex diffusion field in space and time. Previous studies on multi-component systems have mostly focused on the coarsening of dispersed particles [\[86,](#page-278-1) [87,](#page-278-2) [282–](#page-293-5)[285\]](#page-293-7), rather than the evolution of eutectic alloys (particularly in symmetrical phase diagrams), with a few exceptions [\[57,](#page-276-2) [256\]](#page-291-4). Importantly, one cannot necessarily assume infinite dilution for eutectics, since the solid phases are separated by a characteristic spacing that is on the order of a few micrometers. Due to the increasing demand for multi-phase eutectics [\[109,](#page-280-0) [253,](#page-291-1) [286\]](#page-293-8), and recent improvements in real-time imaging capabilities [\[185,](#page-286-0) [242,](#page-290-7) [287,](#page-293-9) [288\]](#page-294-0), the time is ripe to understand the dynamics of coarsening in such morphologically and topologically complex systems. For this purpose, the $Al-Ag_2Al-Al_2Cu$ eutectic is ideal: it has well-established thermophysical properties [\[6,](#page-272-2) [7,](#page-272-3) [22,](#page-273-2) [97,](#page-279-1) [99,](#page-279-2) [113,](#page-280-2) [201,](#page-287-0) [223,](#page-288-2) [259,](#page-291-7) 289, and a relatively low eutectic temperature (T_e) of 773.15 K; in addition, there has been preliminary work on post-solidification microstructural evolution [\[256,](#page-291-4) 290. Lastly, the Al-Ag₂Al-Al₂Cu eutectic forms multiple unique eutectic patterns [\[7,](#page-272-3) [268,](#page-292-4) [289\]](#page-294-1) depending on the alloy composition and growth velocity in directional solidification. This provides different initial conditions that may lead to different end-products upon coarsening.

Despite the extensive research on the $\text{Al-Ag}_2\text{Al-Al}_2\text{Cu}$ three-phase eutectic, many questions remain unanswered about its solid-state evolution. Specifically, what mechanism(s) drive solid-state coarsening in the system, and do multiple rate-limiting mechanisms coexist, as seen in the aforementioned Sn-Ag-Cu eutectic alloy [\[86,](#page-278-1) [87\]](#page-278-2)? Additionally, how does the interfacial anisotropy influence the solid-state evolution? For example, do established low energy interphase boundaries compete with curvature reduction to slow or stop coarsening?

With the aim of answering these questions, we used synchrotron-based X-ray nanotomography to obtain a three-dimensional (3D) view of the microstructural evolution and EBSD to track crystallographic evolution in $Al-Ag_2Al-Al_2Cu$. The former imaging technique allows all three solid phases to be distinguished readily [\[56,](#page-276-5) [201,](#page-287-0) [291\]](#page-294-3), owing to the differences in attenuation contrast, and at high resolution (45 nm/pixel). Conventional micro-tomography is not suitable since the lamellar spacing is on the order of a few micrometers in directional solidification (DS) , *i.e.*, approaching the pixel size $(0.69\mu m)$ [\[180\]](#page-285-0). Instead, our multimodel nano-imaging study focuses on characterizing the morphological and crystallographic evolution in a pseudo-ladder three-phase eutectic pattern [\[97,](#page-279-1) [289\]](#page-294-1), and the correlation of the two. Our efforts are made possible thanks to new hardware developments (a resistive heater at the synchrotron beam-line, enabling in situ experimentation) and new opportunities for multimodal characterization (the integration of X-ray absorption and electron diffraction data [\[180\]](#page-285-0)). These advances enable us to obtained detailed insight on the coarsening mechanism, interfacial anisotropy, and time-dependent bicrystal lattice mismatch.

7.2 Methods

7.2.1 In situ synchrotron X-ray nano-tomography

An alloy of composition Al-42.2 wt%Ag-17.6 wt%Cu (corresponding to the threephase eutectic point [\[22\]](#page-273-2)) was produced using high purity elements (99.999% Al, 99.999% Ag, and 99.999% Cu), vacuum arc remelted at the Materials Preparation

Center at Ames Laboratory (Ames, IA, USA). A cylindrical rod 1 mm in diameter and 10 mm in length was cut from the ingot using electron discharge machining (EDM). The rod was then placed into an alumina crucible and solidified within a vertical three-zone Bridgman directional furnace (MTI Corporation EQ-SKJ-BG). Since the sample diameter was small, radial convection is negligible in DS [\[292\]](#page-294-4). In practice, the sample was directionally solidified via the "gradient freeze" method by imposing a cooling rate, $\frac{dT}{dt}$, of ~0.9 K/min on each zone under a fixed thermal gradient, G, of \sim 1.5 K/mm anti-parallel to gravity. Under these conditions, the sample was expected to grow at a velocity, V, of $\sim 10 \ \mu \text{m/s}$. Following DS, we turned off the furnaces and removed the sample, allowing it to cool in air to room temperature.

Following DS, we hand polished and radially sectioned the sample, hereafter referred to as 'as-cast', approximately halfway along its length. With scanning electron microscopy (SEM), we identified a pseudo-ladder three-phase eutectic morphology [\[97,](#page-279-1) [289\]](#page-294-1). Using Xe plasma focused ion beam (FIB) milling, we milled a ∼45 µm diameter pillar of this material for in situ synchrotron X-ray nano-tomography with the Transmission X-ray Microscope (TXM) instrument. The experiments were performed at beamline 32-ID at the Advanced Photon Source of Argonne National Laboratory (Lemont, IL, USA) [\[190,](#page-286-1) [293\]](#page-294-5). We secured the sample onto an alumina rod with boron nitride spray and placed it on the kinematic mount (see Fig. [7.2\)](#page-180-0). Subsequently, we heated our sample to a homologous temperature of $0.9T_e$ (with respect to the three-phase eutectic temperature of 773.15 K) and annealed it isothermally for 4 hours. To capture the transient eutectic microstructure during coarsening, we took six intermittent TXM scans of the sample at 0.5, 0.75, 1, 2, 3, and 4 hour time-steps at temperature, i.e., without quenching the sample, in addition to an initial or 0 hour scan at room temperature. For the TXM measurements we used a 50nm outerzone width Fresnel Zone plate (FZP) coupled with a mono-capillary condenser. The detector had 2448×2048 pixels, with 45 nm pixel size after magnification. 1004 tomo-

Figure 7.2: Experimental setup for synchrotron TXM, at elevated temperatures at APS beam-line 32-ID. At left is a photograph of furnace used for in situ viewing. Red arrows indicate the X-ray port and direction of the X-ray beam. The sample is placed inside this furnace and rotated to capture images from different views, see schematics at right.

graphic projections were acquired while rotating the samples over 180 degrees. X-ray exposure time per each projection was 0.5 s, resulting in 8.4 min. time per scan. We attempted a continuous or uninterrupted scan between the 0 and 30 min. scans. To prevent blurring artifacts in the reconstruction domain associated with fast-moving features [\[180\]](#page-285-0), we reduced the exposure time to 0.1 s. Unfortunately, however, this resulted in a poor spatial resolution such that we were not able to distinguish the solid-solid interphase boundaries. For this reason, we do not analyze this particular dataset further. Throughout, we used a monochromatic beam of 8.4 keV to achieve reasonable contrast between the three phases.

That said, the high-temperature environment caused significant vibrations that were detrimental to the image resolution. This led to thermal radiation-induced deformations in the X-ray projection images. As a result, when we employed a standard algorithm to reconstruct our tomographic data, the data irregularities propagated into the reconstructed domain, making it difficult to separate phases and trace interfaces. To address this challenge, we used a new technique for compensating sample deformation artifacts and reducing the noise level [\[24\]](#page-273-0). In the following section, we will provide a brief description of this technique.

7.2.2 Optimized tomographic reconstruction

With a conventional method such as Gridrec implemented in the Tomopy pack-age [\[23\]](#page-273-1), a 3D object x can be reconstructed from its projection data d, according to

$$
x = \mathcal{R}^* \mathcal{W} d,\tag{7.2}
$$

where \mathcal{R}^* is the adjoint Radon transform operator and W is a filter, see [\[294\]](#page-294-0) for details. The method has the property of amplifying noise in images due to the filter structure. Therefore, reconstruction in many cases is performed by solving the following optimization problem,

$$
\min_{x} \|\mathcal{R}x - d\|^2 \tag{7.3}
$$

using iterative schemes and without the filtering operation. Commonly used iterative schemes for solving Eq. [7.3](#page-181-0) include the conjugate gradients method and simultaneous algebraic reconstruction technique [\[295\]](#page-294-1). In order to compensate for sample nanodrifts and decrease the noise level, we followed the method in Ref. [\[24\]](#page-273-0) and modified Eq. [7.3](#page-181-0) by adding the total variation (TV) regularization term $\|\nabla x\|_1$ and local deformation estimation operator \mathcal{D}_s that map functions to new coordinates according to local shifts s,

$$
\min_{x,s} \|\mathcal{D}_s \mathcal{R} x - d\|_2 + \lambda \|\nabla x\|_1,\tag{7.4}
$$

where the parameter λ corresponds to a trade-off between the data fidelity term and the regularization term. Higher values of λ lead to more intense noise suppression in reconstructions. Correct estimation of variable s in Eq. [7.4](#page-181-1) leads to compensating sample drifts that, in turn, results in better quality reconstruction. The proposed optimization problem is solved in [\[24\]](#page-273-0) by using the alternating direction method of multipliers [\[296\]](#page-294-2). A GPU-accelerated implementation of the method is publicly available in the TomoAlign package.^{[1](#page-182-0)}

A comparison between Gridrec and TomoAlign reconstructed slices is shown in Fig. [7.14.](#page-207-0) The final reconstructions are shown in Figs. [7.3\(](#page-183-0)a-d), which display the same intermediate slice of the 3D reconstruction as a function of time (in hours).

7.2.3 Segmentation of eutectic phases

We faced another complication due to our decision to capture TXM scans at elevated temperature, which was the increased solubility of Ag in α -Al [\[97,](#page-279-0) [99,](#page-279-1) [107,](#page-280-0) [201,](#page-287-0) [256,](#page-291-0) [259,](#page-291-1) [267,](#page-292-0) [289,](#page-294-3) [290\]](#page-294-4). At 723 K, Ag can dissolve up to ∼12wt% in α-Al before Ag₂Al starts to form (at equilibrium), compared to the $\langle 1wt\%Ag$ solubility at room temperature (RT). Consequently, the Al phase, which is the least attenuating phase at RT, is now more attenuating than the Al₂Cu phase in subsequent in situ reconstructions at the anneal temperature. In addition, the Ag_2Al rods shrink in size and some dissolve completely into the Al matrix. Thus it is challenging to apply a generic segmentation routine to partition the phases and track their evolution from the RT scan to those done at temperature.

To overcome this issue, we used a machine-learning based program, ZEN Intellesis developed by Carl Zeiss AG [\[220\]](#page-288-0), which utilizes a neural network to classify each pixel in a designated image to one of three solid phases. We hand-segmented 20 randomly selected images, which were then used to train the model. Note that we needed two separate training sets to segment the as cast data (at RT) and those captured at elevated temperature. To verify our segmentations, we computed the average recall, precision, and F1-score [\[297,](#page-294-5) [298\]](#page-294-6) for each phase over all seven time steps. Each phase

¹<https://github.com/nikitinvv/tomoalign>

Figure 7.3: Reconstruction slices provide snapshots of the microstructural evolution, at a 0, b 1, c 2, d 3, and e 4 hours of annealing. A magnified view of pseudo-ladder pattern in b is shown in yellow boxed region. This particular, representative slice (see coordinate system in a) is located $\sim 6.5 \mu m$ below the top of the micropillar sample. In **a**, the dark gray color represents Al, the light gray Al_2Cu , and white Ag_2Al . In b-e, the light gray color is instead Al saturated with Ag, the dark gray is $Al₂Cu$, and white is again Ag₂Al. For ease of viewing, Ag₂Al and Al₂Cu are outlined in red and blue, respectively, on the left-hand side.

had an average score greater than 0.9 of 1 for all metrics, where 1 corresponds to a perfect segmentation. This confirms the high degree of reliability of the segmentation procedure. Refer to Appendix [7.5](#page-206-0) for more details.

We also employed a watershed algorithm to improve the detection of the solid-solid interfaces, specifically those of the $\rm Al_2Cu$ phase. Then, the digitized interfaces of the eutectic solids were meshed (i.e., represented by a series of triangles and associated vertices). To remove any spurious staircasing artifacts, we smoothed the mesh by mean curvature flow [\[299\]](#page-294-7). We present our final 3D renderings of the evolving sample in Fig. [7.4](#page-185-0) where the Al, Ag_2Al , and Al_2Cu phases are consistently depicted in green, red, and blue, respectively. Similar to Fig. [7.3,](#page-183-0) Fig. [7.4](#page-185-0) shows the time-evolution of the microstructure over 4 hours.

7.2.4 Electron backscatter diffraction

Our next objective was to evaluate the crystal orientations of the eutectic phases as well as the orientation relationships between them. However, the as-cast microstructure of our TXM sample was no longer available. So, we obtained a fresh sample with the same composition and geometry as the original and recreated the growth conditions in DS. As expected, we found a similar pseudo-ladder three-phase eutectic structure, which we then characterized via electron backscatter diffraction (EBSD). For this purpose, we polished the sample with 1200 grit paper and then reduced the surface roughness further with FIB. We captured Kikuchi patterns of a $23.5 \times 15.0 \mu m^2$ transversal region of as-solidified microstructure, nearly parallel to the thermal gradient G, using a $0.04 \mu m$ step size in a square grid.

Due to the unique mechanical properties of each phase and the $\lt 5\mu m$ lamellar spacing, we weren't able to index the blurry Kikuchi patterns via traditional algorithms. Instead, we turned to dictionary indexing, which has demonstrated robustness against noise [\[195\]](#page-286-0). In short, the backscatter electron yield is simulated for

Figure 7.4: A cubic subvolume of $Al-Ag_2Al-Al_2Cu$ three-phase eutectic, annealed at 90% T_e (723 K). Data shown for **a** 0, **b** 1, **c** 2, **d** 3, and **e** 4 hours. Al, Ag₂Al, and $Al₂Cu$ phases are designated in the colors green, red, and blue, respectively. The gray and black encircled regions highlight regionsof-interest within the evolving microstructure (see text).

a hypothetical single crystal of a specific phase viewed in a geometrical model of our sample-detector configuration. The simulated and experimental patterns are then transformed into Rodrigues-Frank vectors in the fundamental zone. Finally, a dot product of the two vectors is taken and a similarity metric is computed. The simulated pattern most similar to the actual is identified as the crystal orientation [\[195\]](#page-286-0). This automated procedure allowed us to index our EBSD data. We used MTEX open source software [\[261\]](#page-291-2) in the Matlab [\[199\]](#page-287-1) computing environment to process the indexed data and visualize the crystallographic information for each phase (vide infra).

7.2.5 Combining TXM and EBSD data

To determine the crystallographic orientations of the solid-solid interfaces during the coarsening process, we must align the TXM and EBSD frames-of-reference, as a first step. Since we conducted TXM and EBSD scans on two different samples, it is nontrivial to register features in one dataset with those in the other. A second confounding issue is that the Ag₂Al rods are tilted $30°$ with respect to the thermal gradient (taken as the specimen z-axis); meanwhile, it is impossible to identify the angle and direction of any similar tilt within the 2D transversal section imaged by EBSD.

To circumvent these issues, we must make two simplifying assumptions to align the data sets: Firstly, we assume that G in both samples is identical and parallel to the specimen z-axis, which is itself antiparallel to gravity. This assumption is based on the fact that both samples were solidified under identical conditions and held in-place in alumina crucibles, which prevented any macroscopic specimen tilt during DS. Secondly, we assume that the Al_2Cu growth direction is [001], which is also parallel to G and therefore z. This assumption is supported by several past studies [\[22,](#page-273-2) [62,](#page-276-0) [97,](#page-279-0) [113,](#page-280-1) [201,](#page-287-0) [223\]](#page-288-1), which altogether demonstrate that within the Al-

Figure 7.5: Reorientation of reconstructed TXM volume into the crystallographic *frame* and computation of the Ag₂Al-Al and Ag₂Al-Al₂Cu bilateral common planes. In a, the original specimen frame-of-reference is shown with the eutectic phase data, as depicted in Fig. [7.4\(](#page-185-0)b), where again Al, $Ag₂Al$, and $Al₂Cu$ are in green, red, and blue, respectively. In b, the phase data is rotated to align with the EBSD map presented in Fig. [7.9.](#page-195-0) In c, the crystallographic orientations of Ag2Al rods are displayed (referenced to the $Ag₂Al frame$, see standard triangle).

