Solidification Science

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For FY2003-2005 -

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OUTPUT SUMMARY – FY2003-2005

- Invited Conference Presentations: 14
- Other Invited Presentations: 5
- Contributed Presentations: 15
- Journal Papers: 25
- Conference Papers: 11

ABSTRACT AND BACKGROUND

The Solidification Science effort is directed toward gaining an increased fundamental understanding of the thermodynamic and kinetic principles that govern the behavior of crystal-melt interfaces and the physical mechanisms that give rise to phase selection, pattern formation, and the wide variety of solidification microstructures observed in metallic materials. Development of the requisite theory involves descriptions of the physical interactions that operate at spatial and temporal scales ranging over several orders of magnitude, from the microstructural scale \((10^{-6} - 10^{-3})m\) down to the atomistic level \((10^{-8} - 10^{-10})m\). Indeed, the thermodynamic and kinetic properties which originate at the atomistic or even electronic level ultimately govern the dynamics of morphological transitions, and a quantitative understanding of these properties is required for substantive theoretical advancement and the development of predictive capability.

The approach taken in the Solidification Science focus area is to utilize analytical, computational, and experimental tools for the advancement of solidification theory. There are currently five general topics of investigation, with each topic including several specific research efforts. The first topic is the fundamental behavior of solid-liquid interfaces. Motivated by the complex self-selection mechanisms associated with the properties of crystal-melt interfaces, our aim here is to understand the structural origins of anisotropic properties, such as interfacial free energy and mobility. By considering the structure of the interface at equilibrium as well as the general response to prevailing local conditions, our objective is to develop a more comprehensive understanding of interface dynamics and the natural selective processes governing solidification microstructures.

The second topic area involves the investigation of the microstructural dynamics during solidification. The central issues of morphological stability, interfacial properties, transport mechanisms, and phase/morphology selection are investigated using theoretical and experimental techniques. Emphasis is placed on elucidating the microstructural pathways selected during solidification.

The third topic area involves solidification dynamics in multicomponent systems. While significant theoretical understanding has been developed for the thermodynamic and kinetic factors that give rise to solidification microstructures in single component and binary systems, multicomponent solidification has been treated less rigorously. With modern computational capabilities, we now have the tools required to incorporate detailed descriptions of multicomponent phase equilibria
and chemical diffusion into theories for microstructural evolution during solidification. The fourth primary topic area is directed toward understanding the microstructural dynamics involved in multiphase solidification, particularly under cooperative or competitive growth conditions, giving rise to a variety of microstructures. Pattern formation in multiphase systems is complex and requires simultaneous consideration of the various mechanisms involved with stability, nucleation, and growth. A key component of this topic area is the prediction of local conditions, as governed by heat and mass transport. In particular, convective transport may significantly alter the microstructure, and may couple with diffusive processes to give rise to completely novel structures, not predicted by the consideration of diffusion or convection effects alone. Our aim is to isolate these different phenomena and obtain a clearer fundamental understanding of how each influences the microstructure, and how microstructural selection is affected by their simultaneous operation.

The final topic area of investigation is concerned with solidification phenomena that occur under conditions of very high undercooling, i.e. far from equilibrium. Here we focus on the complexities introduced by high interface velocities, high undercooling, limitations to attachment kinetics, decreasing diffusivity, non-equilibrium partitioning, and property changes in the liquid phase with respect to the solidification dynamics in these highly driven systems. The overall objective is to combine computational thermodynamics, atomistic simulation, and continuum modeling strategies with advanced experimental techniques for achieving very high undercoolings and quantifying rapid solidification microstructures to understand the competition between all permissible crystalline and noncrystalline phases and the ultimate selection of phases and morphologies.

TECHNICAL HIGHLIGHTS

• Experimental quantification of the three-dimensional crystal-melt equilibrium (Wulff) shape for the binary Al-Sn system, expressing the interfacial energy and stiffness in terms of the relevant cubic harmonics.
• Identification of detailed mechanistic selection phenomena governing the growth of a twinned bccystaline faceted dendritic array in hypereutectic Al-Si alloys.
• Establishment of a theoretical lower velocity limit for stable melt-pool behavior during free-jet melt-spinning, based on melt-pool oscillation and liquid residence time.
• Establishment of a theoretical upper velocity limit for stable free-jet melt-spinning, based on momentum transfer and volume constraints.
• Theoretical estimate of the crystal-melt interfacial mobility in pure aluminum through atomistic simulation using an embedded-atom model and both mechanical and thermal driving forces.
• Incorporation of a two-state model to describe the thermodynamic properties of the undercooled liquid and the associated low temperature phase equilibria and partitionless crystallization limits in the Al-La binary system.
• Experimental investigation of the pattern evolution in a confined space (thin slab and cylindrical shapes), establishing the lengthscale variation with the sample geometry by using the phase-field model and Hunt/Lu numerical model.
• Experimental discovery a geometrical constraint controlling the lamellar/rod transition and developed a lamellar/rod transition model to include this constraint.
• Establishment of a local growth model to elucidate pattern formation under convective growth conditions.
• Development of a capillary sample solidification technique to access purely diffusive growth conditions for the experimental measurement of the intrinsic solute diffusion coefficient in Al-Cu melts.
INTERACTIONS WITH OTHER PROJECTS AND PROGRAMS

• Interaction with the project titled, “Correlations and Dynamics in Metallic Liquids and Associated Amorphous and Crystalline Systems” (C.Z. Wang, PI), particularly in the area of computational solution thermodynamics.

• Interaction with the Magnetism effort in the area of quantifying the solidification phenomena which occur during free-jet melt-spinning and the associated microstructural features of rapidly solidified ribbons.

• Interaction with the Amorphous and Aperiodic Materials effort regarding the formation of glassy phases in highly undercooled eutectic systems.

• Contribution to both theoretical and experimental efforts within scope of the Computational Materials Science Network (US DOE) project, Microstructural evolution based on fundamental interfacial properties, and the second phase of that project, “The role of impurities at interfaces”, (Tony Rollett, David Srolovitz, and Alain Karma, Principal Investigators).

