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Invariant and univariant eutectic solidification in ternary alloys

Irmak Sargin
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Invariant and univariant eutectic solidification in ternary alloys

by

Irmak Sargin

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University
Ames, Iowa
2015

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DEDICATION

This dissertation is dedicated to my parents Ummuhan and Tahir Sargin.

All I have accomplished and will accomplish are only possible due to their endless love and support.
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ABSTRACT

While solidification structures with a large variety of morphologies and scales continue to be promising candidates for advanced applications in addition to the conventional ones, solidification science has been focused on understanding and building the bridges between theory and application, aiming to describe the solidification process at all length scales and enabling enhanced control over the final microstructure and resulting material properties. The knowledge of solidification built over the decades has been mostly based on simple cases like single phase formation one or two component or coupled growth in peritectic or eutectic alloys, whereas the understanding on much more complex multiphase solidification is very limited. As a result of this, multiphase structure formation, which has been mostly approached as extensions of the simpler cases mentioned above, has many open questions regarding dynamics of the process. Ternary alloys serve as a good example for the onset of understanding of multiphase solidification, where different kinds of reactions could take place along a solidification path. With additional degree of freedom, most of these reaction have different characteristic than their simpler counterparts, and many important aspects which can be disregarded for simpler cases come into play. The main goal of the present study is to understand and quantify the microstructural evolution during directional solidification of ternary Al-Cu-Ag system by focusing on different aspect of formation dynamics. Among many different possibilities with respect to phase and morphology, we focus ternary invariant eutectic, univariant coupled eutectic growth, and finally binary eutectic growth. The first challenge taken is quantification and parameterization of ternary invariant structures. Secondly, we focused on univariant two-phase coupled growth and examined the effect of convection, finally
we study the texture selection in binary eutectic as an initiation of understanding this process in ternary and higher order eutectics. During our experimental studies, we have also come across two more subtopics which are important for comprehensive understanding of microstructural evolution. These are the quantification of the effect of solid state reaction causing deviation from the true solidifications in ternary invariant eutectic Al-Cu-Ag and the other one is effect of pre-holding period which alters the front and in results changing the initial stages of solidification which are carried until the end of the process.
CHAPTER 1. INTRODUCTION

Obtaining new functionality and expanded utility in materials has become increasingly important for next generation innovation in areas such as electric power generation, transportation, medical imaging and many others. An area of new materials design that offers great promise in many such applications is tailored multiphase structures grown directly from the melt through solidification processing. Among these multiphase structures, eutectics hold a very important place due to the property that they took their name from. Eutectic derived from the Greek means ‘most fusible’ [1, 2]. The excellent fusibility of eutectics are coming from their low melting points and small freezing range. These factors have contributed to excellent freezing properties, and most engineering casting alloys are based on well characterized binary eutectic systems, such as Fe-C, Al-Si, Pb-Sn, Cu-Sn, etc. In addition to the freezing characteristics that give rise to good fluidity and casting soundness, the potential for forming ‘in-situ’ periodic composites through eutectic solidification offers great promise for enhanced or new functionality in materials, where unusual optical, electrical, magnetic, and mechanical properties may arise from the interplay between various elements of multi-scale hierarchy. Realization of the expansive range of possible structures calls for the investigation of coupled growth structures involving more than two phases. However, ternary and higher order systems often give rise to a host of complex structures, and controlled production of specific structures with desirable functionality presents substantial challenges with regard to both the theoretical understanding of the governing thermodynamics and kinetics as well as the correlation between processing conditions and structural transformations.

While technological advancements in instrumentation and control of varied energy sources have given rise to an increasing number of viable strategies for materials synthesis and
processing, solidification or crystal growth from an alloy melt remains prevalent. In single-phase materials, control of microstructure (actually reduced to only control of crystallographic texture) during growth-from-melt has been applied successfully; on the other hand, the information and control on microstructure evolution in multiphase growth structures are limited. This is primarily due to non-linear dynamics taking place during the microstructural evolution in multiphase material with increasing degrees of freedom and a high number of arrangements of phases [3, 4].