 Ag_2Al-Al_2Cu eutectic, Al_2Cu grows in the [001] direction, regardless of its incipient growth morphology. With these assumptions in hand, we reoriented our tomography specimen into the EBSD frame-of-reference, as shown visually in Fig. [7.5\(](#page-187-0)a-b).

To transform the interfacial orientations from the EBSD specimen to the crystallographic frame-of-reference, we follow the procedure outlined in Refs. [\[17,](#page-273-3) [122\]](#page-281-0). We begin by computing local orientations (normal vectors) along patches of solid-solid interface, in the specimen frame. By convention, the normal vectors with respect to a given solid phase point outward, i.e., towards its neighbors. The interface unit normal, \hat{n}_i , of mesh triangle *i* is given as

$$
\hat{n}_{i,s} = \frac{\vec{e}_{i,1} \times \vec{e}_{i,2}}{\|\vec{e}_{i,1} \times \vec{e}_{i,2}\|}
$$
\n(7.5)

where $\vec{e}_{i,1}$ and $\vec{e}_{i,2}$ are the edge vectors or triangle i, measured in the specimen s frame.

To convert the normals in Eq. [7.5](#page-187-1) from specimen coordinates, C_S , into crystallo-

graphic coordinates, C_C , we must specify a rotation matrix, g, such that $C_C = gC_S$ [\[192\]](#page-286-1). Each eutectic phase requires a single, unique g matrix (retrieved from EBSD). assuming the phases are single crystals (proved later). Furthermore, for each crystal structure, such as face-centered cubic, hexagonal, and tetragonal for Al, $Ag₂Al$, and Al_2Cu , respectively, there is a set of point group symmetry operators, T_j . These operators represent the 48, 24, and 16 symmetry elements for 432, $6/mmm$, and $4/mmm$, respectively. Since $Ag₂Al$ is hexagonal, we converted its indices to an orthonormal coordinate system, following Ref. [\[300\]](#page-295-0). Ultimately, we obtain all crystallographicallyrelated solutions of the interfacial orientation, $\hat{n}_{i,c}$, as

$$
\hat{n}_{i,c} = T_j g \hat{n}_{i,s} \tag{7.6}
$$

This transformation is shown visually for the Ag_2Al phase in Fig. [7.5\(](#page-187-0)c).

After obtaining $\hat{n}_{i,c}$ for all mesh triangles and all phases, we display the results on a stereographic projection (inverse pole figure), hereby referred to as a crystallographic interface normal distribution (CIND) [\[17,](#page-273-3) [122\]](#page-281-0). For interfaces between phases α and β, the CIND gives the probability of finding a given crystallographic orientation $\hat{n}_{i,c}$ (measured with respect to either α or β). Due to crystal symmetry, we restrict the CIND to the fundamental zone. By plotting CINDs as a function of time (holding g fixed for each phase throughout the anneal), we can track the development of preferred interfacial orientations during coarsening.

7.3 Results and discussion

7.3.1 Interaction between Ag_2Al and Al_2Cu

As mentioned in the introduction, the coarsening dynamics in multi-phase, multicomponent systems differs from their two-phase, binary counterpart. This is because the coarsening behavior of one phase can impact the others, depending on the solubil-

ities and diffusivities according to Eq. [7.1](#page-175-0) [\[282\]](#page-293-0). Thus, to determine the cross-phase interaction between Ag₂Al and Al₂Cu, we calculate Γ_{Ag_2Al,Al_2Cu} and Γ_{Al_2Cu,Ag_2Al} using the thermophysical parameters given in Table [7.1.](#page-189-0) We obtain $\Gamma_{\text{Ag}_2\text{Al},\text{Al}_2\text{Cu}} = -0.014(1)$ and $\Gamma_{\text{Al}_2\text{Cu},\text{Ag}_2\text{Al}} = -0.018(1)$. Since these values are well below unity, we can suppose that the two phases will coarsen independently of each other and can examine the evolution of each separately, for sake of simplicity.

Indeed, this analysis appeals to our need to organize complex information into smaller units. Yet the theory assumes that the two phases are embedded randomly in a matrix, and interact only through concentration fields in that matrix [\[282,](#page-293-0) [283\]](#page-293-1). This assumption is reasonable if the two phases occupy minor volume fractions. Otherwise, we must consider the role of the initial microstructure, namely the spatial correlations [\[301\]](#page-295-1) and topological arrangements [\[7,](#page-272-0) [97\]](#page-279-0) of phases. Below, we show that this effect cannot be fully neglected.

7.3.2 Evolution of Ag_2Al morphology

Initial condition. In Fig. [7.4,](#page-185-0) we examine the reconstructed volumes and focus on the Ag2Al phase (shown in red). This phase is comprised of long fibers tilted at 30 \degree with respect to the z-axis (parallel to G). In the as-cast state at RT, the eutectic pattern can be described as single rods [\[97,](#page-279-0) [105,](#page-280-2) [289\]](#page-294-3). The two intermetallic

Table 7.1: Thermophysical parameters. We estimate the diffusivity D_i of component i in the Al matrix at $T = 723$ K using an Arrhenius relationship, $D_i = D_{o,i} \exp(-Q_i/(RT)).$

Phase n	Ag ₂ Al	$\mathrm{Al}_2\mathrm{Cu}$	Reference
$at\%)$	0.039(7)	$-0.55(1)$	TCAL8 [21]
$'at\%)$	$-0.31(1)$	$-0.013(1)$	TCAL8 [21]
Component i	Αg		Reference
(m^2/s) $D_{o,i}$	1.18×10^{-5}	6.47×10^{-5}	$\left[302\right]$
kJ/mol	116 ± 0.594	135 ± 1.13	302

phases (Ag₂Al and Al₂Cu) alternate back-and-forth within narrow channels in the Al matrix. Yet unlike a regular ladder structure [\[7,](#page-272-0) [22,](#page-273-2) [62\]](#page-276-0), in this case, Al_2Cu partially or completely encases several Ag₂Al rods. As such, Al₂Cu forms an interconnected, bicontinuous structure rather than discrete rods in DS.

Time evolution. In Fig. [7.4\(](#page-185-0)b), we observe the dissolution of Ag_2Al rods into the Al matrix, as we bring the sample from RT to 723 K. Consequently, the entire eutectic pattern undergoes a realignment of Ag_2Al-Al_2Cu chains, as small rods of $Ag₂Al$ disappear. The Al₂Cu phase does not undergo a similar change in volume fraction, resulting in a complete encasement of the newly shrunken Ag_2Al rods by Al_2Cu . Dissolution of Ag_2Al is rapid and has long-lasting effects on the eutectic microstructure. Even so, after the 1-hour mark, the newly established volume fractions remain relatively stable for the rest of the anneal.

As coarsening progresses, smaller $Ag₂Al$ rods gradually disappear while adjacent rods grow in size. One example can be seen in the grey circled region of Fig. [7.4.](#page-185-0) Here, two of the initial three Ag_2Al rods disappear over time-steps (a-e), while the third rod is growing at its neighbors' expense. Meanwhile, in the black circled region, we see three separate rods in (a) that coalesce in (b) to form an irregularly shaped rod. During (c-e), we see the elongated structure undergo curvature reduction and become much less peninsular. By virtue of the 3D data, we do not identify any faults along the Ag_2Al rods, which are characterized by pairs of terminations and branches. Moreover, we see no evidence of discontinuous coarsening [\[145\]](#page-283-0).

Kinetics of rod growth. To determine the operative coarsening mechanism, we used the PolyProc function package [\[303\]](#page-295-3) to assign order parameters to all discrete rods in the reconstructed volume, and track the evolution of each rod across multiple time steps. We computed the equivalent radius r for every identified rod over six time steps t at 723 K; of course, some rods were consumed within the 4-hour experiment. For the coarsening of fibers with a cylindrical geometry (i.e., 2D Ostwald ripening), it can be shown [\[145,](#page-283-0) [304\]](#page-295-4) that

$$
r^3 - r_o^3 = kt \tag{7.7}
$$

where k is the rate constant for coarsening and r_o is the radius at the onset of steadystate ripening. Assuming the relevance of Eq. [7.7,](#page-191-0) we plot in Fig. [7.6](#page-192-0) the radius cubed, r^3 , versus time, t, for each rod. We color the corresponding $\{r, t\}$ datasets by k. The average coarsening rate for all the rods, $\langle k \rangle$, was found to be 1.27 ± 0.0756 \times 10⁻⁶ μ m³/s. This rate constant is notably lower than that reported by Ref. [\[305\]](#page-295-5) for Ag₂Al precipitates in a *binary* Al-10 wt% Ag alloy at 473 K, $k = 8 \times 10^{-4} \ \mu \text{m}^3/\text{s}$, which would suggest a non-negligible influence of $Al₂Cu$ on the coarsening dynamics of Ag₂Al. A closer inspection of the data reveals that many rods have a negative r^3 value at later time-steps since they disappear before the final time-step. In addition, rods with negative k values are shrinking in time. In contrast, other rods appear to have little to no change in r during coarsening, while eleven Ag_2Al rods display a dramatic increase in size with $k > 1 \times 10^{-5} \ \mu \text{m}^3/\text{s}$.

As a robustness check, we estimate from our data the equilibrium volume fraction of Ag₂Al, f_e , noting that the instantaneous volume fraction f should decay slightly with time t [\[306\]](#page-295-6). Thus, we plot f against $t^{-1/3}$, see Fig. [7.7\(](#page-192-1)a). By extrapolating the data to $t \to \infty$, we obtain $f_e = 0.159 \pm 0.0037$. Notably, this value is very close to $f_e = 0.16$ reported by Ref. [\[7\]](#page-272-0) for an alloy of equivalent composition.

Kinetics of rod evanescence. As a system undergoes 2D Ostwald ripening, the number of rods or fibers per unit area, N_A , decreases with time, t, as

$$
N_A \approx \frac{f_e}{\pi \beta k^{2/3}} t^{-2/3} - \frac{(1 - f_e)l}{\langle u \rangle \pi \beta \Delta c_e k} t^{-1}
$$
\n(7.8)

where β is $\frac{\langle r \rangle^2}{\langle r^2 \rangle^2}$ $\frac{\langle r \rangle^2}{\langle r^2 \rangle}$, l is the capillary length, $\langle u \rangle$ is $\frac{r}{\langle r \rangle}$ in Lifshitz-Slyozov-Wagner the-ory [\[128,](#page-281-1) [129\]](#page-281-2) and Δc_e is the equilibrium solubility of the dispersed phase. With Eq. [7.8](#page-191-1) in mind, we plot $N_A t^{2/3}$ vs. $t^{-1/3}$, see Fig. [7.7\(](#page-192-1)b). The y-intercept gives $\frac{f_e}{\pi \beta k^{2/3}}$,

Dynamic scaling of Ag₂Al rods, on a plot of radius cubed, r^3 , vs. time, t, for all individually tracked rods. The discrete data points and corresponding linear fits are color-coded according to the computed rate constant, k , see color-bar. The average dynamics and corresponding 95% confidence interval is conveyed in black with a slope given by $\langle k \rangle$, indicated in the upper left-hand corner.

Figure 7.7: Consistency checks: **a** volume fraction of Ag₂Al, f, and **b** number of Ag₂Al rods per unit area, N_a , vs. inverse cube root of time, $t^{-1/3}$, cf. Eq. [7.8.](#page-191-1) Both plots also indicate their respective 95% confidence intervals. The linear relationships are given in the upper left-hand corner of each plot.

which we find to be 351 ± 15.9 s^{-2/3} μ m⁻². Using $f_e = 0.16$ from Ref. [\[7\]](#page-272-0), $\langle k \rangle$ from Fig. [7.6,](#page-192-0) and calculating β using the list of r at $t = 4$ hours, we directly compute $\frac{f_e}{\pi \beta k^{-2/3}}$ as 359 ± 14.3 s^{-2/3} μ m⁻². The extrapolated and computed values agree within 1%, and it is this self-consistency between the parameters in Eqs. [7.7-](#page-191-0)[7.8](#page-191-1) that indicates the $Ag₂Al phase evolves via 2D Ostwald ripening.$

At first glance, the conformation of our data to the scaling relations may appear somewhat surprising. This is because power law scaling implies the presence of a selfsimilar microstructure $|127|$. Instead, we observe that several Ag₂Al rods changed shape and developed faceted features with long, flat interphase boundaries; we also observe several Ag2Al rods coalesce with neighboring rods, as mentioned previously. Nevertheless, the scaling relations are robustly observed in many other systems without a self-similar morphology, for example, at high volume fractions in a binary system (where coalescence is inevitable) [\[307\]](#page-295-7).

Rod coalescence. To understand the effect of coalescence on the interfacial morphology, we collected the area-to-circumference ratios in 2D sections for all $Ag₂Al$ rods at the 1 hour mark. See Fig. [7.8\(](#page-194-0)a). The black line indicates the "ideal" relationship between area and circumference if the domains would be circular in cross-section. Clearly, the largest domains display the lowest area-to-circumference ratio, deviating from the ideal (see red trend-line) and hence corresponding to coalescence events. Following Ref. [\[280\]](#page-293-2), in Fig. [7.8\(](#page-194-0)b) we scaled the axes by the mean area and mean circumference. From this data it can be seen that the black and red lines intersect around the mean values, indicating that the domains with radii larger than $\sim 1 \times$ the equivalent mean radius are most likely to coalesce.

7.3.3 Evolution of Al_2Cu morphology

Graham and Kraft [\[144\]](#page-282-0) reported that the lamellar eutectic AIA_2Cu evolves through fault migration. According to Weatherly [\[308\]](#page-295-8), these fault lines correspond

Figure 7.8: Morphology of Ag₂Al rods: log-log plots of **a** area vs. circumference and b scaled area vs. scaled circumference of domains captured after 1 hour of annealing. The 'ideal' case (circular cross-sections) is shown in black and the fit to the last 50 data-points is shown in red.

to subgrain boundaries. However, it is uncertain if fault migration is necessarily responsible for coarsening of Al_2Cu within a three-phase eutectic microstructure. As a first step to understanding the morphological evolution of Al_2Cu , we examine the crystallography of the system. Fig. [7.9](#page-195-0) shows a phase map of the three-phase eutectic with corresponding inverse pole figures (IPF) for each phase. We observe that data for $\rm Al_2Cu$ are densely packed into three regions, with the cluster of data-points nearest to {001} accounting for the majority of orientations. The low orientation spread (within 2°) indicates that Al₂Cu has a low incidence of subgrain boundaries, and hence a low fault density, i.e., it is a single crystal.

In the absence of faults, it remains to be determined how Al_2Cu coarsens. Unlike $Ag₂Al$, identifying the underlying mechanism for $Al₂Cu$ is somewhat challenging since it does not show an equiaxed shape. In Fig. [7.4,](#page-185-0) it can be seen that $Al₂Cu$ is highly interconnected and forms a pseudo-ladder structure. For this reason, we replace r in Eq. [7.7](#page-191-0) with the inverse surface area per unit volume S_v^{-1} as an appropriate length-

Figure 7.9: EBSD phase map of as-cast $Al-Ag_2Al-Al_2Cu$ three-phase eutectic, solidified at $G \approx 1.5 \text{ K/mm}$ and $\frac{dT}{dt} \approx 0.9 \text{ K/min}$. Al, Ag₂Al, and Al₂Cu phases are depicted in green, red, and blue, respectively. Inverse pole figure for each phase shown at right.

scale [\[309,](#page-295-9) [310\]](#page-295-10), see Fig. [7.15.](#page-209-0) Since $S_v^{-1} \propto t^{1/3}$ asymptotically, Al₂Cu coarsens *via* 3D Ostwald ripening.

7.3.4 Evolution of interfacial bicrystallography

The lack of self-similarity from the above analysis (particularly for $Ag₂Al$) raises important questions about the changes in interfacial crystallography over time and how they relate to morphological changes. Given the preferential crystal orientations for Al, Ag₂Al, and Al₂Cu (*cf.* Fig. [7.9\)](#page-195-0), we can determine not only the orientation relationships of the three phases, but also the common planes (CPs) of their interphase boundaries (so-called bilateral CPs).