SELECTED PUBLICATIONS


Thermodynamic Prediction of Glass Formation Tendency in Metallic Eutectic Systems

**Personnel:** R.E. Napolitano (PI) and S. Zhou (Post-doc)

**Scope:**

The tendency for glass formation in metallic systems has generally been observed to be considerably lower in binary systems than in higher order systems, where the growth of crystalline phases from the homogenous melt may require more substantial chemical rearrangement and, therefore, may be kinetically limited. However, a reasonably strong tendency for glass formation has been reported in aluminum rare-earth (Al-RE) binary systems. While trends revealed through experimental investigation have given rise to several schools of thought regarding the thermodynamic conditions that may lead to the formation of amorphous phases from the melt, a generally accepted theoretical basis for glass forming tendency in metallic alloys has not been established. Clearly, while any reliable descriptor of glass forming tendency would necessarily include one or more characteristic time scales representing the system kinetics, reliable quantification of relative stability is certainly a prerequisite to meaningful treatment of microstructural dynamics. Unfortunately, detailed thermodynamic descriptions of the Al-RE alloys are generally not well developed, precluding careful investigation of the competition between crystalline and amorphous phases upon cooling from the melt. In the work summarized here, we employ a solution-based methodology to describe the thermodynamics properties of the Al-La binary system and the associated phase equilibria, incorporating first-principles calculations of zero-Kelvin energies where necessary. Remaining model parameters describing the Gibbs free energies associated with the formation of compounds or solution phases are determined through systematic optimization using available experimental data from calorimetry, X-ray diffraction, electron-probe micro-analysis, and optical micrography.

**Research Highlights:**

In treating the Al-La binary system, we have taken a general solution thermodynamics modeling approach to provide a full description of the equilibrium phase diagram, together with constrained or “metastable” phase boundaries. We have also assessed the relevant underlying energetics required to properly treat the nonequilibrium phase compositions which may form at high undercoolings. Specifically, we have used a two-state model for the pure component liquid in the sub-melting temperature regime and a three-species association model to describe the solution or mixing properties of the liquid phase. The resulting liquidus boundaries show better agreement with experimental observation than previously reported models (Fig. 1). In addition, we model both terminal and intermediate phases as solid solutions and compute the values of $T_{liq}$, $T_0$, and $T_k$ corresponding to the conditions $\mu_i^{liq} = \mu_i^s$, $G_i^{liq} = G_i^s$, and $S_i^{liq} = S_i^s$, respectively. For constant temperature and pressure, the first condition is simply the definition of equilibrium and, thus, defines the liquidus, $(T_{liq}, x_L)$ (and associated solidus) boundaries.

![Fig. 1 The computed Al-La phase diagram, showing better agreement with experimental data than a previous model, particularly with respect to the liquidus curves.](image-url)
With a reasonable description of the undercooled liquid, these boundaries can be computed to very low temperatures. The second condition yields the locus \((T_0, x_0)\) or the so-called “T-zero” curve, which defines the temperature below which liquid, of composition \(x_0\), can transform to a given solid phase with no chemical partitioning or associated chemical diffusion. Finally, the third condition defines the locus \((T_k, x_k)\), providing a lower (ideal) limit to the glass transition. All three of these curves, as computed for the liquid-fcc, liquid-\(Al_3La_3\), liquid-\(Al_5La\), and liquid-\(Al_7La\) combinations are plotted in Fig. 2 and compare with experimental observations of glass formation in this binary system. Indeed, this comparison suggests that, as an upper bound to completely partitionless crystallization from the melt, the \(T_0\) temperature may provide a practical limit for the glass formation range.

**Impact:**

We have utilized a solution thermodynamics approach to compute the chemical limits of partitionless crystallization for the Al-La binary system and compared the results with reported observations of glass formation. Considering that partitionless crystallization requires only short range atomic motion, we view the \(T_0\) criterion as a lower bound (i.e. a zero driving force) temperature limit for crystalline solidification, and, therefore, a reasonable inner bound for the glass formation range. Accordingly, we offer the present analysis as a means of assessing the importance of chemical partitioning in the resistance to crystal phase formation. Indeed, thermodynamic descriptions are only a starting point, and quantifying the relative contributions of chemical and structural relaxation kinetics remains an essential step toward a more broad understanding of phase selection upon cooling from the melt, including the formation of stable crystalline phases, metastable crystalline, or amorphous phases.

**Future Work:**

We will continue to model the thermodynamic properties of binary systems and examine the nonequilibrium solidification implications. In particular, we will examine the Al-Sm, Al-Cu, Ag-Sm, and Ag-Cu systems and couple our thermodynamic treatment of these systems with an experimental investigation of thermodynamic properties, applying various calorimetry and diffusion-couple experimental techniques. Finally, we will incorporate both thermodynamic and kinetic properties into analytical and numerical growth models for prediction of phase/composition selection under these far from equilibrium conditions.

**Interactions:**

This project is closely related to the “Correlations and dynamics of metallic liquids” effort, and benefits from close collaboration. In addition, there are several efforts within the Solidification Science focus area which are aimed at the dynamics of eutectic solidification, and a natural interaction exists between those efforts and this project, which is aimed more generally at the many forms of solidification that may occur in highly undercooled eutectic systems.
Anisotropy of Crystal-Melt Interfacial Free Energy

Personnel: R.E. Napolitano (PI), S. Liu (PI), and R. Trivedi (PI)

Scope:

Anisotropic interfacial free energy is a critical factor in any predictive theory or computational treatment of the evolution of solidification microstructures, and its quantification is essential to the development of such treatments. In this project, we have used several approaches to quantify the anisotropic behavior of crystal-melt interfaces and to understand its influence on the dynamics of crystalline phases growing from the melt. We have developed a method for experimentally determining the 3-D equilibrium (Wulff) surface by directly measuring the shape of intragranular liquid droplets. In addition, we have computed the theoretical shape of coupled crystal-melt interfacial grain boundary grooves as a function of anisotropy, orientation of the solid-liquid interface, and orientation mismatch between the grains. These theoretical groove solution trajectories suggest a high sensitivity strategy for the experimental quantification of anisotropy, and we have developed a method for measuring groove shapes along portions of the relevant trajectories. Finally, we have examined the utility of solvability theory with regard to its prediction of the influence of anisotropy on the selection of dendrite tip morphology.