As the understanding of microstructural evolution continues to challenge materials scientists, the most persistent question can be gathered under two main topics: phase and morphology selection [5-15] and interface stability [16-22]. Although recently developed thermodynamic databases have provided versatile information [23-33] most of the open questions still require understanding of the solidification dynamics. From this respect, binary eutectic alloys can be considered as the simplest case of multiphase multicomponent materials with significant complexity in their microstructure formation dynamics at many different levels from grain structure to the periodicity of the phases. At this point in time, it is generally considered that binary eutectic solidification is well understood; however, when the complexity is increased by adding a ternary alloying element to a binary alloy, there is not a comprehensive understanding of evolution of microstructure during solidification.

Academically, examination of solidification structures along the binary eutectic to ternary eutectic point provides a good basis for answering open question as they can give rise to three different microstructural scenarios: binary eutectics, univariant eutectics, and ternary eutectics. By taking challenge of understanding and quantifying microstructural evolution in the three component binary eutectic and ternary structures, this research effort aims to answer
several questions. The first question is how to quantify and parameterize the complex three-phase eutectic structures, where the methods and parameters used for their binary counterparts fall short due to additional degree of periodicity. The second question that we seek answer for is how solutal configuration, which is used to characterize transients, is affected from convection and gravity during univariant eutectic growth. The third question is understanding the kinetics of one of the natural transient, texture selection, in binary eutectic growth since it can be used as a basis for understanding this process in ternary eutectics. In order to form a groundwork on the multiphase solidification, the following section gives an overview of our basic understanding starting from the binary invariant eutectic growth. Then, extension of binary eutectic growth to ternary invariant eutectic is discussed. Finally, general characteristics and additional aspects on univariant eutectic growth is summarized.

1.1 Eutectic Growth

As being one of the most widely used solidification structures, evolution of microstructure in binary eutectics have been a major topic of solidification science. The effort on understanding eutectic solidification has continued since early 1900 [34]. The general milestones on eutectic solidification, which bring us understanding that we have today started with discovery of a minimum solidification temperature at specific compositions in salt-water mixtures and certain metallic alloys by Guthrie in 1884 [2]. This is actually the discovery of invariant eutectic reactions. In 1912, Vogel suggested the coupled growth of eutectics as concluding growth of two phases side by side by based on his work with directionally solidified Zn-Cd eutectic [34]. After revealing of coupled growth, first extensive classification of eutectic microstructures based on their morphology was published [35]. Tamman and Botschwar
showed that the growth rate of primary phases were decreasing as the composition approaches to the eutectic point [36] and based on undercooling one of the competition between primary phases and eutectic structure was won by eutectic. This was the first observation of coupled-zone concept and later it was applied to metallic [37, 38] and to organic systems [39] to explain phase and morphology selection.

Another important aspect of coupled eutectic growth was revealed by crystallographic examination of directionally solidified Zn-Cd eutectics. Straumanis and Brakas showed that in each eutectic grain both phases grow with a specific orientation [40]. Another milestone was presenting solutions to the diffusion equation of pearlitic coupled growth [41, 42], the growth of which is diffusion controlled as that of binary lamellar eutectics. This was major advancement quantified understanding of eutectic growth. In 1946, Zener coupled the effect of diffusion with capillarity declaring the two major determinants of steady-state eutectic growth [43]. In 1957, Hillert extended Zener’s work by assuming a planar solid/liquid interface [44] and calculated the solute distribution ahead of solid/liquid interface for pearlitic structure and the shape of the interface established between austenite and pearlite. In 1958, by accepting the growth conditions in directional solidification, i.e. constant velocity, Tiller accepted a minimum undercooling criterion and wrote an equation for the scaling of microstructure with growth velocity [45]. Jackson and Hunt, presented the most comprehensive theory on steady-state of regular lamellar and rod eutectics [46] based on the former studies.