Orientation relationships. From the EBSD data of the as-cast microstructure, we determine the epitaxial relations: we identify the common directions as $[101]_{\text{Al}}$ $[2110]_{Ag_2Al}$ || $[001]_{Al_2Cu}$, and the common planes as $(131)_{Al}$ || $(0110)_{Ag_2Al}$ || $(110)_{Al_2Cu}$. By transforming the TXM data to the crystallographic frame (see Sec. [7.2.5\)](#page-186-0), we find the bilateral CP between the two intermetallics (Fig. [7.16a](#page-210-0)-c) in the RT data as $(0001)_{\text{Ag}_2\text{Al}}$ || $(110)_{\text{Al}_2\text{Cu}}$. Similar ORs for this three-phase eutectic have been reported elsewhere [\[22,](#page-273-2) [62,](#page-276-0) [113\]](#page-280-1). Additionally, EBSD data was collected from another region of the sample, coarsened for 4 hours. The OR does not change with time (Fig. [7.16d](#page-210-0)-f), indicating there is no grain rotation.

Interfaces of Ag₂Al. We calculated the crystallographic normals ($\hat{n}_{i,c}$ in Eq. [7.6\)](#page-188-0) along all solid-solid interfaces over the course of the anneal, beginning with those bounding the Ag_2Al phase. Fig. [7.10](#page-197-0) illustrates the time-evolution of the bilateral CPs for the ensemble of Ag_2Al rods at three representative time steps. In the top row, we distinguish between Ag_2Al-Al and Ag_2Al-Al_2Cu boundaries in green and blue, respectively. The middle row displays the same solid-solid interfaces such that each patch of interface is colored according to its local orientation, see the standard triangle at left. In the bottom row, we provide the corresponding CIND for each interphase boundary. The color-bar limits are fixed throughout to allow for comparison. Similar to past reports by Ref. [\[22\]](#page-273-2) and others (black points), there is a relatively high probability of finding Ag_2Al-Al and Ag_2Al-Al_2Cu aligned to the basal plane, prismatic plane, or both in its as-cast state. However, upon annealing, the rods appear to evolve into less frequently reported interfacial orientations (e.g., Ag_2Al-Al_2Cu approaches {2203} after 4 hours). This suggests that the reported bilateral CPs of ${0001}$ and ${100}$ may not necessarily be the *lowest* energy interphase orientations.

To disaggregate the above statistics, we focus on a small subset of $Ag₂Al$ rods and tracked their development over 4 hours, see Fig. [7.11.](#page-199-0) The top row shows a classification of interphase boundaries, the middle row the crystallographic orientation of each boundary referenced to $Ag₂Al$, and the bottom row the corresponding CINDs normalized to the same range. We notice in the top row that the Ag_2Al rods coalesced over time. At the 2 hour mark, the center and right rods completely fused into a single misshapen rod. Additionally, we observe the beginning of a similar coalescence event involving the center and leftmost rod. Note that the Ag_2Al rods were separated by

triangle at left. The bottom row gives corresponding CIND plots in the Ag_2A1 frame. All plots have been scaled to and hours. The top row displays Ag₂Al rods colored according to the interphase boundary type, where green is and hours. The top row displays Ag2Al rods colored according to the interphase boundary type, where green is Ag₂Al-Al and blue is Ag₂Al-Al₂Cu. The middle row shows interphase boundaries for Ag₂Al-Al (left) and Ag₂Althe same color-bar limits to facilitate comparison between them. Black squares identify the habit plane orientations Figure 7.10: Coarsening evolution of all $AggAl-Alg$ and $AggAl-Al$ interphase boundaries, shown over three time steps: 0, 2, $\frac{2}{n-2}$ Figure 7.10: Coarsening evolution of all Ag₂Al-Al₂Cu and Ag₂Al-Al interphase boundaries, shown over three time steps: 0, 2, 2, Al₂Cu (right). Each interfacial patch is illuminated according to its crystallographic orientation within the standard Ag₂Al-Al and blue is Ag₂Al-Al₂Cu. The middle row shows interphase boundaries for Ag₂Al-Al (left) and Ag₂Al-
 Al2Cu (right). Each interfacial patch is illuminated according to its crystallographic orientation within the standard triangle at left. The bottom row gives corresponding CIND plots in the Ag2Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them. Black squares identify the habit plane orientations reported in Ref. [22], namely $(000\overline{1})_{\text{Ag}_2\text{Al}}$ and $(1\overline{1}00)_{\text{Ag}_2\text{Al}}$. reported in Ref. [\[22\]](#page-273-2), namely $(0001)_{\text{Ag}_2\text{Al}}$ and $(1100)_{\text{Ag}_2\text{Al}}$. a narrow \sim 250 nm thick region of Al₂Cu. Thus the coalescence of Ag₂Al could only take place because of the elimination of the Al_2Cu phase, *i.e.*, the consolidation of one phase is the direct consequence of the evolution of the other.

According to the bottom row of Fig. [7.11,](#page-199-0) the bilateral CPs of Ag_2Al align with $\{0001\}$ and $\{\overline{1}100\}$ in the as-solidified structure, consistent with past reports [\[22\]](#page-273-2). After the first hour, these planes continue to dominate the CIND. However, after 2 hours (when coalescence begins), the distribution of interfacial orientations is markedly different: the most probable orientation of the Ag_2Al-Al_2Cu boundary shifts to $\{0001\}$, while the Ag₂Al-Al boundary moves to $\{2203\}$. This shift occurs in less than 2 hours before the interfaces appear to 'lock' into the faceted, convex structure seen at the end-state. On closer inspection, we notice that the rods coalesce along {1100} boundary with $\rm Al_2Cu$, which explains why this orientation becomes less probable in comparison to {0001}. We can also compare the {2203} plane against that of other studies. For example, $\{203\}$ differs by 10.7° from the $\{\overline{1}101\}$ plane reported by Friess *et al.* [\[113\]](#page-280-1). Therefore, it is not unreasonable that Ag_2Al displays these interfaces before locking in place. In the case of the Ag_2Al-Al boundary, we observe that the peak in the CIND value has shifted by 35.4◦ , but we have no information about the kinetics that led to this transformation, only the final product.

To quantify the above behavior, we calculate the area fractions that belong to each interphase boundary as a function of time. Fig. [7.17\(](#page-211-0)a) illustrates the evolution of the Ag₂Al-Al boundary and indicates a 53% reduction in $\{0001\}$ planes and a 49% increase in $\{2203\}$ planes. The rate of change of the area fractions drops quickly after 2 hours of coarsening. In Fig. [7.17\(](#page-211-0)b), we observe the transformation of the Ag2Al-Al2Cu boundary, where we again see rapidly changing area fractions before stagnating after the 2 hour mark.

Interfaces of Al and Al_2Cu . Figs. [7.18](#page-212-0)[-7.19](#page-213-0) illustrate the changes in morphology and interfacial orientation of A_2Cu and Al phases in the same, bulk volume

Figure 7.11: Coarsening evolution of three adjacent Ag_2Al rods which coalesce into a single domain. Ag_2Al-Al_2Cu and Ag_2Al-Al_2 interphase boundaries are shown over five time steps: $0, 1, 2, 3$, and 4 hours. The top row shows the isolated Ag₂Al rods colored according to the interphase boundary type, where green is Ag₂Al-Al and blue is Ag₂Al-Al₂Cu. patches are illuminated according to their crystallographic orientation within the standard triangle at left. The Figure 7.11: Coarsening evolution of three adjacent Ag2Al rods which coalesce into a single domain. Ag2Al-Al2Cu and Ag2Al-Al
 The middle row displays the interphase boundaries for Ag₂Al-Al (left) and Ag₂Al-Al₂Cu (right), where interfacial The middle row displays the interphase boundaries for Ag2Al-Al (left) and Ag2Al-Al2Cu (right), where interfacial bottom row displays corresponding CIND plots in the Ag₂Al frame. All plots have been scaled to the same color-bar interphase boundaries are shown over five time steps: 0, 1, 2, 3, and 4 hours. The top row shows the isolated Ag2Al rods colored according to the interphase boundary type, where green is Ag2Al-Al and blue is Ag2Al-Al₂Cu. patches are illuminated according to their crystallographic orientation within the standard triangle at left. The bottom row displays corresponding CIND plots in the Ag₂Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them. limits to facilitate comparison between them.

as in Fig. [7.10.](#page-197-0) We also give a similar set of plots for the smaller field-of-view as in Fig. [7.11,](#page-199-0) see Figs. [7.20-](#page-214-0)[7.21.](#page-215-0) According to the CINDs therein, the Al_2Cu-Ag_2Al interface has a slight preference for $\{110\}$ (referenced to the Al₂Cu crystal) in the as-cast state and evolves to $\{130\}$ during coarsening. In contrast, the Al-Ag₂Al interphase boundaries do not show a clear progression (when referenced to the Al crystal), starting near $\{122\}$ and then shifting towards $\{011\}$ before moving towards {111} in the later stages of coarsening. It is possible that this evolution is part of a larger change that reduces the overall interfacial energy, but this will be proved later in Sec. [7.3.5.](#page-200-0) Taken altogether, the coalescing Ag_2Al rods initially have the bilateral CPs $\{0001\}_{\text{Ag}_2\text{Al}}$ $\parallel \{\overline{1}22\}_{\text{Al}}$ and $\{\overline{1}100\}_{\text{Ag}_2\text{Al}}$ $\parallel \{\overline{1}10\}_{\text{Al}_2\text{Cu}}$, which give way to $\{\overline{2}203\}_{\rm Ag_2Al}$ ∥ $\{\overline{1}11\}_{\rm Al}$ and $\{0001\}_{\rm Ag_2Al}$ ∥ $\{\overline{1}13\}_{\rm Al_2Cu}$ over the 4 hour anneal.

7.3.5 Selection of interfaces during coarsening

To understand why certain orientations dominate as time proceeds, we compute and compare the lattice misfits for the different interphase boundaries from above. Since the interfaces are semicoherent [\[22,](#page-273-2) [256,](#page-291-0) [311\]](#page-295-11), the orientations with the lowest misfits should correspond to the lowest interfacial energies, neglecting thermal and chemical effects. Misfit, δ , is found as

$$
\delta = 2 \frac{\|\rho_{\gamma} - \rho_{\beta}\|}{(\rho_{\gamma} + \rho_{\beta})}
$$
\n(7.9)

where ρ_i represents the atomic density of phase i. In general, the atomic density of a lattice plane is expressed as $\rho = \frac{nd}{\Omega}$ $\frac{nd}{\Omega}$, where *n* is the number of atoms per unit cell in the plane, d is the interplane spacing, and Ω is the volume of the unit cell. However, this definition often leads to varying ρ (and hence δ) since it requires the selection of a specific atomic layer. To overcome this limitation, we adopt the "puckered" interface description [\[281,](#page-293-3) [310\]](#page-295-10), which calculates ρ by taking into account additional atoms that are slightly above and slightly below a given plane. This enables us to determine a minimum δ for a set of bilateral CPs.

Fig. [7.12](#page-202-0) shows the planar density ρ as a function of the thickness of a given layer wherein the "puckered" atoms may be located. Each line represents the contribution of additional atoms to ρ . For each type of interphase boundary, the smallest difference in planar density for the same plane thickness give us the minimum lattice misfit. Table [7.2](#page-204-0) summarizes the results for both the initial (as-cast) and final (4-hour) states. It can be seen that the lattice misfits for both Ag_2Al-Al and Ag_2Al-Al_2Cu interfaces reduce over time, from 8.12% to 5.50% and 10.2% to 3.55%, respectively. This apparent shift suggests that coalescence drives the overall reduction in interfacial energy, for the field-of-view so considered. To lend credence to this idea, in Fig. [7.13](#page-203-0) we plot the surface areas for $\{0001\}_{\text{Ag}_2\text{Al}}$ $\parallel \{\overline{1}13\}_{\text{Al}_2\text{Cu}}$ (in blue) and $\{\overline{2}203\}_{\text{Ag}_2\text{Al}}$ $\parallel \{\overline{1}11\}_{\text{Al}}$ (in green) vs. time, together with snapshots of the $Ag₂Al$ rod cross-sections. The colors of the interfaces match the corresponding data-points. Clearly, consolidation of Ag₂Al leads to the expansion of the $\{0001\}_{\text{Ag}_2\text{Al}}$ interface with Al₂Cu and also a broadening of $\{2203\}_{\text{Ag}_2\text{Al}}$ with Al. We measure the dihedral angle ϕ between these two interfaces and find $\phi \sim 60.3^{\circ} \pm 13.9^{\circ}$; the actual interplanar angle of 51° between ${0001}_{Ag_2Al}$ and ${\overline{2203}}_{Ag_2Al}$ is clearly within this standard deviation. Since both Ag2Al interfaces have comparable and low misfit, it follows that neither plane can expand further without sacrificing the other. As a result, the morphological evolution appears to stagnate, and the two planes 'lock' to form a faceted geometry at long times. The competition between the two interfaces may also explain why $Ag₂Al$ never attains its equilibrium shape with Al (a hexagonal plate [\[305\]](#page-295-5)), at least within the finite duration of our experiment.

We caution that the above puckering analysis provides only a preliminary assessment and does not consider the solubility of Ag in α -Al nor lattice expansion at elevated temperature. It will be necessary to carry out molecular dynamics simula-

Figure 7.12: *Misfit of solid-solid interfaces*. Computed planar density of different crystal orientations, considering all atoms within a certain atomic layer thickness (defined as the distance from the interface into the crystal of the listed phase). Accordingly, we compute the minimum misfit as the smallest difference in atomic planar density of the two solid phases. Using the orientations found for the isolated $Ag₂Al$ rods in Fig. [7.11,](#page-199-0) a displays the planar density of the most prominent orientations in the as-cast state for the two types of hetero-interfaces: $\{0001\}_{\text{Ag}_2\text{Al}}\|\{\overline{1}22\}_{\text{Al}}$ and $\{\overline{1}100\}_{\text{Ag}_2\text{Al}}\|\{\overline{1}10\}_{\text{Al}_2\text{Cu}}$. **b** shows the planar densities of the most prominent orientations after 4 hours of coarsening: $\{2203\}_{\text{Ag}_2\text{Al}}\|\{\overline{1}11\}_{\text{Al}}$ and $\{0001\}_{\text{Ag}_2\text{Al}}\|\{\overline{1}30\}_{\text{Al}_2\text{Cu}}$. Al, Ag₂Al, and Al₂Cu are in green, red, and blue, respectively.

Evolving surface area of Ag₂Al interfaces. Surface area of $\{2203\}_{\text{Ag}_2\text{Al}}$ and $\{0001\}_{\text{Ag}_2\text{Al}}$ habit planes vs. time. A 3D mesh of Ag₂Al rod surfaces at each time step is shown inset, in gray, viewed along the long axis of the rods. Planes which align with $\{2203\}_{\text{Ag}_2\text{Al}}$ and $\{0001\}_{\text{Ag}_2\text{Al}}$ have been colored to match the data points. For display purposes only, the Ag2Al rod mesh is pre-processed to prevent any gaps from smoothing. This leads to a small misalignment between the mesh and the labeled habit planes.

	As cast		4 hours	
Interphase boundary	Ag ₂ A1 Al	$Ag_2Al Al_2Cu$	Ag ₂ Al Al	$Ag_2Al Al_2Cu$
Bilateral CPs	${0001}\ \{\bar{1}22\}$	$\{\overline{1}100\}$ $\{\overline{1}10\}$	$\{\overline{2}203\}$ $\{\overline{1}11\}$	$\{0001\}$ $\{\overline{1}30\}$
Number of atoms in plane	3 3	2 2	11 1	3 6
Planar density (atom/nm^2)	13.(3) 12.(3)	8.5(9) 9.5(6)	$13.(4)$ 14.(1)	13.(3) 12.(8)
Planar misfit $(\%)$	8.12\%	10.2%	5.50%	3.55%

Table 7.2: *Interfacial bicrystallography*, at initial and final time-points of the anneal process.

tions (akin to Ref. [\[312\]](#page-295-12)) to determine the interphase boundary energies and correlate them to the experimental observations. In addition, the high index planes of $Ag₂Al$ at the later temp-steps may display a regular array of steps and kinks. Such an effect would only be visible through high resolution imaging techniques such as TEM. This is an avenue of current research.

In the future, we also intend to develop a clearer picture of the early-stage dynamics, during which fault migration may dominate coarsening [\[150\]](#page-283-1). Although we found limited faults along the Ag_2Al rods in the as-cast structure, terminations and branches have been previously reported for the $Ag₂Al phase$ [\[99\]](#page-279-1), and therefore fault migration cannot be necessarily ruled out. Finally, we aim to investigate the influence of the initial condition: the $A1 \text{Ag}_2A1 \text{Al}_2Cu$ three-phase eutectic produced several distinct patterns during DS [\[7,](#page-272-0) [22,](#page-273-2) [97,](#page-279-0) [107,](#page-280-0) [301\]](#page-295-1), and the arrangement of phases and the ORs between them may impact the coarsening pathway.