Research Highlights:

Driven in large part by recent developments in the ability to estimate interfacial properties through atomistic simulation, we have developed an experimental technique that takes advantage of the crystallographic selection and solute segregation patterns that are characteristic of directional dendritic growth to generate dispersions of fine intragranular liquid droplets in binary alloys. By directly measuring the shape of these droplets, we have experimentally determined the anisotropy of interfacial free energy in several Al-based binary systems. Beginning with Al-Cu (at 868K) and Al-Si (at 853K) alloys, we measured the {001} section of the Wulff plot, reporting our results in terms of the anisotropy parameter $\varepsilon_{40}^{00}$, where the orientation dependent interfacial free energy is given by $\gamma(\theta) = \gamma_0 (1 + \varepsilon_{40}^{00} \cos 4\theta)$. Here, $\gamma_0$ is the mean interfacial free energy and the angle $\theta$ is a rotation about the {001} axis. More recently, we have extended our measurement technique to three dimensions and have quantified the three-dimensional Wulff shape in Al-Sn (at 573-773K). This method involves the measurement of several 2D sections which can be reconstructed to yield the 3D shape. Subsequently, the experimentally determined 3D shape is modeled using spherical harmonics. Specifically, for the case of cubic symmetry, we adopt the cubic harmonics and, using the two leading terms, express the interfacial free energy as $\gamma = \gamma_0 [1 + \varepsilon_1 (Q - 3/5) + \varepsilon_2 (3Q + 66S - 17/7)]$, where the coefficients are assessed as the critical anisotropy parameters. The anisotropy coefficients were determined as $\varepsilon_1 = 1.81 \times 10^{-2} \pm 3.6 \times 10^{-3}$ and $\varepsilon_2 = -1.12 \times 10^{-2} \pm 1.3 \times 10^{-3}$, and the corresponding 3D Wulff shape is plotted in Fig. 1 (left). The importance of this anisotropy is more clearly seen in the interfacial stiffness ($\phi$), a quantity which reflects the free energy ($G$) associated with maintaining an interfacial curvature ($\kappa$), where $dG = \phi d\kappa$. More commonly, the stiffness is expressed in terms of the associated change in the crystal-melt equilibrium temperature (i.e. capillary undercooling), where $\Delta T = \phi \kappa \Delta S_f = \Gamma \kappa$. Here, $\Delta S_f$ is the melting entropy, and $\Gamma$ is known as the Gibbs-Thompson coefficient. Because of the relationship with the equilibrium interface temperature, the interfacial stiffness is the quantity which best indicates the influence on microstructural dynamics. Based on our determination of the

Fig. 1 The normalized interfacial free energy and stiffness, showing the anisotropy in Al-Sn (573-773K).
anisotropy coefficients, we plot a normalized interfacial stiffness in Fig. 1 (right), illustrating the high degree of anisotropy.

Using variational techniques along with a numerical direct-minimization method, we have computed the morphology of coupled crystal-melt grain boundary grooves as a function of (i) the orientation of the involved grains, (ii) the orientation of the crystal-melt interface, (iii) the rotational symmetry of the crystal, and (iv) the magnitude of the anisotropy of interfacial free energy. Computed solution trajectories in various orientation coordinates have shown that groove depth and grain-boundary angle may be very sensitive indicators of anisotropy. In addition, we have begun to employ our predictions of coupled groove shape for direct measurement of interfacial free energy and its anisotropy in transparent organic metal-analogs. With this technique, we have measured $\gamma_0 = 9.28 \pm 0.06$ mJ/m$^2$ and $\varepsilon_4 = 0.0051 \pm 0.001$ for succinonitrile. Preliminary results have also shown that $\gamma_0 = 2.78 \pm 0.05$ mJ/m$^2$ and $\varepsilon_4 = 0.023 \pm 0.012$ for pivalic acid.

The microscopic solvability theory relates the dendrite tip radius ($\rho$) selection to $\varepsilon_4$, the anisotropy in interfacial energy through the relationship:

$$\sigma^* = D \Gamma / m C_o (k - 1) V \rho^2 \times \left( \varepsilon_4^{0.01} \right)^{1/4}$$

where $D$ is the solute diffusivity in the liquid, $m$ is the liquidus slope (negative), $k$ is the equilibrium partition coefficient, $V$ is the growth rate and $C_o$ is the alloy composition. Due to the scarceness of reported $\varepsilon_4$ values, no systematic comparison has been reported between the predictions of this solvability theory and observed dendritic growth selection in metallic alloys. With our measured values of $\varepsilon_4$ for Al-Cu alloys, we have examined directional growth in Al-4.0wt%Cu under purely diffusive control, carefully quantified dendrite tip radii, and found that the predictions of the solvability theory agree well with our experimental results (Fig. 2).

**Impact:**

The intrinsic properties of crystal-melt interfaces play a major role in phase selection and morphological dynamics during alloy solidification. As such, the quantification of crystal-melt interfacial free energy is a critical issue in the understanding of interfacial behavior involving both theoretical advancement and the development and interpretation of predictive models. Given this importance and the absence of experimental reports of interface energy anisotropy, our work here has been instrumental in the substantial fundamental gains that have been made over the past several years in this area.

**Interactions:**

Understanding the fundamental properties that characterize the intrinsic interfacial response is critical to all solid-liquid transformations, including nucleation, non-equilibrium solidification, and the formation of amorphous materials from the melt. Accordingly, the work described above has clear ties to the project titled “Solidification in eutectic systems driven far from equilibrium” (R.E. Napolitano, PI). This project also benefits from interactions with the project titled, Correlations and Dynamics in Metallic Liquids and Associated Amorphous and Crystalline Systems (C.Z. Wang, PI), which seeks to determine liquid structure, both experimentally and theoretically, and examine the role of the liquid structure on the pathways to the resultant low temperature phases. Reaching beyond the scope of Ames Laboratory, the research outlined here has been contributory to the collaborative efforts of the Computational Materials Science Network (CMSN) project titled, “The role of impurities at interfaces,” (Pls: A. Rollett, Carnegie Mellon University, D. Srolovitz, Professor, Princeton Materials Institute, and A. Karma, Northeastern University), which is a second-phase project, following the very successful CMSN effort, “Microstructural Evolution Based on Fundamental Interfacial Properties.” Other interactions here include J.R. Morris (Oak Ridge National Laboratory), M. Asta (U.C. Davis), and J.J. Hoyt (Sandia National Laboratory).
Mechanistic Selection in Faceted Crystal Growth

Personnel: R.E. Napolitano (PI), H. Meco (Post-doc), C. Jung (Grad. Student), and M.J. Kramer (PI)

Scope:

During the directional growth of primary silicon from a binary Al-Si liquid, competing atomistic mechanisms at the crystal-melt interface are “selected” in accord with their ability to facilitate more efficient long-range chemical diffusion, thus promoting optimization of the overall morphology. At low growth rates, primary structures grow as faceted “dendrites” comprised of two interpenetrating silicon twin-crystals. The dominance of this morphology suggests that the twinned structure is strongly favored in the dynamical sense. Here, we examine this hybrid selection phenomenon and propose a twin-plane migration mechanism, where a complex configuration of high-mobility coherent twin boundaries provides the requisite morphological responsiveness. With compelling experimental evidence to support our claim, we conclude that the observed behavior is indeed a hybrid phenomenon where mechanistic selection of the twinned bicrystal is critical to the morphological selection of the primary array.