The application of coupled zone concept to highly off-eutectic alloys and producing of coupled growth structures by applying high thermal gradient to velocity ratio was opened the door for phase and morphology selection studies [46]. Following to these, most of the research efforts were relaxing the assumption of Jackson-Hunt analysis and make it applicable a larger
variety of eutectics instead of just regular lamellar and rod ones. These studies which are
detailed below also showed that operating point selection is more complex than it was thought
and it requires a quantitative stability analysis. These treatment were conveyed by Strassler
and Scheinder [47] and Datye [17]. One of the recent milestones can be stated as presentation
of thermodynamic databases combined with numerical codes which are extremely useful for
handling complex phase equilibria not just for binary eutectics but also for higher-order
solidification reactions [47]. Another milestone can be given as employing directional
solidification of transparent thin eutectic samples. Since dynamics of the advancing front can
be closely examined many question have been answered on front dynamics and stability of
eutectic patterns [4, 48-59] as well as initial stages and effect of initial condition on these
stages [35, 60, 61]

At this point, it is important to mention the classification of eutectics in order to make
the discussion of the theory more understandable. The eutectics can be classified according to
growth configuration, stability of the solid/ liquid interface, growth mechanism, interface
structure, and geometric arrangement of phases [62]. Table 1 shows the classification of
eutectics. Growth configuration is determined by the heat extraction. The stability of the
solid/liquid interface will be detailed under the univariant growth. The following subsections
covers the growth mechanism, interface structure, geometric arrangement of the phase coupled
zone concept, binary eutectic growth theories, modifications of Jackson-Hunt theory,
operating point selection, as a subtopic of regular eutectics.
1.1.1 Growth mechanism

Formation of eutectics could be governed by three different mechanisms: coupled growth, divorced growth, and symbiotic growth. Coupled growth is made possible by the exchanging of solute atoms between two solid phases. As a result of this mutual relationship, they grow simultaneously, forming a common interface [63, 64]. In divorced eutectic growth, there is no connection or mutual relationship between the phases; they grow independently but in successive manner. Symbiotic growth was observed during binary eutectic solidification in univariant alloys by Hecht et al. in the presence of foreign particles which act as nucleation sites for one of the phases [65, 66].

1.1.2 Interface structure

Here the interface structure refers to the solid/liquid interface of the individual phases. The phases may have either faceted or non-faceted interfaces. A faceted interface forms if the dimensionless entropy of fusion is over a critical value [64]. This value was suggested by Hunt and Jackson in 1966 [67] as

\[ \alpha = z^* \frac{\Delta S_f}{R} \]  

where \( z^* \) is the ratio of the number of near neighbor atoms in the plane of the solid/liquid interface to the total number of near neighbor in the bulk. \( \Delta S_f \) is the entropy of fusion, and \( R \) is the ideal gas constant. An \( \alpha \) value larger than 2 indicates a faceted interface, whereas \( \alpha \) value less than 2 indicates a tendency for non-faceted growth. Due to their low entropy of fusion, most metallic interfaces are non-faceted.

The interface structure has a direct influence on the eutectic structure formed. Faceted interfaces are associated with irregular morphologies, whereas regular structures are limited to
situations where both phases have a low entropy of fusion, which allows the eutectic growth to be free from crystallographic limitations. The difference between regular and irregular structures appears as their adherence to periodicity in the structure. In this study, our focus will be on regular eutectics. The most frequently observed regular eutectic structures are called lamellar and rod-like. The lamellar eutectic structure consists of alternating plates, whereas in the rod-like structure, one of the phases has a rod-like morphology and is distributed in a matrix formed by the other phase. In regular eutectics alloys with isotropic interface energies, the distinguishing parameter between these morphologies is the volume fraction of the phases. If one of the phase has a phase fraction lower than 0.28, rod-like structure forms to decrease the interfacial area [64].