7.4 Conclusions

We probed the coarsening dynamics of a model three-phase eutectic *via in situ* 4D X-ray nano-imaging coupled with EBSD. This investigation led to the following conclusions:

• We demonstrated a method to reconstruct X-ray micrographs corrupted by noise from thermal vibrations. Using TV-regularized reconstruction with deformation compensation and machine learning segmentation, we characterized the three eutectic phases and their respective interphase boundaries.

- Based on this data, we found that two of the phases $(Ag_2A1$ and $Al_2Cu)$ obey a temporal power law for their average length-scales, matching the predictions of theory. Even so, the eutectic microstructures are not self-similar in time.
- One reason for the absence of self-similarity is the coalescence of neighboring Ag₂Al rods, which involves the elimination of an intervening Al_2Cu channel. This demonstrates that the coarsening of one phase (Ag_2A) is limited by the other (Al_2Cu) , in a multi-phase system with comparable volume fractions.
- By correlating our absorption and diffraction data, we identified the common planes at the solid-solid interfaces. In this way, we determined that coalescence leads to a selection of interfaces that possess low misfit, and by extension, low energy.

Acknowledgements

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7.5 Appendix: Segmentation performance

To ascertain the reliability of our segmented data, we compare a digitally segmented image to one that is hand-segmentated, taken as ground truth. All pixels are divided into four classes: true positives (TP) , true negatives (TN) , false positives (FP) , and false negatives (FN) . Mapping the pixels in this manner allows us to computed the average recall (R) , precision (P) , and $F1-score$ for each of the three phases [\[297,](#page-294-5) [298\]](#page-294-6). Sometimes called sensibility, recall describes the capability of a segmentation to identify all instances of a designated class $(i.e., R = TP/(TP + FN)).$ Meanwhile, precision, or sensitivity, describes the ability to identify only the designated class (*i.e.*, $P = TP/(TP + FP)$). Finally, the F1-score, otherwise known as the Dice loss score, gives the harmonic mean of the precision and recall $(i.e.,$ $F_1 = 2(P * R)/(P + R) = 2TP/(2TP + FN + FP)$. The recall, precision, and F1-score range from zero to one, with values closer to one indicating a higher accuracy.

To perform these calculations, we selected the central-most reconstructed slice for each of our time-steps and segmented it by hand, i.e., tracing over the solid-solid interfaces as best as possible. We then compared each ground truth slice to the respective one automatically segmented and computed the precision, recall, and F1-score. In order to account for human error in the hand segmentation, we selected a tolerance threshold of 4 pixels (*i.e.*, 2% of image width and height). Table [7.3](#page-208-0) gives the results. We find that the average recalls for Al, Al_2Cu , and Ag_2Al are 0.92 ± 0.02 , 0.92 ± 0.01 , and 0.99 ± 0.01 , respectively. Average precisions for Al, Al₂Cu, and Ag₂Al are 0.90 ± 0.03 , 0.92 ± 0.02 , and 0.97 ± 0.1 , respectively. Finally, the average F1-scores for Al, Al_2Cu , and Ag_2Al are 0.91 ± 0.02 , 0.92 ± 0.01 , and 0.98 ± 0.01 , respectively. All of these values display a high level of similarity and accuracy (comparable to other works [\[219,](#page-288-2) [313\]](#page-295-13)), confirming that our automated segmentation is reliable.

0.9266 0.9266 0.9266 0.9801 0.92809 0.9333 0.92809 0.9272 0.9285 0.9271 0.9275 0.9286 0.9271

0.9226 0.9256 0.9932 0.8789 0.9004 0.9461 0.9002 0.9128 0.9691

0.8789
0.9022

0.9932
0.9842

0.9256
0.9300

 0.9004
 0.8927

 0.9691
 0.9734

0.9128 0.9110 0.9090

 0.9002
 0.9150

0.9461
0.9628

0.9800 0.9814 0.0076

0.0104

 0.9206

0.9098 0.0201

0.9178

0.9620 $\frac{0.9703}{2}$ 0.0139

0.9282 0.9300 0.9842 0.9022 0.8927 0.9628 0.9150 0.9110 0.9734

 $4\hskip 1.6cm 1.9330\hskip 0.2cm 0.9303\hskip 0.2cm 0.9987\hskip 0.2cm 0.8886\hskip 0.2cm 0.9620\hskip 0.2cm 0.9178\hskip 0.2cm 0.9090\hskip 0.2cm 0.9800$ $\mathrm{Avg.}\quad\begin{array}{|l|} \hline \text{Avg.}\hline \text{0.9203}\hline \text{0.9203}\hline \text{0.9229}\hline \end{array}$ 0.936 0.9703 0.9703 0.988 0.9814 $\text{Std.} \qquad \begin{array}{|l|} \text{0.067} \quad 0.0066 \quad 0.00631 & 0.0268 \quad 0.0245 \quad 0.0139 & 0.0201 \quad 0.0104 \quad 0.0076 \end{array}$

0.9032

0.9987 0.9929

0.9303 0.9229 0.0066

0.8886

0.9187 0.0245

0.8996

0.0268

0.00631

Table 7.3: Contour matching scores. Recall, precision, and $F1$ -score of the Al, Al_2Cu , and Ag_2Al phases computed by comparing comparing Table 7.3: Contour matching scores. Recall, precision, and F1-score of the Al, Al₂Cu, and Ag₂Al phases computed by comparing

 $\overline{2}$

0.9226 0.9282 0.9330 $\frac{0.9203}{5}$ 0.067

 $\overline{\mathfrak{c}}$

4

Avg. $\overline{\overline{\mathrm{std}}}$.

Dynamic scaling of Al_2Cu domains. Plot of S_v^{-1} vs. $t^{-1/3}$ during the annealing process. The line-of-best-fit is shown in blue along with the 95% confidence interval. The linear regression equation is given in the top-left corner $(\tilde{R}^2 = 0.9626)$.

Figure 7.16: Orientation relationships: **a-c** as cast sample and **d-f** one coarsened for 4 hours. **a**, **d** common directions $\overline{[101]_{\text{Al}}}\left\|\overline{[2110]}_{\text{Ag}_2\text{Al}}\right\|\overline{[001]}_{\text{Al}_2\text{Cu}}$ **b**, **e** CPs $(\overline{131})_{\text{Al}} \parallel (01\overline{10})_{\text{Ag}_2\text{Al}} \parallel (110)_{\text{Al}_2\text{Cu}}$, and **c**, **f** bilateral CP $(0001)_{Ag_2Al}$ ||(110)_{Al2Cu}. Al, Ag₂Al, and Al₂Cu grains are colored in green, red, and blue, respectively.

Figure 7.17: Evolving area fractions of Ag₂Al interfaces: **a** Bilateral CPs shared with Al, $\{0001\}_{\text{Ag}_2\text{Al}}$ and $\{\overline{2}203\}_{\text{Ag}_2\text{Al}}$, and **b** CPs shared with Al₂Cu, ${\overline{1100}}_{Ag_2Al}$ and ${\overline{0001}}_{Ag_2Al}$, as a function of annealing time. All data are plotted with 95% confidence intervals.

Top row: Al phase colored by the interphase boundary type where red is $A1-Ag_2A1$ and blue is $A1-A1_2Cu$. Middle Figure 7.18: Coarsening evolution of Al-AggAl and Al-AlgCu interphase boundaries, shown at three time steps: 0, 2, and 4 hours.
The more manimum and the column of Al-AggAl and Al-AlgCu interphase boundaries, shown at thre row: interphase boundary for Al-Ag₂Al (left) and Al-Al₂Cu (right). Interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: corresponding CIND plots in the Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison. Black squares identify the Top row: Al phase colored by the interphase boundary type where red is $A1-Ag_2A1$ and blue is $A1-A1_2Cu$. Middle Figure 7.18: Coarsening evolution of Al-Ag₂Al and Al-Al₂Cu interphase boundaries, shown at three time steps: 0, 2, and 4 hours. row: interphase boundary for Al-Ag2Al (left) and Al-Al2Cu (right). Interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: corresponding CIND plots in the Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison. Black squares identify the habit plane orientation reported in Ref. [22], $(1\overline{13})_{\text{Al}}$. habit plane orientation reported in Ref. $[22]$, (113) _{Al}.

4 hours. Top row: Al_2Cu phase colored by the interphase boundary type where red is $\text{Al}_2\text{Cu-Ag}_2\text{Al}$ and green is $A_{12}Cu-A1$. Middle row: interphase boundary for $A_{12}Cu-A_{52}Al$ (left) and $A_{12}Cu-A1$ (right). Interfacial patches are Figure 7.19: Coarsening evolution of $A l_g C u$ - $A g_g A l$ and $A l_g C u$ - $A l$ interphase boundaries, shown over three time steps: 0, 2, and A and 4 hours. Top row: Al₂Cu phase colored by the interphase boundary type where red is Al₂Cu-Ag₂Al and green is colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND plots in the $\mathrm{Al}_2\mathrm{Cu}$ frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them. Black squares identify the habit plane orientations reported in Ref. [22], namely $(1\overline{1}0)_{A1_2Ou}$ and between them. Black squares identify the habit plane orientations reported in Ref. [\[22\]](#page-273-2), namely $(110)_{A1_2Cu}$ and Figure 7.19: Coarsening evolution of $AlgCu-Ag_2Al$ and $AlgCu-Al$ interphase boundaries, shown over three time steps: 0, 2, and Al₂Cu-Al. Middle row: interphase boundary for Al₂Cu-Ag₂Al (left) and Al₂Cu-Al (right). Interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND plots in the Al_2Cu frame. All plots have been scaled to the same color-bar limits to facilitate comparison (110) Al₂Cu.

Figure 7.20: Coarsening evolution of the Al-AggAl interphase boundary along the coalescing AggAl rods in Fig. 7.11, shown over
first time at the contract of the Al-AggAl interphase boundary along the coalescing AggAl rods five time steps: 0, 1, 2, 3 and 4 hours. Top row: Ag₂Al phase colored by the interphase boundary type where red is Al-Ag₂Al. Middle row: interphase boundary for Al-Ag₂Al. Interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND plots in the Figure 7.20: Coarsening evolution of the Al-Ag2Al interphase boundary along the coalescing Ag2Al rods in Fig. [7.11,](#page-199-0) shown over five time steps: $0, 1, 2, 3$ and 4 hours. Top row: Ag₂Al phase colored by the interphase boundary type where red is Al-Ag2Al. Middle row: interphase boundary for Al-Ag2Al. Interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND plots in the Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them. Al frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them.

Figure 7.21: Coarsening evolution of the AlgCu-AggAl interphase boundary along the coalescing AggAl rods in Fig. 7.11, shown
 $\frac{c}{2}$ Coarsening evolution of the AlgCu-AggAl interphase boundary along the coalescing AggAl over five time steps: $0, 1, 2, 3$ and 4 hours. Top row: Ag₂Al phase colored by the interphase boundary type where red is Al₂Cu-Ag₂Al. Middle row: interphase boundary for Al₂Cu-Ag₂Al where interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND Figure 7.21: Coarsening evolution of the Al2Cu-Ag2Al interphase boundary along the coalescing Ag2Al rods in Fig. [7.11,](#page-199-0) shown plots in the Al₂Cu frame. All plots have been scaled to the same color-bar limits to facilitate comparison between over five time steps: 0, 1, 2, 3 and 4 hours. Top row: Ag₂Al phase colored by the interphase boundary type where red is A_2Cu-Ag_2A l. Middle row: interphase boundary for A_2Cu-Ag_2A1 where interfacial patches are colored according to crystallographic orientation within the standard triangle at left. Bottom row: Corresponding CIND

and the corresponding CIND plots in the Al2Cu frame. All plots have been scaled to the same color-bar limits to facilitate comparison between them.
CHAPTER VIII

Peritectic Solidification Patterns in Three- and Four-Dimensions

This chapter centers around work done with my colleague Dr. Shanmukha Kiran Aramanda, without whom this project would not have been possible and shares cofirst authorship. The chapter is based on an article that has been submitted for publication in Acta Materialia as of February 2024.

Abstract: Microstructure selection in two-phase peritectic alloys has been a longstanding topic of fundamental importance. The bicontinuous microstructures arising from peritectic solidification have presented significant challenges for analysis due (in part) to our reliance on two-dimensional (2D) sections, which limits our ability to interpret the full three-dimensional (3D) complexity. Additionally, understanding growth mechanisms based solely on postmortem data has proven to be challenging because the extent of the solid-state peritectic transformation is unknown. Here, we employed X-ray imaging techniques to acquire detailed 3D data and visualize in real-time the dynamics of peritectic solidification in a model system of composition Zn-9.53 wt.% Ag. This paper offers a detailed examination of the origin of twophase $(Zn) + AgZn₃$ microstructures during directional solidification: specifically, our work investigates the influence of velocity, thermal gradient, and sample size on microstructure selection, namely, rod-like, single-banded, and multiply-banded struc-

tures. Importantly, we find at low velocities V (0.07-0.1 μ m/s) and a low thermal gradient G (3 K/mm) the emergence of peritectic (Zn) channels, interwoven within and between primary $AgZn₃$ columnar grains. While these microstructures are suggestive of coupled growth morphologies, real-time imaging proves that the two solids are instead decoupled at the growth front. Meanwhile, at thermal gradients $10\times$ higher, we observe a partially dendritic and partially banded structure that has not been reported before, to the best of our knowledge. We initiate a discussion on the formation of such structures, with broad implications to a wide range of metallic, semi-metallic, and organic peritectic alloys.

8.1 Introduction

Peritectic equilibria can be found within numerous phase diagrams. At the peritectic temperature T_p in binary systems, there exists an equilibrium between two solid phases (the primary phase, denoted α , and the peritectic phase, β) and a liquid phase, often represented as α + liquid $\leftrightarrow \beta$. This reaction is encountered in the solidification of steels [\[41\]](#page-275-0), copper [\[8,](#page-272-0) [314](#page-296-0)[–316\]](#page-296-1), aluminum [\[152\]](#page-283-0), titanium [\[157\]](#page-283-1), zinc [\[317,](#page-296-2) [318\]](#page-296-3), and superalloys [\[319\]](#page-296-4). It plays a pivotal role in the development of permanent magnets [\[320,](#page-296-5) [321\]](#page-296-6) and high-temperature superconductors [\[322,](#page-296-7) [323\]](#page-296-8). Therefore, it is of fundamental interest and technological importance to investigate the evolution of microstructures during peritectic solidification.

In particular, alloys with a composition between that of the α phase and that of the β phase at T_p show two-phase $\alpha - \beta$ microstructures of varying complexity [\[9,](#page-272-1) [40,](#page-275-1) [54,](#page-276-0) [324,](#page-296-9) [325\]](#page-296-10). Some of these variations may be attributed to the stability of the α -liquid and β -liquid interfaces, which can either remain morphologically stable or develop perturbations, leading to cellular or dendritic structures in directional solidification (DS). Exotic morphologies emerge when both solids are planar, as will be reviewed below.

In this context, one interesting scenario is the emergence of *banding* [\[165,](#page-284-0) [166\]](#page-284-1) wherein alternating layers of the two phases form perpendicular to the growth direction. The peritectic phase nucleates below the peritectic temperature and spreads across the primary-liquid interface, inducing a decline in solute concentration near the front. Consequently, the interface temperature rises, allowing the primary phase to re-nucleate above T_p . This cyclic process perpetuates, giving rise to banded microstructures, driven by the constitutional undercooling of the liquid ahead of the growth front [\[165\]](#page-284-0). It is worth noting that this theory [\[165\]](#page-284-0) assumes growth in a diffusive regime and is hence relevant to thin samples. In thicker samples, convection becomes significant and can impact the banding behavior [\[11,](#page-272-2) [326\]](#page-297-0). Moreover, the concept of banding relies on re-nucleation of primary and peritectic solids, relevant to infinitely thin specimens. In the case of thicker samples, additional growth modes may be accessible that do not require re-nucleation, see, e.g., Ref. [\[11\]](#page-272-2).

Closely related to the above is the formation of discrete regions referred to as islands or partial bands within the continuous matrix of the other phase [\[9,](#page-272-1) [167\]](#page-284-2). The transition from bands to islands was studied through phase-field simulations [\[9\]](#page-272-1). These simulations revealed that when the volume fraction occupied by the peritectic phase is low, the prevailing trend is the formation of islands. Conversely, in scenarios where the primary and peritectic phases approach similar volume fractions, banding is the dominant morphology. Between these two regimes, a compositional range emerges that accommodates the formation of both islands and bands. Importantly, the specific morphology is determined by the distance between nuclei, with island formation requiring a distance below a certain critical threshold, which is contingent upon the composition.