Research Highlights:

The primary silicon structure that evolves during low-velocity directional growth from a binary Al-13 wt% Si solution is shown in Fig. 1. This faceted growth morphology is comprised of broad plates which are approximately 1-5 microns in thickness, extending radially from a central stem or core in what we describe as a star-like dendritic morphology, with a common primary growth axis aligned along a <001> crystallographic direction. The sideplates exhibit characteristic interplate angles that alternate between 36.87 and 53.13 degrees, a rotational offset consistent with previously reported twinning about the {210} planes. The central core may be compact and roughly cylindrical or elongated and irregular in shape. The angular dendrites tend to have eight side-plates, but fewer or more side-plates are commonly observed. The sideplates extend radially in [100] directions with neighboring sideplates typically emanating from opposed twins. The exposed leading S-L facets are {111} planes with <011> ridges running along the center of the sideplate edge.

Using serial milling and 3D image reconstruction, we have investigated the growth mechanisms that lead to the observed rapid lateral propagation of the bicrystalline dendritic twin-grains and have shown (Fig. 2) the critical role of twinning in the formation of the sideplates, a necessary feature for selection of this diffusive growth morphology. The migration of twin boundaries within the dendritic core enables efficient twin boundary reconfiguration, permitting diffusion-based evolution of sideplate structures, new primary core formation, and the associated selection of primary array spacing. Considering the possible “simple” core structures that would result in the eight-pointed starshape morphology, we classify.

Fig. 1 The faceted tip of twinned bicrystal primary Si.

Fig. 2 The growth tip at a central core revealing radial instability and new sideplate formation (large arrows) between twin boundaries (small arrows).
the cores into three types, according to the connectivity of the individual twins. Using electron backscatter patterns (Fig. 3), we have confirmed all three core types, and through the analysis of many such twin structures we have shown that the twin boundaries are comprised predominantly of segments with \{310\} and \{210\} orientations (Fig. 4). With direct evidence supporting this claim, we have proposed a structure for the dendritic core that includes a combination of \{310\} and \{210\} symmetric coherent twins and have described an associated twin boundary migration mechanism, at the atomistic level, which would facilitate reconfiguration of the core structure and the sideplate generation required for efficient response to radial supersaturation gradients.

**Impact:**

While scientific understanding has led to a high level control in the primary growth of nonfaceted dendritic crystals, the fundamental principles and mechanisms of selection for the growth morphology of faceted crystals are not well understood. In this work we establish a hybrid mechanistic/morphological selection phenomenon and make a direct connection between the atomistic structure of the twin boundaries on the growth interface, twin boundary migration during primary growth, the mechanisms of sideplate formation, and the evolution of the overall primary morphology. Such connection may be a critical step in the understanding of growth phenomena in more complex phases, such as multifunctional or coupled-response materials.

**Future Work:**

We will investigate the selection mechanisms and primary silicon growth morphology in Al-Si alloys of increasing silicon content. As the silicon content is increased, the axial growth velocity can be increased without entering the coupled zone for eutectic growth. We will measure composition profiles, tip temperature, and primary spacing as a function of growth velocity and reconcile the observations with an appropriate growth model. A key issue here is the velocity above which the overall selection is no longer diffusive in nature and where the kinetics of step migration on the silicon surface become limiting.

**Interactions:**

The kinetics of silicon growth from the Al-Si melt is a critical issue in several other projects within the MEP Program, including, “Rapidly solidified hypereutectic Al-Si alloys” (Anderson, Chumbley). In addition, the role of twinning in impurity modified Al-Si eutectics is being investigated as a part of the DOE-CMSN project “The role of impurities at interfaces” (A. Rollett and A. Karma).
Non-equilibrium Chemical Partitioning and Phase Formation in Rapidly Solidified Binary Eutectic Systems

Personnel: R.E. Napolitano (PI), M.J. Kramer (PI), and H. Meco (Post-doc)

Scope:

New experimental and computational methods offer effective means to address many fundamental questions that remain unanswered regarding the competition between various morphologies during rapid solidification. A critical issue, central to microstructural selection at high undercoolings, is the role of non-equilibrium solute partitioning and the formation of metastable phases. When local chemical equilibrium constraints break down at very high undercoolings, solidification dynamics are influenced by limitations to atomic attachment kinetics, decreasing solute diffusivities, changing thermodynamic driving forces, and the energetics of ordering or clustering in the liquid phase. Under such conditions, prediction and control of these solidification dynamics involving non-equilibrium chemical partitioning along with metastable crystalline and amorphous phases requires more comprehensive understanding of these phenomena and more general models capable of describing the non-equilibrium effects in these highly driven systems. The project highlighted here is part of a larger effort aimed at such fundamental understanding, where the novelty of our approach is that we consider the mesoscopic reduction in free energy density to be the sole thermodynamic constraint and where the partitioning of all dissipative forces are considered simultaneously in the selection process. The scope of the current subtask is to employ free-jet melt spinning along with advanced e-beam and x-ray microanalysis techniques to investigate non-equilibrium chemical partitioning and metastable phase formation during rapid solidification in Al-Sm and Ag-Sm binary systems.

Research Highlights:

High undercooling solidification has been investigated in Al-Sm and Ag-Sm binary alloys and typical microstructures resulting from free-jet melt-spinning are shown in Fig. 1 for Al-3at%Sm and Ag-10at.%Sm (i.e. eutectic composition). In both cases, the SEM micrographs reveal a relatively featureless wheel-side structure with radial multiphase nodules evident nearer to the free side. While the structures in these two alloys appear similar, further TEM, EDS, and XRD analysis has shown that they are quite different. For the Al-Sm alloy, the nodules consist of a primary Al solution phase (fcc) which grows with a fine cellular morphology, with a metastable Al$_{11}$Sm$_3$ (tetragonal) phase in the intercellular regions. Closer to the wheel surface, these phases are present in a much finer structure, with no evidence of amorphous phases. In the case of Ag-Sm, however, we have observed that the radial nodules consist of a supersaturated primary cellular Ag solution phase (fcc) with a Sm-rich amorphous phase in the intercellular regions (Fig. 2). In this system, the equilibrium diagram has been reported to contain an intermediate Ag$_{51}$Sm$_{14}$ solution phase (hexagonal), which is roughly the same composition as the Al$_3$Sm phase (hexagonal). In both cases, this phase appears to be kinetically limited, resulting in the formation of the Al$_{11}$Sm$_3$ phase in the Al-Sm case or the glassy phase in the Ag-Sm case on rapid cooling from the melt. This behavior

Fig. 1 Rapid solidification microstructures after melt-spinning at 20 m/s: (a) Al-3at%Sm, (b) Ag-10at%Sm.
suggests that both chemical diffusion and structural rearrangement may play dominant roles in governing kinetic efficiency. Thus, non-equilibrium chemical partitioning, as permitted by the underlying thermodynamics, becomes integrally linked to crystallization interface kinetics. Accordingly, we have begun to investigate the degree of non-equilibrium partitioning in these rapidly solidified eutectic alloys. We have employed x-ray diffraction and applied a Rietveld refinement technique to accurately determine the lattice parameter as a means for measuring the amount of solute trapped within a given phase. Surprisingly, for the Al-Sm alloy, preliminary results have shown that the supersaturated primary fcc-Al phase has a lattice parameter that is smaller than that for a pure Al phase, despite the larger atomic radii of Sm.