The microstructure of a regular eutectic consists of three definite level of structures: grain, subgrain and the eutectic mixture as shown in Figure 1. In a eutectic grain, crystallographic orientation of each phases and their microscopic angular orientation is fixed. Although, at the beginning of a directionally solidified sample there are many grains, which may or may not have a fixed orientation relationship are present, with increasing growth distance, number of grains decreases and finally one grain with a fixed crystallographic orientation between phases forms the microstructure [68-73]. This selected grain was observed to align parallel to the growth distance many time in experimental studies [74-76]. Although the crystallographic orientation is fixed within a grain, subgrains, which are separated from each other by eutectic fault lines, are formed by several degrees of deviation from the mean crystallographic orientation [69].
1.1.3 Coupled zone concept

It is important to state here that the eutectic microstructures are defined as the cooperative growth of two phases from the liquid in case of binary alloys, which does not require the exact eutectic thermodynamic equilibrium [77]. This means a eutectic microstructure can be formed at composition far away from the eutectic composition. The composition and temperature which determines the limits for cooperative growth of two phases are called coupled zone. Tammann and Botscharw suggested that this limit is determined by competition between dendritic single phase growth and eutectic growth [36]. So, the transition between these two morphologies is determined by a highest temperature or in other words minimum undercooling criterion. The shape of the coupled zone is determined by the entropy of fusion of the solid phases [77]. For the eutectic phases which tend to form non-faceted interfaces, the coupled zone is symmetric, however if one the phases is faceted the coupled can be skewed. The example for these two types is given in Figure 2 schematically.

1.1.4 Binary eutectic growth theories

The first theories of lamellar eutectic solidification was offered in early 1900. Tammann suggested that two phases forms alternatively in 1908 [78]. According to his explanation, first one phase nucleates and this causes the enrichment of liquid with respect to one of the constituents and results in formation of other phases. On the other hand, the simultaneous growth of phases first suggested by Vogel [34], substantiated by Lamplough and Scott with the decrease in spacing with increasing solidification rate [79]. Later, edge-wise simultaneous growth of lamellar eutectic was verified by experiments with controlled heat extraction [40].
The progress on explanation of coupled growth was based on pearlitic growth and started with solution of diffusion equations [42]. The following step taken was combining physical reasoning with analytical solutions to the diffusion equations, which required consideration of capillary effect [43]. In this study, Zener suggested a maximum rate criterion at a definite undercooling and presented the first formal theory of coupled growth by showing the reverse relationship between undercooling and lamellar spacing. The need for maximum rate criterion was based on the fact the growth of periodic structures as a balance between diffusion and capillarity results in multiple solutions. An important contribution was development of a mathematical model for Brandt’s solution for pearlitic growth and calculation of solid/liquid interface shape as a function of growth conditions by Hillert [44]. In 1958, Tiller applied Zener’s reasoning to the lamellar eutectic growth and changed maximum growth rate condition to an extremum growth condition, which means growth takes place at spacing which requires the minimum undercooling [45]. As a result of this analysis, the relationship between velocity and eutectic spacing was analytically determined. Jackson-Hunt extended the earlier coupled growth analysis by Zener [43], Hillert [44], and Tiller [45] to regular lamellar and rod-like geometries for steady-state growth [67]. Although, their work was based on the previous attempts, they were first to explain eutectic spacing selection. Additionally, they proposed that the adjustment of the eutectic spacing is possible by motion of the faults within the eutectic structure and also suggested a qualitative range for spacings that can be selected.

Their analysis could be summarized as selection of the factors affecting the growth morphology and determination of the relationships between interface undercooling, eutectic spacing and growth velocity. It is important to state that the eutectic growth theory, as its name
implies, does not consider nucleation. The name “growth” is used as attachments of the solute atoms to the solid at the solid/liquid interface. Effectively, any present solid is actually considered as a seed.