The opposite of banding is peritectic *coupled growth* (PCG), wherein the solidsolid interfaces are aligned with the growth direction, and both solid phases grow simultaneously into the liquid. This behavior is thought to resemble coupled growth in eutectic systems. However, in peritectic systems, both solid phases reject the same component into the liquid. PCG has thus remained a subject of extensive discussion and investigation over time. The feasibility of isothermal PCG in hypoperitectic compositions was initially postulated by Chalmers [\[161\]](#page-284-3). Building upon the arguments presented by Uhlmann and Chadwick [\[327\]](#page-297-1), Chalmers [\[328\]](#page-297-2) later proposed that peritectic solidification mechanisms differ from the "lamellar mechanism of eutectics." Kurz et al. [\[162\]](#page-284-4) suggested PCG in Sn–SnSb alloys during DS on the basis of metallographs that showed SnSb fibers within a (Sn) matrix. However, in a study on peritectic Sn–Cd alloys with hypo- and hyperperitectic compositions, Boettinger [\[163\]](#page-284-5) did not observe isothermal coupled growth. To explain the conditions that favor PCG, he employed the Jackson–Hunt model, originally developed for eutectics [\[329\]](#page-297-3), and suggested that a negative undercooling (superheating) was essential for PCG to take place.

In most peritectic systems, experimental endeavors to induce PCG have remained elusive, resulting in the formation of banded structures instead [\[9,](#page-272-1) [11,](#page-272-2) [165,](#page-284-0) [167,](#page-284-2) [326,](#page-297-0) [330\]](#page-297-4). This is largely because the stability field of PCG hinges on the morphological stability of both phases [\[10\]](#page-272-3). Yet under such conditions, islands will form according to phase-field modeling [\[9\]](#page-272-1). In Ref. [\[167\]](#page-284-2), Karma, Kurz, and coworkers explored the interplay between island banding and coupled growth, ultimately concluding that island banding can either persist or serve as a precursor to the initiation of coupled growth, depending on the stable range of the interphase spacings and the mean distance between the islands.

Among the few experimental studies on PCG, Lee et al. [\[331\]](#page-297-5) investigated Ni–Al alloys and found lamellar morphologies therein. Their experiments on quenched DS samples revealed that the solid–liquid interface, seemingly coupled, remained isothermal and slightly below the peritectic temperature (in sharp contrast to Boettinger's predictions [\[163\]](#page-284-5)). Likewise, Busse et al. [\[155\]](#page-283-2) reported lamellar morphologies in the

Ti-rich Al-Ti system. Concurrently, Vandyoussefi et al. [\[164\]](#page-284-6) and Dobler et al. [\[10\]](#page-272-3) investigated two-phase Fe–Ni alloys. The resulting microstructures in Fe–Ni alloys were generally dependent on the growth conditions and local composition. Metallography indicated that the lamellar growth front was isothermal but slightly above the peritectic temperature in this Fe–Ni alloy system. Yet due to radial macrosegregation of Ni, such patterns coexist with multiple other microstructures within the same sample [\[164\]](#page-284-6). Aligned two-phase structures emerged within a specific growth window, contingent upon the tie line and critical G/V ratio. When the composition closely approximates that of the peritectic phase, the minor phase exhibits stable growth in either a fibrous or lamellar configuration. However, when the peritectic phase fraction exceeded 0.1, the authors observed an oscillatory behavior in two-phase growth, analogous to the 2- λ instabilities found in off-eutectic alloys. Notably, the observed spacings were considerably larger, in general one order of magnitude greater than that of eutectics.

Importantly, PCG has been documented only in specific systems such as Ni-Al, Ti-Al, and Fe-Ni. This could be due to relatively narrow solidification range ΔT_0 for the primary phase, defined as the difference between the primary liquidus temperature and T_p . The Cu–Sn peritectic system [\[8,](#page-272-0) [314,](#page-296-0) [332\]](#page-297-6) is a notable exception: despite a considerably larger ΔT_0 , it forms a pattern of alternating regions of singleand two-phase growth, the latter of which may arise from PCG. A diversity of morphologies, encompassing lamellar, rod-shaped, and mixed morphologies was found in the two-phase regions [\[8\]](#page-272-0). The thermophysical factors governing the transitions between these morphologies remain unclear to-date.

Despite these landmark studies, our understanding of peritectic phenomena lags behind that of other polyphase processes, such as eutectic solidification. This knowledge gap arises firstly from the complex interplay of multiple potential growth modes in peritectic systems which may operate simultaneously or sequentially. Adding to

the complexity is *secondly* the occurrence of thermosolutal convection resulting from both thermal and concentration gradients in DS, particularly pronounced at low velocities due to the substantial solidification range of the primary phase. In many cases, achieving conditions that favor planar front growth using a conventional Bridgman apparatus is exceptionally challenging. This is because it demands extremely low velocities to ensure a planar front and also necessitates capillary samples to suppress thermosolutal convection [\[292\]](#page-294-0). A third challenge is that the majority of previous studies in this domain have predominantly relied on *postmortem*, two-dimensional sections which limit our understanding of an inherently 3D phenomenon. That is, the connectively between phases in 3D may not be evident in 2D images [\[8,](#page-272-0) [11,](#page-272-2) [314,](#page-296-0) [332\]](#page-297-6). Therefore, 3D imaging is warranted since 2D sections can obscure or destroy internal features. An example is given in Fig. [8.1](#page-222-0) which shows the microstructure of a Zn-9.53 wt.% Ag alloy directionally solidified at a velocity $V = 0.1 \mu m/s$, and a thermal gradient $G = 3.0 \text{ K/mm}$. A scanning electron metallograph (Fig. [8.1\(](#page-222-0)a)) appeared to indicate a single band transition from primary to peritectic phase along the growth direction. However, X-ray tomography (Fig. [8.1\(](#page-222-0)b)) revealed the presence of a concealed interior conical pit of peritectic phase embedded within the primary phase. This discrepancy underscores the indispensable role of 3D visualization. Understanding how this two-phase microstructure comes to be necessitates in situ imaging which, notably, has been so far limited to organic systems [\[51–](#page-275-2)[53,](#page-276-1) [333–](#page-297-7)[340\]](#page-298-0), which may not be relevant to metallic ones (especially regarding fluid flow effects in solidification [\[252\]](#page-291-0)).

To meet the above challenges, we leveraged the recent advancements in 3D and 4D (i.e., three spatial dimensions and time) X-ray imaging to investigate the Ag-Zn peritectic system, as alluded to previously. At hypoperitectic compositions, the alloy consists of the primary solid solution (ϵ -AgZn₃) and the peritectic phase (Zn). The difference in the concentration of the Ag constituent offers attenuation contrast between

Figure 8.1: Microstructure of the sample obtained under thermal gradient of 3 K/mm and a velocity of 0.1 μ m/s. A) presents an image acquired through SEM by polishing perpendicular to the growth direction. B) illustrates a crosssectional slice obtained from a tomographic reconstruction of the region highlighted purple in (A) . The approximate location of the reconstructed slice is indicated by a white line. C) and D) represent the 3D reconstructed isosurfaces of the primary and peritectic phases, respectively. The sample produced a single conical pit of peritectic which penetrates into the primary phase near the sample center, stretching \sim 400 μ m along z. This same pit cannot be seen in SEM. For clarity, the primary phase is shown in red and the peritectic in blue.

the solid phases. Prior studies on this system are well-documented [\[159,](#page-284-7) [327,](#page-297-1) [341](#page-298-1)[–343\]](#page-298-2) but are limited to rapid solidification and postmortem 2D imaging techniques. Here, we utilize both laboratory and synchrotron-based X-ray imaging (namely radiography and tomography) to gain 3D insights into the selection of two-phase peritectic patterns as a function of V, G, and sample diameter \varnothing in DS. Our research aims to deepen our understanding of peritectic solidification and shed light on the origins of the growth modes outlined above. Below we provide some brief background on the analytical techniques employed, present our results, and draw corresponding conclusions on the basis of the 3D and 4D data so-obtained.

8.2 Experimental methods

8.2.1 Sample preparation

An alloy with a composition of Zn-9.53 wt.%Ag was cast using high-purity elements (99.999% Zn and 99.999% Ag) *via* vacuum arc remelting at the Materials Preparation Center at Ames Laboratory (Ames, IA, USA). Subsequently, cylindrical rods measuring 20 mm in length by 1 mm in diameter were sectioned from the ingot using electric discharge machining. To investigate the impact of sample size on microstructure selection, we prepared rods with diameter \varnothing between 0.5 to 2 mm. Rods with α < 1 mm were produced through a cold wire drawing process, while those with $\beta = 2$ mm were obtained by melting the material in crucibles with a 2 mm inner diameter. These samples were sealed within quartz ampoules for ex situ DS.

For the sake of monitoring the evolution of microstructures in situ via X-ray absorption imaging, we require samples of uniform thickness. This ensures that any variation in the forward transmitted signal stems from chemical partitioning alone. Sheet-like samples were made by cold rolling sections of the as-cast ingot. This process resulted in sheets 50 to 100 μ m thick for the *in situ* X-ray radiography studies.

8.2.2 Directional solidification experiments

In this work, we have used three different types of DS apparatuses, as follows:

8.2.2.1 Three-zone Bridgman apparatus

Most of our solidification experiments were conducted using a vertical three-zone Bridgman furnace (MTI Corporation EQ-SKJ-BG) fixing G at 3 K/mm. We varied V in the range of 0.035 to 1 μ m/s and β from 0.5 to 2 mm for these experiments. In this setup, the sample was held stationary while the furnace moved upward thereby solidifying the material antiparallel to gravity.

8.2.2.2 Modified Bridgman apparatus with water cooling

To investigate the impact of a significantly higher G , we conducted DS under \sim 32 K/mm. This G is roughly ten times greater than that employed above (Sec. [8.2.2.1\)](#page-224-0). We performed these experiments with a modified Bridgman apparatus equipped with water cooling, as detailed in Ref. [\[344,](#page-298-3) [345\]](#page-298-4). To mitigate thermosolutal convection associated with the higher G, we utilized 0.5 mm \varnothing cylindrical samples.

8.2.2.3 In situ directional solidification

The thin sheet-like samples (described above, Sec. [8.2.1\)](#page-223-0) were subject to in situ experiments at beamline 2-BM at the Advanced Photon Source of Argonne National Laboratory (Lemont, IL, USA). At the beamline, we affixed our samples to alumina rods secured on kinematic mounts, and coated them with a layer of boron nitride spray for mechanical stability. Utilizing a two-zone directional viewing furnace, we imposed $G \sim 18-21$ K/mm. The furnace temperature at the sample location was calibrated using a K-type thermocouple. To directionally solidify our samples, we employed the "gradient freeze" approach, wherein we lowered the temperature at a rate T ranging from 0.3 to 3 K/min. (under fixed G, oriented anti-parallel to gravity). For a stationary sample, the isotherms will move upwards at a constant velocity given by \dot{T}/G . This frame-of-reference is notably different from other in situ DS studies wherein a sample is "pulled" through a fixed G , leading to an imaged field-of-view (FOV) with static isotherms [\[51](#page-275-2)[–53,](#page-276-1) [337\]](#page-297-8).

During solidification, a monochromatic X-ray beam with an energy of 30 keV penetrated the sheet sample along its thinnest dimension. Transmitted X-rays were captured and converted into visible light by a Eu-doped Gd–Ga–Garnet scintillator. We employed a FLIR Oryx camera with a field-of-view measuring 1.632×2.422 mm² and a pixel size of 1 μ m/pixel. The solidification dynamics were recorded with an exposure time t_e of 180 ms and a frame rate between 0.1 to 1 Hz.

To investigate the 3D connectivity of the fully solidified microstructure, we captured a postmortem, 3D X-ray tomographic scan of the sample. We used a 30 keV energy monochromatic X-ray beam (as before) to acquired 1500 projections over 180° of rotation. With an rotation speed of $0.6^{\circ}/s$ and the same t_e as above, each scan took approximately ∼9.5 min. to complete.

8.2.3 Materials characterization

Following in-house DS (Sec. [8.2.2.1-](#page-224-0)[8.2.2.2\)](#page-224-1), we employed a Zeiss Xradia Versa 520 X-ray microscope to conduct $ex\ situ$ X-ray tomography. To optimize absorption contrast and transparency, we employed a beam voltage of 150 kV at 10 W power. During the scan, transmitted X-rays were directed onto a CsI scintillator, converting them into visible light images. These images were further optically magnified and captured using a CCD camera (all samples were magnified using a $4\times$ lens, except for the high-gradient solidified sample, which was magnified to $21\times$). We acquired 1601 projections in total covering a 360° rotation of the sample. Certain samples necessitated multiple tomographic scans to capture an extended view of the microstructure (along the growth direction). Consequently, these scans were manually 'stitched' together to facilitate a comprehensive analysis. The acquisition parameters for each sample are outlined is Table [8.1.](#page-250-0)

To characterize the crystal orientations in the fully-solidified material, we first prepared the surfaces of the specimen using 1200-grit polishing paper and then conducted further surface milling with a Xenon plasma-focused ion beam to minimize sample roughness. We then used a TESCAN MIRA3 FEG scanning electron microscope (SEM) with an attached EDAX Hikari camera to perform electron backscatter diffraction (EBSD) on the sample surface. We used a 30 kV beam voltage and working distance of 20 mm to collect 285 \times 372 μ m² EBSD maps with a 1 μ m step size in a hexagonal grid.

8.2.4 Post-processing of images

8.2.4.1 In situ directionally solidified samples

After the in situ experiments, we processed the radiographs in order to illuminate the microstructural dynamics. We used so-called 'constant' and 'sequential division' techniques [\[200\]](#page-287-0) to differentiate between different phases and solid-liquid interfaces, respectively. In constant division, we normalize all radiograph images by a single, fixed image of the liquid phase, in order to remove beam artifacts; in sequential division, we instead normalize each radiograph N by the $(N-50)$ th image in the image stream, to show the changes in the microstructure over a time-interval of 50 s (corresponding to 50 images).

Tomographic reconstruction of the solidified sample (see Sec. [8.2.2.3\)](#page-224-2) was carried out using the Gridrec algorithm within the Tomopy package [\[23\]](#page-273-0). Due to residual strain in cold rolling, the sheet-like samples exhibited mild buckling, leading to some tilt with respect to the specimen z -axis (corresponding to the rotation axis), which resulted in positional shifts within the reconstructed slices (in the specimen $x - y$ plane). To correct for this effect, we registered the reconstructed slices using an affine

transformation. This was done in an automated manner using a genetic algorithm, see Ref. [\[303\]](#page-295-0). The classification of each pixel within the images into the two solid phases (*i.e.*, segmentation) was facilitated *via* a neural network technique in the ZEN Intellesis program by Carl Zeiss AG [\[220\]](#page-288-0). We then used MATLAB [\[199\]](#page-287-1) to further improve the segmented slices by conventional image processing. Finally, we generated triangular meshes, defined by a series of triangles and associated vertices, to represent the phase-interfaces of the primary and peritectic solids. To eliminate staircasing artifacts, we smoothed the mesh by mean curvature flow [\[299\]](#page-294-1).

To gain a comprehensive perspective of the solidification process in both 3D space and in time, we implemented the "pseudo-4D" imaging technique, as detailed in Ref. [\[17\]](#page-273-1). The reduced thickness of our ribbons allowed us to assume negligible microstructural changes within this spatial dimension. Consequently, the solid-liquid interfaces captured through X-radiography were digitally interpolated onto the postmortem reconstruction, assuming no tilt of the solidification front in the direction of the X-ray beam. Furthermore, because we take the morphology of as-solidified primary phase to be the same as that seen during the growth process, we assume that the solid-state peritectic transformation [\[40\]](#page-275-1) is negligible on the time-scales of DS. We test the validity of this assumption in Sec. [8.3.1.](#page-228-0) By combining the *in situ* and postmortem data, the pseudo-4D technique provides both the high temporal resolution of X-radiography (limited solely by the camera frame rate) and the high spatial resolution of room-temperature X-ray micro-tomography (free from solidification- or thermal-radiation-induced deformations). An additional benefit of the pseudo-4D technique is that we do not need to rotate the sample during the DS experiment (as is the norm for the acquisition of 4D data [\[346\]](#page-298-5)), which eliminates convection due to the centripetal acceleration of the sample.

8.2.4.2 Ex situ directionally solidified samples

We used the Zeiss 'Scout-and-Scan Control System' to reconstruct ex situ tomography scans into 3D. For samples that required additional scans, we manually identified the overlapping $x - y$ image slices and merged the corresponding volumes. In MATLAB, we then segmented the phases using Otsu's method [\[203\]](#page-287-2) and subsequently generated and smoothed the mesh of the phase-interfaces (following the same protocol as in Sec. [8.2.4.1\)](#page-226-0). We employed the open source toolbox MTEX [\[261\]](#page-291-1) to analyze our EBSD data.