**Impact:**

In this project, the use of emerging characterization capabilities and new-generation rapid solidification methods with increased control (coupled with other experimental and theoretical studies currently in progress) will shed new light on the dynamics of microstructural evolution and amorphous phase formation in eutectic systems driven far from equilibrium. In particular, through the work described here and in concert with other ongoing efforts, we will gain new understanding and predictive power with respect to thermodynamic limits for local equilibrium and partitionless crystallization, the effect of solute diffusivity and its temperature dependence, and the relationship between interface mobility and solute partitioning.

**Future Work:**

Using advanced solidification and characterization methods, we will continue experimental investigation of the undercooling dependence of the solute partitioning behavior in both stable and metastable phases. The data gathered as a result of this work will ultimately be used for a more accurate thermodynamic description of phase equilibria in the high undercooling regime. In parallel with this experimental work are three theoretical efforts that are essential to the project. First, we are developing solution-based models for accurate and comprehensive thermodynamic description of the binary systems we are investigating. This work will include first principle calculations along with experimental determination of critical thermodynamic features. Second, we will employ atomistic simulations to investigate the relationship between interface kinetics and chemical partitioning (See highlight entitled: “Computer simulation of solid-liquid interface migration.”). Third, we will incorporate the detailed thermodynamic models and interface behavior into a phase-field model for prediction of phase selection, non-equilibrium partitioning, and even glass formation.

**Interactions:**

This project is closely related to several efforts within the Materials and Engineering Physics Program, including: “Prediction of of thermodynamics limits for partitionless crystallization from the melt” (Napolitano), “Thermodynamics of eutectic solidification” (Napolitano), “Computer Simulation of Solid-Liquid Interface Migration” (Mendelev and Napolitano), and “Rapidly solidified hypereutectic Al-Si alloys” (Anderson, Chumbley, and Trivedi), which are all part of the Solidification Science focus area. In addition, there is direct interaction with the project titled “Correlations and dynamics of liquid metals,” (C.Z.Wang, PI).
**Coupled Growth: Far From Equilibrium**

**Personnel:** R. Trivedi (PI), N. Wang (Visiting Scientist), and J. Teng (Grad. Student)

**Scope:**

Eutectic growth under large undercooling conditions is important since it gives rise to nanoscale spacing, and it can lead to the formation of amorphous materials. The aim of this project is to develop a coherent program based on combined experimental and theoretical approaches that examine coupled growth that occurs under conditions far from equilibrium. The current theoretical model is based on the Zener hypothesis that considers the two-phase microstructure to be controlled solely by the diffusion in the parent phase and interfacial energy. These considerations give rise to a simple scaling law that gives $V \lambda^2 = \text{constant}$, where $V$ is the growth velocity and $\lambda$ is the lamellar spacing. When the coupled growth is obtained at a large undercooling, a significant deviation from this scaling law is observed, indicating that other fundamental physics need to be included in the model. Since the precise quantitative analysis of experimental studies at very high velocity is difficult, we shall consider a more general formation of two-phase coupled growth that exists in polymer systems, as well as during the solid-state transformations. This is because the new phenomena that need to be included for high velocity eutectic growth in alloys are operative in these systems at low velocities so that controlled experiments can be carried out to validate the general model. The new physics taken into account include the interface kinetic effects, strain energy effects at the interface, and the additional solute transport by interface diffusion. Concurrent experimental studies are also being carried out in Al-Cu, Al-Sm, Fe-C (eutectoid) and Polyethylene Glycol (PEG)-1, 4-DibromoBenzene (DBBZ) polymer blend.

**Research Highlights:**

Current theoretical models of eutectic growth are based on solute transport in the parent phase and interface energy effects, where the boundary conditions at high velocity are derived from the Baker-Cahn non-equilibrium model. When this model is applied to eutectic growth in the Al-Cu system, it is found that a steady-state eutectic growth can no longer be stable beyond the velocity of 1.0 m/s. This is due to the presence of large undercooling, or low interface temperature, at high velocity that significantly reduces the solute diffusion coefficient in the liquid. The limiting eutectic spacing is found to be about 17 nm. These results lead to the following observations.

1. The model is based on solute diffusion in the liquid only. However, as the diffusion coefficient in the bulk liquid becomes very small, transport by interface diffusion can become of primary importance.

2. At very high undercooling, the eutectic spacing becomes very fine, on the order of a few nanometers, and the composition difference in the solid between the two phases becomes larger. Very high solute gradients will be present along the interface that will produce significant strain energy effect that must also play a critical role in the stability of the eutectic microstructures. We have included this effect in the model.

3. Interface kinetics effects become important at large undercooling and appropriate kinetic models need to be developed and included in the overall treatment.

A conceptual model that includes all these phenomena is developed. Since the model is complicated, several specific systems are examined experimentally in which the different physics outlined above can be isolated so that a rigorous model for limiting cases can first be developed and tested.
It should be noted that rapid solidification is not related to high velocity, but it is related to high interface undercooling. For eutectic growth, rapid solidification occurs when the Peclet number, \( P \), is larger than one, where \( P = \frac{V\lambda}{2D} \). Since the Peclet number also depends on \( \frac{\lambda}{D} \), \( P=1 \) corresponds to velocities on the order of 1.0, \( 10^{-4} \) and \( 10^{-5} \) m/s for coupled growth in Al-Cu, Fe-C eutectoid and polymer system of PEG-DBBZ, respectively. The Peclet number, however, is directly related to interface undercooling, which can be large at low velocities for systems with small diffusion coefficient values and/or large interface kinetic effects. Experiments are thus carried out in several eutectic, eutectoid and polymer systems in which the diffusion coefficient varies by several orders of magnitude. These include:

1. Directional solidification of Al-Cu and Al-Sm, alloys, since Al-Sm has a smaller diffusion coefficient and larger atomic size so that interface diffusion and interface strain contribution may become important near the limit of stability of the eutectic.

2. Directional transformation of Fe-C eutectoid in which the strain energy effects would be important since the variation in lattice parameter with solute is large. We have used these general concepts to explain the results in Fe-C eutectoid in which the experimental spacing has been found to be a factor of three larger than the theoretically predicted value by using the Zener approach.