The first step of doing such an analysis is to determine the contributing factors to the interface undercooling. In the analysis of JH, these factors were treated as deviations from the equilibrium liquid solute concentration and the energy required to form new interfaces. The energy required for attachment of solute atoms to the interface was disregarded, because it is very small in comparison to the other contributors to the undercooling. This is mostly true for metals with non-faceted growth characteristics. The total interface undercooling can be given as:

$$\Delta T = \Delta T_C + \Delta T_R,$$  \hspace{1cm} (2)

where $\Delta T_C$ is the diffusional, and $\Delta T_R$ is the curvature undercooling. These two contributors of the undercooling are assessed separately.

The diffusional undercooling is calculated by solving diffusion equations for the moving solid/liquid interface at constant velocity to determine the liquid composition ahead of each phase, and by multiplying the deviation from the eutectic composition with the liquidus slope. The condition of constant velocity makes this problem steady-state and its equation is

$$\nabla^2 C + \frac{V}{D} \left( \frac{\partial C}{\partial Z} \right) = 0,$$  \hspace{1cm} (3)

where $V$ is growth velocity, $C$ is composition, $D$ is diffusion coefficient and $Z$ is the growth distance. Although the solution to this equation is different for the lamellar and rod-like morphologies, given in Figure 3, due to different boundary conditions dictated by geometry of solid/liquid interface, it is possible to state general assumptions without considering morphological differences. It is assumed that the structure is periodic and growing into the
liquid with a planar interface in addition to being steady-state. These assumptions dictate the boundary conditions as

\[ C = C_E + C_\infty \text{ at } z = \infty \]  
\[ \frac{\partial C}{\partial x} = 0 \text{ at } x = 0 \text{ and } x = S_\alpha + S_\beta \]

for the lamellar eutectic. \( C_\infty \) is the difference between the initial and eutectic compositions. \( S_\alpha \) and \( S_\beta \) are the half widths of phases \( \alpha \) and \( \beta \). Also, by conservation of mass JH determined that the solute rejected or accepted by the solid phases are equal to the amount of solute at the interface in the liquid. This is expressed by

\[ \left( \frac{\partial C}{\partial z} \right)_{z=0} = -V(C_E - C_S^\alpha) \text{ for } 0 \leq x < S_\alpha \]  
\[ \left( \frac{\partial C}{\partial z} \right)_{z=0} = V(C_S^\beta - C_E) \text{ for } S_\beta < x \leq S_\alpha + S_\beta \]

where \( C_S^\alpha \) and \( C_S^\beta \) are the solubility limits of \( \alpha \) and \( \beta \) phase respectively at eutectic temperature.

Following the boundary conditions, the solution to the diffusion equation is

\[ C = C_E + C_\infty + \sum_{n=0}^{\infty} B_n \cos \left( \frac{n\pi x}{S_\alpha + S_\beta} \right) \exp \left( -\frac{Vz}{2D} - \sqrt{\frac{V^2}{4D^2} + \left( \frac{n\pi}{S_\alpha + S_\beta} \right)^2} \right) z, \]

for \( \frac{2n\pi}{\lambda} \gg \frac{V}{D} \), it simplifies to

\[ C = C_E + C_\infty + B_0 \exp \left( -\frac{Vz}{D} \right) + \sum_{n=1}^{\infty} B_n \cos \left( \frac{n\pi x}{S_\alpha + S_\beta} \right) \exp \left( -\frac{n\pi x}{S_\alpha + S_\beta} \right), \]

where \( \lambda = 2(S_\alpha + S_\beta) \). \( B_0 \) is the composition of the solute boundary layer coming from the solubility differences of the phases and by the phase diagram it is

\[ B_0 = \frac{(C_E - C_S^\alpha)S_\alpha - (C_S^\beta - C_E)S_\beta}{S_\alpha + S_\beta} \]  
\[ B_n = \frac{2}{n\pi^2 (S_\alpha + S_\beta)} \frac{V}{D} (C_S^\beta - C_S^\alpha) (\sin \left( \frac{n\pi S_\alpha}{S_\alpha + S_\beta} \right)) \]
By integrating the diffusion solution over the half period average, the composition in front of each phase can be calculated at the interface (\(z=0\)).