8.3 Results and discussion

8.3.1 Effect of growth velocity

8.3.1.1 Ex situ directionally solidified samples

We begin by considering the influence of growth velocity on microstructure selection (holding all else constant). Fig. [8.2](#page-230-0) gives the 3D microstructures of two cylindrical samples, each with 1 mm \varnothing . These samples were solidified at $V = 0.035$ and 0.07 μ m/s under $G = 3$ K/mm. In what follows the peritectic (Zn) phase is represented in blue, and the primary $AgZn_3$ in red, for sake of clarity. At the lower velocity (Fig. [8.2\(](#page-230-0)a)), we observe the emergence of a distinctive single band separating the peritectic and primary phases, in contrast to the interior conical channel shown in Fig. [8.1.](#page-222-0) Turning our attention to Fig. [8.2\(](#page-230-0)b), we encounter another interior channel of the peritectic phase, positioned near the center of the sample. The rod-like morphology extends a vertical distance of 2.7 mm into the primary phase while maintaining a relatively narrow width, never exceeding 0.15 mm. The peritectic phase is not wholly cylindrical, displaying regions of both convexity and concavity. In addition, the peritectic rod tends to increase in thickness as it approaches the uppermost interphase boundary. It follows that the channel morphology is not the result of PCG, which should produce fully convex cylinders, in principle, but rather a product of secondary instabilities of the primary phase, perpendicular to the growth direction (*vide infra*).

We caution that the final, two-phase microstructure is the product of solidification and solid-state transformation of the primary phase into peritectic phase. To assess the volume of primary phase consumed in the peritectic reaction, assuming it is diffusion-limited, we calculate the characteristic diffusion length $\ell \propto$ √ $D\tau$, where D is the solid diffusivity and τ is time. Neumann and Tujin [\[347\]](#page-298-6) have reported that the self-diffusivity of Zn at 400 °C is 6.33×10^{-13} m²/s, which we take to represent D here due to lack of data on the binary Ag-Zn system. If we consider the height of the observed FOV (along the specimen z direction) as the region where the peritectic front interacts with the primary and liquid phases in DS (conservatively, this is 400 μ m, based on Fig. [8.1\)](#page-222-0), and given the solidification front velocity (0.1 μ m/s), then $\tau \sim$ 4000 s. Consequently, $\ell \sim 50 \mu m$, which is notably smaller than the depth of the conical pit. This suggests that solid-state diffusion is not, by itself, responsible for the peritectic channels.

We also note that the pit described above did not originate at a grain boundary (GB) groove. To prove this point, we sectioned the same sample from Fig. [8.1](#page-222-0) just below the peritectic pit and imaged it via EBSD (Sec. [8.2\)](#page-223-1). We found no GBs (Fig. [8.10\)](#page-249-0), instead observing a single crystal of the primary $AgZn₃$ phase.

8.3.1.2 In situ directionally solidified samples

To identify the growth mechanism of the peritectic channels seen in Figs. [8.1-](#page-222-0)[8.2,](#page-230-0) we turned to in situ X-radiography to observe the DS process. Figs. $8.11-8.3$ $8.11-8.3$ show snapshots of thin films of Zn-9.53 wt.%Ag at various time-points during solidification. For these "gradient freeze" experiments, we use two sets of conditions: $\dot{T}=0.3$ K/min and 0.7 K/min, with $G = 21$ K/mm and 18 K/mm, respectively. Figs. [8.11-](#page-251-0)[8.3\(](#page-232-0)a) show an image stream processed via "constant division" while Figs. [8.11-](#page-251-0)[8.3\(](#page-232-0)b) dis-

Figure 8.2: Microstructure selection as a function of growth velocity V under a constant thermal gradient of 3 K/mm. A) $V = 0.035 \ \mu \text{m/s}$ yields a singleband transition between the primary and peritectic phases (artificially separated for better visibility). Additionally, precipitates of the primary phase are distributed throughout the peritectic regime of the sample (these form during subsequent cooling). B) $V = 0.07 \mu m/s$ (*i.e.*, doubling the velocity) produces a peritectic column, spanning 2.7 mm along z before reaching the primary-to-peritectic transition. For clarity, the primary phase is shown in red and the peritectic in blue.

plays the same result by a different approach, "sequential division" as described in Sec. [8.2.4.1](#page-226-0) (videos provided in online supplementary material for manuscript). In Fig. [8.11,](#page-251-0) we see the primary phase forms initially, growing as columnar grains at $V = 0.08 \ \mu \text{m/s}$. These grains are separated by channels of Zn-enriched liquid. As the primary phase advances, the primary solids may coalesce and coarsen into a single band of material (described later). After ∼230 min., the peritectic phase begins to solidify at a rate of 0.24 μ m/s. The sample solidified under a higher cooling rate (Fig. [8.3\)](#page-232-0) also shows columnar grains of the primary phase, which grow first, this time at a rate of 0.18 μ m/s, before beginning to coarsen. However, the peritectic front forms after only \sim 36 min., growing at a velocity of 0.67 μ m/s, and eventually it overtakes the primary phase before the primary solids can fully ripen. Ultimately, the resulting microstructure resembles that obtained in PCG, although it is sequential in nature.

To contextualize the above results, we compute G/V ratios for the in situ experiments and compare them to the *postmortem* DS studies. Single bands result when $G/V = 88 \times 10^{-3}$ Ks/ μ m² (Fig. [8.11\)](#page-251-0), which matches well to $G/V = 85 \times 10^{-3}$ Ks/ μ m² (Fig. [8.2\(](#page-230-0)a)). Likewise, columnar grains from when $G/V = 28 \times 10^{-3} \text{ Ks}/\mu\text{m}^2$ (Fig. [8.3\)](#page-232-0), as compared to $G/V = 30 \times 10^{-3} \text{ Ks}/\mu\text{m}^2$ (Fig. [8.2\(](#page-230-0)b)). Thus, we can relate the *in situ* observations to the *postmortem* 3D studies without loss of generality and ultimately demonstrate a self-consistent behavior. While both in situ experiments show columnar grains initially, and hence the imposed velocity V exceeds the critical V^* above which the primary phase is morphologically unstable, one key distinction between them is the local solidification time t_f . By definition, $t_f = \Delta T_0/GV$ where ΔT_0 is the equilibrium freezing range [\[348\]](#page-298-7). We find t_f to be 17900 s and 7690 s for Figs. [8.11](#page-251-0) and [8.3,](#page-232-0) respectively, *i.e.*, a difference of over $2 \times$ between the two experiments.

As described in Sec. [8.2.4.1,](#page-226-0) we can combine the X-radiography and tomogra-

Figure 8.3: Snapshots from X-radiography showing hypo-peritectic solidification in Ag-Zn at $\dot{T} = 0.7$ K/min and $G = 18$ K/mm. Data were collected continuously over a period of 84 minutes. Images were processed through A) 'constant division' and B) 'sequential division', see text for details. The latter shows contrast at the solid-liquid interfaces. As before, the primary phase is shown in red and the peritectic in blue.

phy data into a pseudo-4D representation of the solidification process. Fig. [8.4](#page-234-0) shows a pseudo-4D visualization of the sample solidified under $\dot{T} = 0.7$ K/min. and $G = 18$ K/mm. Several channels between the primary cellular grains have begun to coalesce. The liquid surrounding and in between these grains enriches in Zn and solidifies into (Z_n) below T_p , halting any further semisolid coarsening of the primary phase. In Fig. [8.4\(](#page-234-0)b), we zoom-in on one exemplar liquid channel within the tomographic volume. We see the pocket of liquid herein is not connected to any other channels elsewhere (within the experimental resolution), and so the (Zn) nucleates heterogeneously along the bottom most primary-liquid interface *(i.e.*, the coldest point of the interior channel). It then grew along the G until it merged with the outer layer of peritectic (Zn). Eventually, the channels of the peritectic solids meet the primary-liquid front, and at this point, the remainder of the sample solidifies as the peritectic phase. This behavior is somewhat reminiscent of that seen in the succinonitrile-(D)camphor transparent eutectic alloy investigated during DS by Serefoğolu and Napolitano [\[73\]](#page-277-0), wherein the eutectic structure originated from a liquid film trapped between two GBs.

Our in situ experiments conclusively demonstrate that the channel formation did not result from the nucleation of peritectic (Zn) on a planar $AgZn₃$ front. That is, the conical channel of the peritectic seen in Fig. [8.1](#page-222-0) is likely formed within the inter-cellular regions which are unable to coarsen (by curvature reduction) at the higher velocities and cooling rates. Within the channels, the peritectic-liquid front grows considerably faster than the primary-liquid front. This disparity in growth rates is attributed to solutal depletion ahead of the primary-liquid interface, leading to a variation in liquidus temperature and a reduction in interfacial velocity. In general, the peritectic phase has a higher partition coefficient compared to the primary phase [\[40\]](#page-275-1) and hence is less hindered by the rejected solute. Consequently, the peritectic-liquid front can overtake the primary-liquid front, as illustrated in Fig. [8.3](#page-232-0) and as quantified below. This relatively high velocity of (Zn) diminishes the likeli-

Figure 8.4: Pseudo-4D reconstruction of hypo-peritectic solidification in Ag-Zn at $T = 0.7$ K/min and $G = 18$ K/mm. Listed times are relative to the first appearance of peritectic (Zn) phase within the imaged FOV. A) shows snapshots of the full volume over a duration of 33 minutes. B) depicts a zoomed-in view of microstructure evolution within the yellow boxed region, namely, the formation of an interior channel of peritectic (Zn) from supersaturated liquid within intercellular spaces of primary $AgZn₃$, cf. Figure 2(b). The primary phase is shown in red and the peritectic in blue.

hood of nucleating peritectic solids that become enclosed within the primary matrix, thereby excluding the possibility of island formation (Sec. [8.1\)](#page-217-0).

We tracked the average positions of the primary and peritectic fronts for samples solidified under $\dot{T} = 0.3, 0.5, \text{ and } 0.7 \text{ K/min.}$ and computed a moving time-average of their respective velocities (see Figs. [8.12-](#page-252-0)[8.13,](#page-253-0) and [8.14,](#page-254-0) respectively). When the peritectic overtakes the primary phase, indeed the $AgZn₃$ front decelerates (or *recoils*, see, e.g., $[53]$, due to a shift in the interface temperature, as discussed above. The recoil of the primary front increases the G/V ratio, thus stabilizing the primary-liquid interface and flattening some primary columns into a more planar front. This effect is most clearly seen in the case where $\dot{T} = 0.7$ K/min. (Fig. [8.14\)](#page-254-0) where we measure $V < 0$ as the columnar tips remelt partially to yield a flattened morphology. Taken altogether, these results indicate that the recoil of the primary-liquid interfaces may help to stabilize the primary front; meanwhile, a longer solidification time acts in concert to reduce or eliminate the highly-curved liquid channels that percolate below the front. In the limit that the primary front is planar and all liquid channels have been removed via coarsening, we should attain a single-band transition along the growth direction (see again Fig. [8.11\)](#page-251-0).

8.3.1.3 Analysis of interfacial curvatures

Capillarity is the driving force for coarsening by Ostwald ripening such that surfaces will evolve to remove highly curved interfaces over time [\[127\]](#page-281-0). Therefore, we can ascertain to what extent the primary phase coarsens as a function of cooling rate, and by extension the effect it has on pattern selection, by quantifying and comparing the (solid-liquid) curvatures of the primary phase. We computed the curvatures κ of the primary phase for the cooling rates so-investigated $(i.e., 0.3, 0.5, 0.7,$ and 2.0 K/min.) by determining the principle radii, r_1 and r_2 , of each patch of the mesh, see also Refs. [\[57,](#page-276-2) [349–](#page-298-8)[351\]](#page-299-0). By definition, $\kappa_1 = 1/r_1$ and $\kappa_2 = 1/r_2$ where $\kappa_1 \leq \kappa_2$. We

then plot the two principal curvatures as a bivariate histogram or an interface shape distribution (ISD) [\[141\]](#page-282-0) which displays the probability that a randomly selected surface has κ_1 and κ_2 . Accordingly, the interfaces may be categorized into *convex* shapes (with respect to the primary phase), when $\kappa_1 < 0$ and $\kappa_2 < 0$; concave shapes when $\kappa_1 > 0$ and $\kappa_2 > 0$; and saddle shapes when $\kappa_1 < 0$ and $\kappa_2 > 0$. When either $\kappa_1 = 0$ or $\kappa_2 = 0$ (but not simultaneously), the surface is locally cylindrical in shape; $\kappa_1 = \kappa_2 \neq 0$ defines a spherical shape; and finally, $\kappa_1 = \kappa_2 = 0$ indicates planarity.

The ISDs for all four cooling rates are shown in Figs. $8.5(a-d)$. We normalize the principle curvatures by the surface area to volume ratios (S_V) so we may compare shapes irrespective of length-scales. At low \dot{T} , the primary interfaces are predominantly planar or nearly planar. Meanwhile, at high \overline{T} (corresponding to high V and low t_f), the ISD shows long tails along the two axes (*i.e.*, $\kappa_1 = 0$ and $\kappa_2 = 0$), suggesting that the increased cooling rate correlates with the proliferation of cylindrical-like patches of interface. We can distill these trends into a single measure of the interfacial curvedness, defined as

$$
C \equiv \sqrt{\frac{1}{2} \left(\frac{\kappa_1}{S_V}\right)^2 + \frac{1}{2} \left(\frac{\kappa_2}{S_V}\right)^2}
$$
\n(8.1)

Mathematically, C is proportional to the distance from the origin of the ISD. A sphere of radius r has $C = 1/r$. Fig. [8.5\(](#page-237-0)e) shows cumulative distributions of C for the four aforementioned cooling rates. We see that the two slow-cooled samples display an initial jump at $C = 0$ (as expected from their ISDs, cf. Fig. [8.5\(](#page-237-0)a-b)). By comparison, the samples solidified under higher cooling rates display some remnant curvedness. In Fig. [8.15,](#page-255-0) we display the primary phase for each \dot{T} , colored by the local curvedness. These results underscore the importance of channel coarsening during directional peritectic solidification.

Figure 8.5: Interfacial shape distributions of primary crystal grown under cooling rates of A) 0.3, B) 0.5, C) 0.7, and D) 2.0 K/mm. The principal curvatures, κ_1 and κ_2 , have been normalized by the total surface area to volume ratio of the primary phase, S_V . The color bar represents the probability, P, of finding a patch of interface with the set of curvatures $\{\kappa_1, \kappa_2\}$. E) Cumulative area fraction of the interfacial curvedness, C, defined in section [8.3.1.3.](#page-235-0) Decreasing the cooling rate by nearly one order-of-magnitude (i.e., increasing the solidification time) leads to significant curvature reduction.

8.3.2 Effect of sample geometry

Fig. [8.6](#page-239-0) depicts tomographic reconstructions of two cylindrical samples solidified under $G = 3$ K/mm (as before) and $V = 0.07 \mu m/s$. These samples differ only in diameter, with one measuring 0.5 mm \varnothing (Fig. [8.6\(](#page-239-0)a)) and the other 2 mm \varnothing (Fig. 8.6(b)). The 0.5 mm \varnothing sample presents a flat, single-band transition separating the peritectic and primary phases. This microstructure, contrasting with that of its 1 mm β coun-terpart (Fig. [8.2\(](#page-230-0)b)), suggests that for the given growth conditions G and V , there exists an instability wavelength λ^* between 0.5-1 mm at which the primary front destabilizes and peritectic channels begin to form. Samples with $\beta < \lambda^*$ should thus solidify with a planar front.

Turning to Fig. [8.6\(](#page-239-0)b), we encounter a significantly different microstructure. The radial segregation pattern suggests that solidification was no long in a diffusive regime, but rather a convective one. Variations in density may lead to fluid flow during DS which would in turn alter the local morphology. The fluid velocity is characterized by the Rayleigh number Ra, which scales with \varnothing to the fourth power [\[292\]](#page-294-0). By doubling \varnothing , Ra increases by 16 \times , giving rise to significant fluid flow and solute segregation.