3. We have completed initial set of experiments in a polymer system, PEG-DBBZ, which show that the interface kinetics effect are very large and the composition variation in the bulk liquid is nearly zero. In this case, the eutectic growth is governed by interface diffusion, interface kinetics and interface strain energy effects. This is a significantly different model than the one used currently for eutectic growth. The interface kinetic laws for this system have been characterized experimentally, and were found to be governed by the nucleation process at the interface. These results are now being analyzed by using the model that takes into account these specific concepts.

**Future work:**

The general model, which is now developed conceptually, will be completed with a rigorous thermodynamic and mathematical analysis. Experiments will be continued in other selected systems that allow proper validation of the effect of specific new physics introduced in the model. For example, several previous experimental studies in directionally transformed eutectoids have found the scaling law as \( V\lambda^n = \text{constant} \), where \( n \) is found to vary from 2 to 4 (including the fractional values). This clearly indicates that different physics play key roles in different alloy systems. Similarly, different scaling laws have been reported in different polymer blends. To isolate the relevant physics, we shall carry out experimental studies in selected systems in which each physical contributor plays a dominant role. These experimental results will be used to fine tune the general model of coupled growth that occurs under far from equilibrium conditions.

**Interactions:**

We have significant interactions with Fred Yost (Sandia Laboratories, Albuquerque) and Alain Karma (Northeastern University) in the development of the model.
Crystal-Melt Interface Mobility Prediction by Atomistic Simulation

Personnel: M.I. Mendelev (PI) and R.E. Napolitano (PI)

Scope:

The scope of this effort was to establish a reliable method for the determination of solid-interface mobility. In the work presented here, we consider a single-component system, but the method will ultimately be applied to multicomponent alloys. The crystal-melt interface mobility is a fundamental property indicating intrinsic resistance to motion of the interface by atomic attachment and detachment mechanisms. The mobility is most often given as a simple kinetic coefficient, $\mu$, which is defined by the relation,

$$V = \mu (T - T_m) = \mu \Delta T \quad (1)$$

where $V$ is the solid-liquid interface (SLI) velocity and $T_m$ is the melting temperature. This expression is valid when $|\Delta T|$ is small and undercooling (i.e. the bulk free energy difference) is the only driving force. The situation is more complex when $|\Delta T|$ is large (far away from solid-liquid equilibrium) or when there are other contributors driving the interface, such as SLI curvature. In this case, the SLI velocity is a function of the total driving force $P$. Our goal was to establish a reliable simulation method for quantifying the relationship between the driving force and the interface velocity when the system is far from equilibrium. We considered two methods to drive the interface: 1) heating/cooling of the system at zero stress and 2) applying external stress at $T=T_m$. The first method has been well established in the literature; therefore, here we discuss the second method.

Research highlights:

We used a simulation cell with periodic boundary conditions in the $x$ and $y$ directions, which are parallel to the interface, and open surfaces in the $z$-direction. Thin liquid layers were created in the top and bottom parts of the simulation cell (see Fig. 1). A constant strain was applied in the $x$ and $y$ directions at $T=T_m$. Since liquid does not support strain, this increased only the free energy of the crystal and served as the source of the driving force. During the simulation, the liquid layers grew toward the center of the simulation cell. This simulation scheme allowed us to keep constant stress (and, therefore, the driving force) during the SLI migration and thus avoid difficulties associated with using the Parrinello-Rahman technique. In order to get a reasonable simulation time, we had to apply a rather large strain (up to 2%). Since under this strain, the linear elasticity theory is no longer valid, we determined the stresses in the bulk crystal for several strains and found the constants in the following expression:

$$\sigma_x + \sigma_y = \lambda_1 \epsilon + \lambda_2 \epsilon^2 \quad (2)$$

The driving force was then calculated as $P = \frac{1}{2} \lambda_1 \epsilon^2 + \frac{1}{3} \lambda_2 \epsilon^3 \quad (3)$

In order to test the proposed method, we determined the SLI mobility in pure Al. An embedded-atom method (EAM) potential, which properly describes the solid and liquid properties was developed within the framework of the “Correlation and Dynamics
in Metallic Liquids” effort. J.R. Morris (Oak Ridge National Lab) showed that this potential provides correct predictions for the SLI free energy. The velocity – driving force relationship for the <100> SLI is shown in Fig. 2. This figure demonstrates that the relationship is linear at all applied strains. The slope to this plot gives the SLI mobility, which was found to be 65, 54 and 53 m/(s·G Pa) for the <100>, <110> and <111> SLIs, respectively. The kinetic coefficient was calculated from these data by using the Gibbs-Helmholtz equation (using additional simulation data, which are not discussed here). The kinetic coefficient was also determined directly from the simulation where ΔT was used as the driving force. The comparison of the kinetic coefficient values obtained by two different techniques demonstrated that the SLI mobility does not depend on the source of the driving force. The experimental value for Al with -0.5wt% Be is 66 cm/(s·K). This comparison clearly demonstrates the reliability of our simulation.

Impact:
The proposed computer simulation method allows for the determination of reliable data on the solid-liquid interface mobility. It was shown that the SLI mobility does not depend on the source of the driving force.

Future work:
We will perform the simulation under the imposed conditions of simultaneously undercooling and applied strain as the source of the driving force. This study will allow us to determine a velocity – driving force relationship for temperatures much below the equilibrium melting temperature. We will then extend our simulation to the case of two-component alloys. The obtained velocity – driving force relationships will be used for development of analytical and numerical solidification models. In particular, we will examine the relationship between driving force, interface velocity, and chemical partitioning.

Interactions:
This research is performed in collaboration with Dr. J.R. Morris (Oak Ridge National Lab) who performs the parallel study of the SLI free energy and nucleation in the same system and Prof. D.J. Srolovitz (Princeton University) who performs the parallel study of the SLI migration in pure Ni. There is a strong interaction with the work described in “Non-equilibrium Chemical Partitioning and Phase Formation in Rapidly Solidified Binary Eutectic Systems,” (Napolitano).
Lamellar/Rod Eutectic Transition

Personnel: S. Liu (PI), R. Trivedi (PI), J. Lee (Visiting Scientist), and E. Simsek (Asst. Scientist)

Scope:

Eutectic microstructures generally consist of a rod or a lamellar morphology. Current models of lamellar to rod transitions are based on a competitive growth assumption in which the minimum undercooling required for the two morphologies under steady-state growth conditions are compared. We have examined this transition by specifically considering two critical aspects that are lacking in current models: (1) the transition occurs dynamically so that the stability of each morphology needs to be considered; and (2) a range of spacing (or undercooling) exhibits stability under given growth conditions, significantly influencing the transition condition.