8.3.3 Effect of thermal gradient

We also explored microstructure selection under a higher thermal gradient of ∼32 K/mm, approximately $10\times$ greater than above (Sec. [8.3.1](#page-228-0)[-8.3.2\)](#page-238-0). With this relatively high G, we conducted DS experiments with $V = 0.3 \ \mu \text{m/s}$, $0.5 \ \mu \text{m/s}$, and $1 \ \mu \text{m/s}$. Remarkably, the microstructures in the three samples showed similar features: an initial transient structure, followed by the formation of a primary front instability after a certain distance along the solidification direction. Below, we focus on the initial transient region which shows a highly unusual two-phase pattern, likely because the samples experienced the highest thermal gradients due to the water cooling process. Fig. [8.7](#page-241-0) shows a representative reconstruction from postmortem X-ray tomography

Figure 8.6: Microstructure selection as a function of sample geometry. Both samples solidified under identical conditions, *i.e.*, $G = 3$ K/mm and $V =$ 0.07 μ m/s. A) shows a cylindrical sample with diameter of 0.5 mm, within which there is a single-band transition from primary to peritectic phase. B) displays another cylindrical sample, but with an increased diameter of 2 mm. This led to a radial segregation pattern, as shown in the two cross-sections at right. The primary phase is given in red and the peritectic in blue.

of the sample solidified at $V = 1 \mu m/s$. Figs. [8.7](#page-241-0)[-8.8\(](#page-242-0)a) display banded structures consisting of single-phase peritectic regions and two-phase regions consisting of both primary and peritectic phases.

As alluded to above, the primary distinction in the experiments herein lies in the reduced thermal length of the mushy zone, $\Delta T_0/G$, due to the higher thermal gradient. In contrast, in our previous experiments, we achieved planar solidification fronts through either a reduction in V to below V^* or \emptyset to below λ^* . In those cases, due to the very low velocities (e.g., 0.07 and 0.1 μ m/s), the diffusive length, D/V , was greater than the thermal length. This longer diffusion-boundary layer led to a change in the composition of the liquid ahead of the primary-liquid interface, resulting in segregation of Zn into the liquid and the formation of a single band transition from primary to peritectic phase. Conversely, in the current case, characterized by a smaller D/V and $\Delta T_0/G$ compared to our previous studies, we observe *multiple* bands, which could arise from a growth competition between phases as suggested by Ludwig et. al. [\[53,](#page-276-1) [339\]](#page-298-9) in an organic system.

Within the two-phase regions, we observe predominantly rod-like morphologies, as indicated in Fig. [8.7\(](#page-241-0)b). Moreover, the two-phase structures exhibit characteristics of 2D surface dendrites (when viewed in cross-section). The spreading of these 2D surface dendrites along existing peritectic-liquid interfaces closely resembles the "invasion" phenomenon well-documented in eutectic systems [\[5\]](#page-272-4). In between the dendritic arms, the peritectic phase can grow. Thanks to the 3D prespective, we detect filaments of the primary phase that appear to extend through the peritectic-containing bands and connect with other primary bands, as highlighted by circles in Fig. [8.7\(](#page-241-0)a). That is, the peritectic microstructure is *bicontinuous* in 3D. This kind of interconnectivity, forming a banded tree-like structure, has been seen also in Pb-Bi [\[11\]](#page-272-2) and Sn–Cd bulk alloys [\[352\]](#page-299-1). The distinction here, however, is that the microstructure is partially banded and partially columnar (within the bands), due to a morphological

Microstructure selection under $10\times$ higher thermal gradient. 0.5 mm dia. sample directionally solidified under $V = 1 \mu m/s$ and $G = 32 \text{ K/mm}$. A) 3D rendering showing multiple bands perpendicular to the growth direction. The bands are connected to a long primary grain (far left). In addition, filaments of the primary crystal bridge the peritectic bands, giving rise to a bicontinuous microstructure. Three such filaments are circled in white. B) shows six cross-sectional slices from the reconstructed volume. The bands appear as dendrite arms growing from the primary rod and spreading along the peritectic surface (akin to an invasion of surface dendrites). As before, the primary phase is shown in red and the peritectic in blue.

Figure 8.8: Crystallographic characterization of the same sample depicted in Figure 8. A) Cross-sectional slice showing the multiple bands of primary and peritectic phases. The primary phase is shown in red and the peritectic in blue. B) Corresponding EBSD map of a region that contains three bands. Ag Zn_3 and (Zn) phases have hexagonal crystal structures and are colored using the same standard triangle on the bottom. Both phases are monocrystalline.

instability of the primary phase. The interplay between instability and banding has not been observed before, to the best of our knowledge.

Inverse pole figure maps from EBSD are shown in Fig. [8.8\(](#page-242-0)b). They indicate that the orientations of the primary and peritectic phases remain consistent throughout. This finding, together with the interconnectivity of the solids as noted above, supports the idea that re-nucleation is not responsible for the partially-banded microstructure. It stands to reason that Trivedi's banding model [\[165\]](#page-284-0), which represents discrete bands that are generated by re-nucleation, is applicable primarily to samples with vanishingly small thickness. In that case, re-nucleation is a necessity since one phase will completely cover the other. However, in bulk solidification, if one phase (say, α) extends laterally, it will reduce the fraction of the other phase (β) exposed to the liquid (assuming finite \emptyset), causing the diffusion field of the β phase to become three-dimensional. Consequently, the β -liquid interface accelerates as the fraction of β becomes smaller [\[352\]](#page-299-1). Furthermore, the lateral rejection of solute by one phase impedes the lateral spread of the other phase. Based on this reasoning, the possibility of interconnection precludes the need for re-nucleation.

8.3.4 Influence of defects

In addition to V, G, and \varnothing ,, we investigated the influence of microstructural defects, specifically cracks that extend radially from the surfaces of the cylinder to its interior. Fig. [8.9](#page-245-0) shows a 2 mm wide cylindrical sample grown in parallel with $(i.e.,$ under the same conditions as) those samples shown in Fig. [8.6\(](#page-239-0)b). The difference in the two cases is that the former displays extensive cracks throughout the bulk with a crack spacing of λ_c . A cross-sectional slice of the reconstructed volume reveals primary phase which appears throughout the length of the sample, as opposed to a single band transition as in Fig. [8.2\(](#page-230-0)a). Indeed, the primary phase follows the curvature of the cracks at several different points suggesting that the $AgZn₃$ phase renucleates at the crack surfaces. In addition, the band spacing correlates with λ_c . The 3D rendering in Fig. [8.9\(](#page-245-0)a) makes evident the prevalence of these defects and their relationship to the solidified microstructure.

The preference for renucleation instead of growth competition may be attributed to a change in the nucleation undercooling of the primary phase and the impact of the pre-existing sites. Under steady-state conditions with a high G/V ratio, banded or partially banded microstructures may become stable [\[168\]](#page-284-8). According to Trivedi, the formation of multi-band morphologies in thin specimens is highly dependent on the nucleation undercooling of both the primary and peritectic phases [\[165\]](#page-284-0). Pre-existing cracks provide a location for heterogenous nucleation which would in turn reduce the undercooling. The contact angles of embryos along cracks may also be more favorable than those on the reciprocal phase [\[353\]](#page-299-2), further reducing the nucleation undercooling. Therefore, such defects increase the likelihood of multi-band formation.

8.4 Conclusions

In this article, we employ 3D imaging in the laboratory and at the synchrotron to investigate solidification microstructures in an off-peritectic Ag-Zn alloy. We observe a great diversity of two-phase patterns that emerge in DS. We draw the following conclusions, regarding the

• Influence of velocity. At high velocities (exceeding the instability threshold V^* of the primary phase), we identified in 3D the formation of a conical pit of peritectic (Zn) encased by a matrix of primary $AgZn₃$. Under relatively lower velocities (but still exceeding V^*), the interior columns of peritectic phase were replaced by a single-band transition. Synchrotron-based in situ X-radiography revealed the origin of such a structure: the peritectic channels formed from sequential growth of the phases, with the (Zn) -liquid front far behind the AgZn₃-liquid

Figure 8.9: 3D characterization of a sample directionally solidified under $G = 3$ K/mm and $V = 0.07 \mu m/s$. A) Volume rendering showing primary phase re-nucleating on pre-existing cracks. Here, the primary phase is depicted in red and the peritectic phase in blue/purple. The darkest blue regions are the cracks. B) displays representative cross-sectional slices of the reconstruction in the $y - z$ and $x - y$ orthogonal planes (see green lines). The light gray regions belong to the primary phase, the dark gray to the peritectic, and the black to the cracks.

front. That is, $AgZn₃$ was in the form of columnar grains separated by highly curved liquid channels; these channels were later invaded by (Zn). At lower cooling rates (and hence longer solidification times $\Delta T_0/GV$), coalescence and Ostwald ripening eliminated the channels so as to form a single band of primary phase onto which the peritectic nucleated.

- Influence of specimen geometry. We determined an instability wavelength λ^* between 0.5-1 mm for $V = 0.07 \ \mu \text{m/s}$ and $G = 3 \ \text{K/mm}$, as evidenced by the single-band morphology which appeared in cylindrical samples with ≈ 0.5 mm. In contrast, large samples (on the order of $2-4\times\lambda^*$) displayed evidence of thermosolutal convection which led to radial segregation patterns. Furthermore, the presence of microstructural defects, such as cracks that are perpendicular to solidification direction, led to renucleation of the primary phase and, in turn, the formation of a multi-banded structure.
- Influence of thermal gradient. Relatively high thermal gradients $G(10\times \text{that of})$ our above studies) led to a partially banded microstructure that has not been reported before. Small interconnecting filaments of primary $AgZn₃$ connected the separate bands. EBSD confirmed a nearly identical crystal orientation across different bands, which indicates that renucleation was of minor importance to the final microstructure. Instead, the microstructure formation is controlled by solute redistribution leading to time-dependent growth rates and hence growth competition between the two phases in DS. This situation is encountered when the thermal length of the mushy zone $\Delta T_0/G$, and hence the separation of the two growth fronts, is minimized.

Beyond G/V and alloy composition C_0 [\[163,](#page-284-5) [168,](#page-284-8) [224\]](#page-288-1), our results indicate that additional axes like the solidification time $\Delta T_0/GV$ and the thermal length of the mushy zone $\Delta T_0/G$ are needed to more accurately predict the selection of peritec-

tic microstructures. In terms of the latter variable, we have shown that exceptionally low thermal lengths may drastically impact the morphology of the two-phase microstructure. The prevalence of high G in additive manufacturing (exceeding 5×10^6 K/mm [\[354\]](#page-299-3)) suggests that simultaneous growth of the two phases may be achievable. Preliminary results (not pictured) indicate that the interphase spacing of laser-remelted off-peritectic Ag-Zn is $\leq 1 \mu$ m, necessitating synchrotron-based X-ray nanotomography for 3D analysis. Another avenue of further inquires involves forming defects along the sample surface (through, e.g., nicks along a sample edge), potentially facilitating to the formation of banded or partially banded structures with a desired band spacing. This outcome, traditionally pursued through DS alone [\[165\]](#page-284-0), could be achieved more controllably through the deliberate introduction of defects. Further exploration may consider nucleation site geometry, such as curved or straight interfaces. Additionally, incorporating nonreactive ceramic particles in the melt may address the need for re-nucleation while avoiding the potentially detrimental effects of sample defects. Finally, an exploration of other peritectic alloys of technological importance (e.g., Fe-Ni, Fe-C, etc.) through contemporary in situ and 3D techniques is also warranted to fully understand the conditions under which PCG may occur, as a function of $\Delta T_0/G$ in DS. All of these inquiries inspire further research.

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8.6 Supplementary Material

Figure 8.10: EBSD phase (left) and orientation (middle) maps of region \sim 500 µm below the conical channel of peritectic shown in Fig[.8.1](#page-222-0) (*i.e.* $G = 3$ K/mm and $V = 0.1 \mu \text{m/s}$. The inverse pole figure of AgZn₃ is shown on the right.

Table 8.1: Acquisition parameters for tomography using Zeiss Xradia Versa 520 X-ray microscope and the corresponding figures.
Acquisition parameters for tomography using Zeiss Xradia Versa 520 X-ray microscope and the cor FOV refers to field-of-view; 'high G' to the conditions indicated in Sec. 8.2.2; and 'cracked' to the sample described Table 8.1: Acquisition parameters for tomography using Zeiss Xradia Versa 520 X-ray microscope and the corresponding figures.
FOV refers to field-of-view; 'high G' to the conditions indicated in Sec. 8.2.2.2; and 'cracked

Figure 8.11:

X-radiography showing DS of off-peritectic Ag-Zn alloy at \dot{T} of 0.3 K/min and $G = 21$ K/mm. Snapshots over a 255 minute time period are given, processed through constant division A) and 50 frame sequential division B). The primary phase is shown in red while the peritectic phase is blue.

 $\dot{T} = 0.3$ °C/min

Figure 8.12: Position (A) and C) and velocity (B) and D) of primary (red) and peritectic (blue) fronts with time, under at \dot{T} of 0.3 K/min. C) and D) show magnified views of boxed regions in A) and B), respectively.

 $\dot{T} = 0.5$ °C/min

Figure 8.13: Position (A) and C) and velocity (B) and D) of primary (red) and peritectic (blue) fronts with time, under at \dot{T} of 0.5 K/min. C) and D) show magnified views of boxed regions in A) and B), respectively.

 $\dot{T} = 0.7$ °C/min

Figure 8.14: Position (A) and C) and velocity (B) and D) of primary (red) and peritectic (blue) fronts with time, under at \dot{T} of 0.7 K/min. C) and D) show magnified views of boxed regions in A) and B), respectively.

Figure 8.15:

Reconstructions of primary surface grown under cooling rates of A) 0.3, B) 0.5, C) 0.7, and D) 2.0 K/mm, colored according to the curvedness, C, of the local interface (refer to section [8.3.1.3\)](#page-235-0). \bf{C} ii) provides a magnified view of the boxed region in C i). All volumes are colored according to the color bar on the right and thus comparable.

Part III

Conclusions and Outlook

CHAPTER IX

Conclusions

This dissertation demonstrates the ability of modern imaging and computational tools to comprehensively characterize the kinetics of naturally formed multi-phase materials. Each chapter delves into a poorly understood aspect of the formation and evolution of multi-phase eutectic or peritectic microstructures, contextualizing the experimental findings with relevant theory. Leveraging synchrotron X-ray imaging and machine learning tools allows for in situ and/or ex situ perspectives on morphological development in three dimensions.

In summary, the key findings are as follows:

- 1. As a first step, we leveraged machine learning to understand under what conditions a wholly three-phase eutectic microstructure can solidify. More specifically, genetic optimization aided in solving for the velocity-undercooling relationships for each potential growth form within the Al-Ag-Cu ternary system. On the basis of the competitive growth criterion, we then mapped the threephase eutectic coupled zone in composition-velocity space. The derived coupled zone is 90% accurate with respect to experimental results. The model was subsequently enhanced to include a kinetic term, addressing the slow growth kinetics of faceted Al_2Cu interfaces.
- 2. We then explored the growth kinetics of the three-phase eutectic in undercooled

solidification. We used a slightly Cu enriched Al-Ag-Cu alloy, placing it along the $Al₂Cu$ boundary of the coupled zone (determined from above). Employing a multi-modal approach that combines focused ion beam (FIB) tomography and X-radiography, we captured highly anisotropic eutectic growth velocities. That is, the eutectic front exhibited rapid tangential growth with the primary Al_2Cu interfaces, surpassing velocities predicted by the Jackson-Hunt model for minimal undercooling. Scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and 3D FIB tomography demonstrated that this behavior is due to an invasion-type process in solidification, whereby pseudo-2D surface dendrites or 'fingers' of Al and Ag_2Al zip across the Al_2Cu surfaces, thereby setting up eutectic patterns normal to the surface. Furthermore, we ascertain a notable crystallographic and morphological correlation between the primary $Al₂Cu$ and the surrounding eutectic $Al₂Cu$. Protrusions of $Al₂Cu$ originating from the primary rod were observed stretching between interdigit spacings of Ag2Al fingers merging with the surrounding eutectic. Finally, we proposed a model based on local supersaturation and spacing between dendritic fingers to account for the diverse array of two- and three-phase microstructures surrounding the primary rod.

3. We also examined the stability of the three-phase microstructure against annealing. By implementing the total variation regularization reconstruction method, we obtained an in situ perspective on the temperature-dependent evolution of the solid-solid interphase boundaries in $Al-Ag_2Al-Al_2Cu$. The combination of diffraction and absorption data provided a comprehensive view of both crystallographic and morphological changes, respectively, and their correlations. We find that the Ag_2Al and Al_2Cu phases both followed the temporal power law for their average length-scales, despite the lack of self-similarity. The absence of self-similarity in the Ag_2Al phase was partially attributed to the coalescence of rods along high-energy interface boundaries, eliminating the intervening $A₂Cu$ channels in the process. This illustrates the influence of one phase on the other in a system with comparable volume fractions.

4. Finally, we explored pattern formation in a two-phase peritectic alloy. Leveraging laboratory and synchrotron X-ray imaging capabilities, we conducted the first comprehensive and three-dimensional study to explore the impact of growth velocity, thermal gradient, sample geometry, and sample defects on the directional solidification of an off-peritectic Ag-Zn alloy. Our investigation revealed the development of conical channels of peritectic Zn, originating from the solidification of intercellular liquid. Under slow growth rates, these channels disappeared as solid-liquid coarsening of primary $AgZn₃$ led to the coalescence of the columns into a single-phase band, upon which the peritectic nucleated. This demonstrates that solidification time is a key criterion for predicting morphology and is not considered in existing models and theories. Meanwhile, an increase in the thermal gradient resulted in the formation of an unreported partially banded structure, where interconnected filaments of $AgZn₃$ connected the bands. EBSD revealed identical crystal alignment across different bands, indicating that re-nucleation is of minor importance and that the microstructure originates from competitive growth between primary and peritectic phases.

As noted above, the research presented in this dissertation delves into various aspects of pattern formation and solid-state evolution in multi-phase materials. Moreover, it showcases the capabilities of modern tools, such as machine learning and in situ X-ray imaging, in capturing and comprehending such phenomena. For example, chapter [V](#page-120-0) demonstrates the potential of leveraging existing experimental data, coupled with machine learning tools, to construct robust analytical models for predicting the stability fields of a three-phase eutectic as a function of growth conditions. Chapters [VI](#page-150-0) and [VII](#page-173-0) provide insights into how multi-phase pattern formation may be affected by imperfect casts or under elevated temperatures, of fundamental importance but also common scenarios in industrial-scale operations. A key takeaway from these chapters is the influence of the interphase boundary relationships and energies, which contribute the spreading of one phase on the other in solidification and also to the stagnation of coarsening in the solid-state. Chapter [VIII](#page-216-0) builds on the preceding chapters by illustrating the expansive capabilities that tools like Xray imaging offer in capturing dynamic phenomena that were previously obscured by two-dimensional sections. Enhancing our understanding of how pattern formation in multi-phase materials provides valuable insights into how we can control their formation and, consequently, their properties.

CHAPTER X

Outlook

10.1 Outlook on future experimental opportunities

The field of microstructure evolution in multi-phase materials, encompassing both solidification and coarsening, offers numerous opportunities for future experimentation.

10.1.1 Eutectics

10.1.1.1 Solidification

Starting with eutectics, further refinement of the coupled zone in the Al-Al-Cu ternary system is in order. In the model described in Chapter [V,](#page-120-0) certain simplifications were made due to the limited availability of experimental data for the genetic algorithm (GA). The next logical step involves compiling experimental data from the literature, covering a wide range of compositions and growth conditions. The growth constants can then be separated into phase- and/or microstructure-specific components before being fed into the GA. This approach allows for not only determining the phase(s) with the lowest undercooling but also deriving functional representations of compositionally dependent variables, such as the partition coefficient. The result would be a more comprehensive coupled zone map in composition-velocity space.

Additional data could also provide insight into compositional effects on pattern formation within the three-phase eutectic (e.g., ladder, irregular, etc.). While morphology changes in two-phase eutectics, such as the rod-to-lamellar transition, have been shown in situ $[17, 355]$ $[17, 355]$, changes in morphology and topology of multi-phase eutectics have yet to be captured. By further expanding our coupled zone to include morphology changes, one could more accurately predict the conditions under which such a transition could be captured in directional solidification. Furthermore, parameters, such as thermal gradient, which were neglected in the model for simplicity, play a key role in determining the coupled zone of Al-Ag-Cu and should be considered in future studies. Finally, we can adopt the same approach to map the eutectic coupled zone of a wide array of industrially important materials, such as Sn-Ag-Cu. We also believe that this work should be integrated with large materials property data mines like PRISMS, the Materials Project, and CALPHAD. By doing so, we could potentially reach the point when kinetic coefficients would be available in these data repositories. In order to use multi-phase materials in modern applications, it is paramount that we determine the stability field of eutectics to their fullest extent.

Much of the in situ studies on eutectics presented in this dissertation has delved into the analysis of microstructures grown under equiaxied or undercooled conditions, with the effect of thermal gradient beyond the scope of this work. However, directional solidification may inform standard casting procedures. High thermal gradients are typically preferred for their stabilizing effect on the solid-liquid interface [\[356\]](#page-299-1). Recently, the Brookhaven National Laboratory National Synchrotron Light Source II beamline 18-FXI developed a two-zone in situ viewing furnace capable of achieving a maximum thermal gradient of 20 $^{o}C/min$ with 0.1°C temperature precision [\[357\]](#page-299-2). Through either in situ X-ray nano-tomography or radiography, the thermal gradient can be adjusted as the solid-liquid front progresses, enabling us to see, e.g., the transition from cellular to planar eutectic and the concomitant adjustment in lamellar spacings. Additionally, as of this dissertation, there has been no in situ observation of a growing three-phase $Al-Ag_2Al-Al_2Cu$ eutectic front with the spatial resolution discriminate between the eutectic solids and hence capture their interphase boundaries. The recent advancements in X-ray imaging with n-CT provide the means to probe the selection of interfaces in directional solidification, which has so far been examine only postmortem.

10.1.1.2 Solid-state evolution

The solid-state evolution of the three-phase eutectic microstructure described in Chapter [VII](#page-173-0) represents just the beginning of future analyses in this field. For instance, we were unable to visualize in detail the dissolution of Ag into Al at high temperatures, only observing the resulting shift in volume fractions. Through in situ X-ray nanotomography, this elusive phenomenon becomes accessible and can potentially provide more insights into the disappearance of rods. Furthermore, the initial thirty minutes of coarsening, which we were unable to observe, may reveal additional dynamical events, such as fault migration/annihilation, that dominate solid-state evolution in the early stages before becoming negligible later on, as compared to Ostwald ripening [\[31,](#page-274-0) [145\]](#page-283-0). Finally, we investigated an as cast, directionally solidified sample coarsened at atmospheric pressure. These are very idealized initial conditions which are often absent in real world applications. Further work could include introducing initial strain, adjusting the pressure, or changing the initial conditions.

In addition to observing the early stages of coarsening, another area where this work may be expanded upon is the exploration of variations in three-phase eutectic patterns that solidify. For instance, Steinmetz et al. have shown that the 'crossed' eutectic morphology evolves differently while annealing compared to the regular morphology as a result of solid-state crystalline anisotropy [\[256\]](#page-291-0). The clear next step in this work is an *in situ* three-dimensional characterization of the various morpholo-

gies found in the $Al-Ag_2Al-Al_2Cu$ three-phase eutectic system during heat treatment. The CIND analysis described in Chapter [VII](#page-173-0) also allows us to isolate the low-energy habit planes that are selected as coarsening progresses. We may also capture the solid-state evolution of other three-phase eutectic systems to ascertain their interfacial dynamics and compare them with $AI-Ag_2AI-Al_2Cu$. Aramanda *et al.* have shown the existence of faceted planes within the Ag-Cu-Sb three-phase eutectic microstructure [\[105\]](#page-280-0). Faceted solid-solid interphase boundaries will often impede coarsening due to the low interfacial energy [\[271\]](#page-292-0). The design of coarsening-resistant, multi-phase materials is a topic of further study and technological importance.

10.1.2 Peritectics

Turning to peritectic alloys, there remain many areas of research left to explore. As of this dissertation, there has been no real-time observation of coupled peritectic growth within metallic systems. We expect that PCG may be attainable under the high G present in additive manufacturing (exceeding 5×10^6 K/mm [\[354\]](#page-299-3)) as the thermal length of the mushy zone $\Delta T_0/G$ is minimized. Furthermore, there is much yet to be understood about the transition from one pattern to another, for example, island banding to PCG [\[167\]](#page-284-0) and isothermal coupled growth to cellular coupled growth [\[10\]](#page-272-0). Many industrially relevant metallic alloys, such as the Fe-Ni and Cu-Sn systems, have very limited in situ studies. These studies are particularly worthwhile because understanding the growth conditions that lead to different morphologies can better improve solidification procedures, reducing cost and yielding better products. Additionally, *in situ* studies of model organic and metallic peritectic systems, such as Ag-Zn, are not wholly representative of all types of peritectic growth. The time is ripe for a renewed investigation of peritectic solidification.

To investigate the potential for PCG during additive manufacturing and obtain some preliminary insights, we again turned to our Ag-Zn system as an idealized system. We selected three compositions in the vicinity of the peritectic point, 2, 4, and 6 wt% Ag-Zn, to investigate its effect on the pattern formation. 2 cm long cylindrical ingots were cast in an inert argon environment at the Materials Preparation Center at Ames Laboratory (Ames, IA, USA). To ensure homogeneity, the liquid was systematically agitated to ensure thorough mixing before quenched in an oil bath.

The microstructure of the as cast ingots still showed a lack of homogeneity (evidence later). In an attempt to further homogenize the sample surface, we then cut the samples in half with a band saw before using a Trumpf HLD 4002 Disk laser (Yb:YAG) with 1030 nm wavelength to remelt the samples. A 3.2 mm wide laser rastered from top to bottom of the cylinder as a scan speed of 10 m/min, across the sample surface multiple times over a 6 mm diameter regime. Two different powers were used to homogenize, 800 and 1000 W.

To examine the effects of both beam power and scan speed on the solidification microstructures of the homogenized samples, we performed five scans on each half of the homogenized sample, where one half had a fixed power of 600 W while the speed varied between 5-15 m/min and the other had a fixed speed of 10 m/min and the power varied from 450-650 W. A 0.75 mm laser was used to remelt the sample surface, each new line separated by a 2 mm gap. Finally, we again cut each half cylinder in half so as to separate the different homogenization powers. Now, we had 12 unique samples (*i.e.*, 3 compositions \times 2 halfs \times 2 power used in homogenization), each with five different melt pools as described above, resulting in a total of 60 unique scans. A cumulative list of all scan parameters are given in Table [10.1.](#page-271-0) Finally, each sample was polished using SiC grinding paper and diamond polishing fluid and placed on a TESCAN RISE SEM with a beam energy of 30 keV to capture the microstructures within the different melt pools.

Observing the microstructure surrounding the different melt pools, we determined that the homogenization attempt through laser remelting was generally ineffective due

to the low power density. The depth of the melted region was small (15-20 μ m fromt he sample surface), which was exceeded by all the subsequent scans. Thus the melt pools were composed of primarily unhomogenized material wherein primary dendrites of AgZn₃ still appeared within the as cast material.

Within all the compositions, we observed peritectic dendrites surrounded by thin layers of a dark phase (see Fig. [10.1\)](#page-267-0). Energy dispersive X-ray spectroscopy (EDS) confirmed these dark regions are enriched with Zn, suggesting that they were liquid channels where excess Zn segregated to when the peritectic phase formed before being quenched. The microstructure within the melt pool formed within the Zn-2 wt% Ag sample from a 600 W laser moving at 12.5 m/min appears featureless, even at the highest achievable spatial resolution. The alloy compositions with higher Ag concentration (*i.e.*, Zn-4wt% Ag and Zn-6wt% Ag) displayed AgZn₃ dendrites spread throughout the matrix, in addition to the two Zn phases, as seen in Figs [10.2](#page-267-1) and [10.3.](#page-268-0)

Looking more closely at the $Zn-4wt\%$ Ag sample (Fig. [10.2\)](#page-267-1), we can see that along the edge of the melt pool near the heat affected zone (HAZ), the laser appears to have melted these $AgZn₃$ dendrites, but Ag had insufficient time to diffuse away before resolidification. The $AgZn₃$ appeared to have reformed into smaller dendrites with primary trunk diameters of \sim 1 µm (see Fig [10.2B](#page-267-1)). Surrounding the primary phase, peritectic Zn formed 0.75 μ m diameter peritectic Zn cells separated by thin channels of Zn enriched material, as shown in Fig [10.2C](#page-267-1). These cells appear very uniform in size, spacing and growth direction within a single grain. These cells are absent from regions where no primary phase can be found, suggesting their formation is dependent on the increased Ag concentration from the liquidifed primary dendrites. The small size and alignment of these cells may explain why they have been identified as lamellae in PCG [\[343\]](#page-298-0). Further evidence that these are cells is the formation of secondary arms at at several points within the microstructure, which man only occur

Laser remelted microstructure of a Zn-2 wt% Ag alloy with a beam power of 600 W and a laser scan speed of 12.5 m/min. A) shows entire melt pool and surrounding microstructure. B) shows a magnified view of the red box shown in \bf{A}). The light gray phase is the peritectic \bf{Z} n while the dark gray is quenched liquid enriched with Zn.

Figure 10.2:

Laser remelted microstructure of a Zn-4 wt% Ag alloy with a beam power of 550 W and a laser scan speed of 10 m/min. A) shows entire melt pool and surrounding microstructure. B) shows a magnified view of the red box shown in A). C) shows a magnified view of the cyan box shown in \bf{B}). The white phase is primary AgZn₃, light gray phase is the peritectic Zn, and the dark gray is quenched liquid enriched with Zn.

Figure 10.3:

Laser remelted microstructure of a Zn-6 wt% Ag alloy with a beam power of 600 W and a laser scan speed of 5 m/min. A) shows entire melt pool and surrounding microstructure. B) shows a magnified view of the red box shown in A). C) shows a magnified view of the cyan box shown in A). D) shows a magnified view of the green box shown in C). The white phase is primary AgZn3, light gray phase is the peritectic Zn, and the dark gray is quenched liquid enriched with Zn.

Figure 10.4:

Laser remelted microstructure of a Zn-4 wt% Ag alloy with a beam power of 600 W and a laser scan speed of 7.5 m/min. A) shows the entire melt pool and surrounding microstructure. B) shows a magnified view of the red box shown in \bf{A}). C) shows a magnified view of the cyan box shown in \bf{B}). The white phase is primary AgZn₃, light gray phase is the peritectic Zn, and the dark gray is quenched liquid enriched with Zn. Mullins-Sekerka instabilities along the peritectic Zn cells have begun to form along the interphase boundary as seen in \mathbf{C}).

from Mullins-Sekerka instabilities (see Fig. [10.4\)](#page-269-0).

The melt pool found in the Zn-6wt% Ag sample (Fig. [10.3\)](#page-268-0) appears to be much deeper and well-homogenized compared to the pools shown in the Zn-2wt% Ag and Zn-4wt% Ag alloys. This is attributed to the low scan speed and high beam power to yield a high energy density. Within this homogenized region, we again see evidence of peritectic Zn cells (Fig. [10.3B](#page-268-0) and D), but this time without any nearby $AgZn_3$ dendrites. Instead, we see several ∼1 µm diameter near-circular particles of AgZn³ scattered throughout the microstructure. We hypothesize these are precipitates of the primary phase which formed after the solidification (likely while the sample cooled). Solid-state annealing of the sample may determine the validity of this theory as we would expect additional precipitation and coarsening over time.

The only observed effect of the power and scan speed appeared to be a decrease in melt pool size and thus a fine cellular growth at high scan speeds and low powers.

An additional area which is yet to be explored thoroughly is the transition to solute trapping during peritectic solidification. This process is thought to promote the formation of banded microstructures within off-peritectic alloys [\[40\]](#page-275-0). To confirm that the potential for solute trapping, we estimate the Péclet number $Pe \approx V l/D$ [\[1\]](#page-272-1). Here, V is the growth velocity, l is the characteristic length $(i.e.,$ the cellular spacing). and D is the solute diffusivity in the liquid. We determined D from Ref. [\[341\]](#page-298-1) and back-calculated V from the cell spacing using the relationship $\lambda = 14V^{-1.1}$ also given in therein. Using these values, we computed an approximate Péclet number of 4.64. As Pe is greater than 1, the system is solidifying without partitioning solute at the solid-liquid interface. The results above indicate that within the Ag-Zn sample, we may be observing solute trapping of Ag which allows for precipitation of the $AgZn₃$ particles within a Ag-Saturated matrix. We do not believe they are forming purely precipitation under near-equilibrium conditions as we do not observe their formation in the as cast microstructure far from the melt pool.

These results point to many explored avenues of peritectic solidification which have yet to be captured in real time, such as the fine microstructures formed through laser remelting. The sub-micrometer diameter of the peritectic Zn trunks indicate that Xray nano-tomography is needed to investigate their formation, although we still lack the temporal resolution needed to capture it in situ. The solid-state precipitation and coarsening of two-phase peritectic alloys is another untapped area of research worth exploring. Little is known of how stable different two-phase peritectic patterns may evolve under at elevated temperatures, especially in the face of solute trapping.

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