Two sets of critical experimental studies in the Al-Cu system have been carried out to examine the lamellar to rod transition. In the first set, directional solidification is performed using capillary samples to obtain diffusive growth conditions, and the selection of morphology under steady-state conditions is established. In the second set, a concentration variation along the radial direction is introduced, and the dynamics of the transition are examined. It is shown that this transition is not sharp, but occurs over a range of compositions or volume fractions where both morphologies coexist. The presence of a spectrum of spacings and the constraints imposed by the dynamics of the transition play an important role in the selection of the morphology. These findings are incorporated into the lamellar-rod transition model, and the results are summarized in a microstructure map in the volume fraction-interface energy space that establishes rod, lamella and rod-lamella coexistence regions.

Research Highlights:

One of the key questions in most two-phase pattern formation processes in nature relates to the fundamental physics that govern the selection of a given morphology. For eutectic growth, the morphological selection occurs between the lamellar or rod morphologies. The current theory for selection is based on a competitive growth model that assumes that morphology selection is governed by the relative undercooling values under steady-state growth conditions. It also assumes that each morphology grows with a unique spacing (or a unique undercooling value), which is not valid. Furthermore, transition dynamics are not taken into account, yet these must also be critical in the selection process. The current model predicts a sharp transition condition that depends on the volume fraction of the minor phase and on the relative values of the interfacial energies between the two solid phases.

In this study, detailed experimental work on the rod/lamellar transition is examined in the Al-Cu system over a wide range of compositions (i.e., a range of volume fractions). The growth was carried out in a capillary sample (<1.0mm in diameter) where diffusive growth prevailed and a uniform steady-state eutectic microstructure formed in hypoeutectic alloys (<33.2wt%Cu). For the hypereutectic alloys, purely diffusive growth was not possible, but the macrosegregation allowed us to study the effect of composition on the morphological transitions. The key finding through this study is that the lamellar/rod transition is not sharp, but rather occurs over a composition range (20.0–26.0wt%Cu), which corresponds to the volume fraction of θ (CuAl2) phase from 0.24 to 0.36. This gradual transition is shown to be due to the presence of a spectrum of stable spacing for both lamellar and rod eutectic morphologies. A model is proposed that incorporates the effect of the spectrum of spacings on the transition criterion.

A critical aspect of the dynamics of this transition is the stability of the lamellar morphology, involving a mechanism where the lamellae break into rods. We investigated this feature of the transition through experimental studies where composition variation was introduced in the radial direction so that the process of lamellae transforming into rods could be directly observed. The process is found to be very dynamic, where the lamellae break up into rods and then the rods may rejoin to form lamellae depending on the local spacing (Fig. 1). Instability in a lamella initiates at one end, most often at the fault boundary, and then propagates to form a sinusoidal perturbation. A coupling of instabilities in adjacent lamellae is...
observed that shows a phase difference in the instability of the two lamellae, as seen in the lower left corner in Fig. 1. This phase difference in the instability of the adjacent lamellae leads to the formation of a hexagonal arrangement of rods. This observation shows that the rod spacing at the transition is not the same as the lamellar spacing, as assumed in current models, but rather that the ratio of spacing ($\frac{\lambda_R}{\lambda_L}$) is 1.16. This spacing ratio indicates that the dynamics of the process places an additional constraint on the transition that must be taken into account in the model.

Two critical aspects observed in this study are the range of stable spacing and the dynamical constraint. A theoretical model was developed that incorporated these effects into the lamellar-rod transition criterion. The results of the model are summarized into a morphological map, Fig. 2. In this figure S is the ratio of average interfacial energy of the rod eutectic to that of the lamellar eutectic, and $f_{V\theta}$ is the volume fraction of the minor phase. It clearly demonstrates the complex interplay between the anisotropy factor and the volume fraction factor in the selection of eutectic morphologies.

Impact:
This research provides an understanding of the complex physics that govern the selection of morphology in two-phase systems. The proposed model incorporates dynamical effects of the instability process that lead to a rod-lamellae coexistence region. The ability to produce rod morphology for in-situ composite growth is critical and the present results, based on the physics of transition, will provide optimum composition and processing conditions.

Future Work:
Future work will concentrate on the 3D reconstruction of the lamellar/rod transition process, and on the development of a more rigorous stability model based on shape perturbations.

Interactions:
We are interacting with Dr. M. Plapp (CNRS/Ecole Polytechnique, France) who is developing a phase-field model for the lamellar to rod transition. In addition, this research is closely related to the project “Solidification in Eutectic Systems Driven Far From Equilibrium.”
Morphological Evolution in Confined Space

Personnel: S. Liu (PI) and R. Trivedi (PI)

Scope:

Although significant studies are devoted to solidification microstructures as a function of processing conditions, microstructural evolution is significantly influenced by the size of the system. Specifically, when solidification is carried out in micron or submicron systems, the stability conditions for different morphologies are significantly altered compared to larger-scale systems. This effect of system size on solidification microstructures is investigated through directional solidification studies in SCN-0.7wt%Salol in cells of 12, 50, 100 and 200 µm thicknesses. With fixed alloy composition, temperature gradient and growth velocity, the growth morphology is found to change significantly as the sample thickness becomes very small. For example, in a 12 µm thick sample, only dendritic structures are formed even at very low velocity where planar front stability is predicted for a bulk sample. Experimental results are compared with phase-field model predictions, showing good agreement for the variation in tip radius and primary spacing as a function of the thickness of the sample.

Research Highlights:

Early quantitative studies on interface morphologies in metallic alloys and in transparent systems are carried out in samples of finite thickness that represent the morphological evolution in bulk materials. Most theoretical models are based on large systems, and it is critical to examine how microstructural evolution is affected by system size. The effect of sample thickness on solid/liquid interface stability in CBr₄-Br₂ was first examined by de Cheveigne et al. who found that the critical velocity for planar interface stability decreased for a sample thickness less than 50 µm. The authors attributed this to the curvature of the solid/liquid interface in the direction of thickness due to the requirement of mechanical equilibrium at the solid/liquid/glass junction. However, there is no systematic study on the effect of sample thickness on the evolution of cellular and dendritic microstructure in thin samples. The objective of this study is to quantitatively evaluate the effect of sample thickness on interface stability, cell/dendrite shape, and associated spacing selection. A theoretical model is also developed to compare with the experimental results. Important results are:

(1) The critical velocity for planar front stability and the cell-dendrite transition are reduced as the sample size becomes smaller than 50 µm. For a 12 µm sample, neither a planar nor a cellular front is stable, and only a dendritic morphology is observed even at a very low velocity (e.g., V= 0.25 µm/s) where a planar front is predicted to be stable in bulk samples.

(2) The tip radius in a 12 µm thick sample is very large at low growth rates, facilitating careful study of the dendrite tip growth behavior. It was found that dendritic growth in a very thin film sample clearly shows the oscillating growth mode, with each oscillation generating a pair of side arms. The overlap of the dendritic shape is shown in Fig. 1 for one oscillating cycle τ~340 seconds.

(3) Over the velocity range 0.25 to 15.0 µm/s, only the dendritic morphology is stable in the 12 µm thick sample, and the primary arm spacing decreases monotonically. When the thickness is increased to 50µm, the spacing increases into the cell/dendrite coexistence regime and then decreases when the morphology is completely dendritic. When the thickness is increased to 100 µm or higher, the primary spacing becomes independent of the sample thickness and shows the behavior predicted for the bulk sample.
Phase-field calculations show that $\rho^2 V$ ($\rho$ is tip radius and $V$ is velocity) is not constant for dendritic growth in a confined space and that the primary spacing is larger than that in a bulk sample. The calculation agrees with the experimental observation.

**Impact:**

The constraints imposed by the system size dominate pattern formation in a solidification process. It changes the criteria for solid/liquid interface stability and the primary arm spacing selection. The dendritic tip pulsation generates a train of side arms, which offers a clear mechanism for side arm generation. These results clearly show that solidification theory, developed for bulk samples, needs to be modified when the system size becomes very small. This is significant for applications in the production of metal-matrix composite materials and for the thin-film soldering in micro-electronics.

**Future Work:**

Studies on thin-film samples will be complimented with crystal growth in cylindrical samples of capillary dimensions, and the experimental work will be coupled with theoretical calculations based on the phase field model.

**Interactions:**

We have maintained a close interaction with Prof. J. A. Dantzig at University of Illinois - Urbana for the analysis of experimental results by using the phase-field model. For theoretical modeling of pattern formation in capillary cylindrical samples, we are interacting with Prof. Alain Karma at Northeastern University and Prof. Shuzu Lu at Michigan Technological University.
High Undercooling Solidification in Hypereutectic Al-Si Alloys

Personnel: L.S. Chumbley (PI), I.E. Anderson (PI), E. Simsek (Asst. Scientist), E. Kalay (Grad. Student)

Scope:

Solidification morphology and non-equilibrium solute partitioning at high solidification rates are investigated for the Al-Si binary system over a hypereutectic composition range. A gas atomization technique is employed to achieve very high undercoolings, and we build upon prior work, where we have used eutectic spacing measurements to correlate undercooling with particle size and have mapped the Al-Si coupled zone to low temperatures. In the present study morphology and composition are characterized using scanning and transmission electron microscopy (SEM, TEM) and x-ray diffraction (XRD). SEM results reveal four distinct microstructures, selected at different undercoolings (i.e. particle sizes). In order of increasing undercooling, the dominant growth modes are (i) primary silicon, (ii) eutectic, (iii) dendritic primary aluminum, and (iv) cellular primary aluminum. XRD lattice parameter measurements were used to estimate the silicon content of the fcc-Al phase as a function of alloy composition, and TEM results have yielded preliminary estimates of chemical partitioning and solute segregation.

Research Highlights:

Rapidly solidified specimens of three hypereutectic compositions (15, 18 and 50 wt% Si) were produced using high pressure gas (He and N₂) atomization. We employ x-ray diffraction to measure lattice parameter as a means of estimating phase composition and the degree of solute partitioning. Preliminary results have been obtained for particles less than 5 μm in diameter, indicating very high undercooling (see Fig.1). Silicon phase peak broadening was observed with decreasing silicon content in the alloy, indicating a decrease in silicon phase particle size, a trend that was confirmed in associated electron microscopy studies. For the fcc aluminum-rich solid solution phase, the observed x-ray peak shift indicates a lattice parameter increase with increasing silicon content in the alloy melt. A Nelson-Riley extrapolation function was used to calculate the lattice parameters of this phase to be 4.0419, 4.0400, and 4.389 Å, for the 15, 18, and 50 wt% Si alloys, respectively. Based on these measurements, we employ the results of Bendikl et al., who reported a change of 1.9x10⁻⁵ Å/at.% for Si in the aluminum solution, to estimate the silicon content as 3.84, 4.84, and 5.42 at%, respectively.

Recent SEM analyses conducted for Al-18Si at different particle sizes showed several distinct types of microstructure associated with different particle size ranges, correlating to different undercooling regimes. Analyzing the 15 wt% and 18 wt% alloys, we have used eutectic spacing measurements to correlate melt undercooling (relative to the eutectic temperature) to the particle diameter, as shown in Fig.1. Examining the microstructures, we find that particles with diameters from 32 to 45μm (ΔΤ≈35K), exhibit both primary aluminum (dendritic) and primary silicon (faceted, light contrast particles), along with a considerable amount of the Al-Si eutectic (Fig. 2). Smaller particles, with diameters from 20 to 32μm (ΔΤ≈45K), exhibit a smaller amount of the primary phases and the microstructure is largely eutectic (Fig. 3). For particles with diameters from 10 to 20μm

![Fig.1 Undercooling vs particle size, estimated from average eutectic spacing measurements.](image-url)
(ΔT≈65K), a microstructure consisting of either dendritic or cellular type Al growth was generally observed, with the distinction between cells and dendrites being difficult to make.

Due to the spatial resolution limitations of SEM, TEM has been utilized extensively to examine powders of the smallest diameters. Although sample preparation is extremely difficult for these powders, excellent results now are being obtained. A nanocrystalline structure with a grain size of approximately 25 nm was identified in Al-18Si particles with diameters of ~0.5µm (Fig. 4), indicative of extremely high undercooling.

**Impact:**

The TEM studies of small particles (<5µm) are starting to yield useful information about solidification morphologies at high cooling rates in the high Si alloys, which currently have been unexplored due to the difficulty of sample preparation. Coupled with other experimental methods for rapid solidification and theoretical prediction of thermodynamic and kinetic properties, it is expected that these studies will contribute significantly to the understanding of chemical partitioning and microstructural selection far from equilibrium.

**Future Work:**

TEM investigation of particles with a diameter of <5µm is currently in progress for Al-15Si, Al-18Si, Al-25Si and Al-50Si. Further studies will also include 3-D computer reconstruction of the microstructure of the larger powder samples. Measurement of eutectic and cellular spacing to verify the recently published theories will also be undertaken. This work will be conducted in combination with levitation melting experiments, where undercooling and solidification velocity can be directly measured.

**Interactions:**

This work constitutes an effort in examining structures that result when solidification is pushed to far-from-equilibrium conditions. Frequent technical discussions occur and a close working relationship is maintained with the team headed by R. Napolitano, S. Liu, and R. Trivedi.