\[
\overline{C}_\alpha = C_E + B_0 + \frac{2(S_\alpha + S_\beta)^2}{s_\alpha} \frac{\nu}{D} (C_S^\beta - C_S^\alpha)P \tag{9a}
\]

\[
\overline{C}_\beta = C_E + B_0 - \frac{2(S_\alpha + S_\beta)^2}{s_\beta} \frac{\nu}{D} (C_S^\beta - C_S^\alpha)P \tag{9b}
\]

\[
P = \sum_{n=1}^{\infty} \frac{1}{(n\pi)^3} [\sin(n\pi f_\alpha)]^2 \tag{9c}
\]

where \(f_\alpha\) is the phase fraction of the \(\alpha\) phase. The undercooling is \(\Delta T_C = m_i[C_E - C(x)]\) where \(m_i\) is the liquidus slope. For determination of the composition fields of the rod-like eutectics, the boundary conditions are changed before calculation of diffusional undercooling due to different periodicity in these structure.

The second contribution to the interface undercooling of the interface stems from the interfacial curvature, which is a function of eutectic spacing and contact angle. A larger contact angle means a larger interface area, and a smaller eutectic spacing means a larger curvature. The average curvature is given by

\[
\overline{k}_\alpha = \frac{2\sin(\theta_\alpha)}{f_\alpha \lambda} \tag{10a}
\]

\[
\overline{k}_\beta = \frac{2\sin(\theta_\beta)}{f_\beta \lambda} \tag{10b}
\]

where \(\theta_\alpha\) and \(\theta_\beta\) are the contact angles of the \(\alpha\) and \(\beta\) phases at the triple junction. The curvature undercooling is \(\Delta T_R = \Gamma \kappa\) where \(\Gamma\) is the Gibbs-Thomson coefficient.

After calculating the two contributors to the undercooling separately, Jackson and Hunt accepted equal undercooling in the liquid at the interface in front of each phase, and determined the relationship between eutectic spacing, interlamellar for lamellar growth and rod spacing for rod-like growth, and velocity. The total average undercooling becomes

\[
\Delta T = K_C \lambda V + (K_R / \lambda) \tag{11}
\]
and the relationship between velocity and eutectic spacing is

\[ \lambda^2 V = \left( \frac{K_R}{K_C} \right) \]  

where \( K_C \) and \( K_R \) are material dependent constants.

\[ K_C = \frac{\bar{m}(c_\beta^S - c_\alpha^S)}{D_f^\alpha f_\alpha} \]  

\[ K_R = 2\bar{m}\left( \left| \Gamma_\alpha \right| \frac{\sin(\theta_\alpha)}{|m_\alpha| f_\alpha} + \left| \Gamma_\beta \right| \frac{\sin(\theta_\beta)}{|m_\beta| f_\beta} \right) \]

The undercooling gives a minimum with respect to eutectic spacing at a constant velocity. This is called extremum growth condition, which dictates the growth takes place at the minimum undercooling. The major contributor to the undercooling is by deviation from the equilibrium composition; however, as the velocity increases the interface energy becomes dominant factor. As a result, there will be a minimum in a spacing versus undercooling plots, which indicates the highest rate of growth (Figure 4). The validity of JH analysis was tested by both experimental and theoretical studies. In these studies relaxing of the assumptions and extending the use of JH analysis by modifications have been achieved. Furthermore, determination of the operation point selection has also been assessed.

1.1.5 Modification of JH analysis

Series et.al. based on their experiment with electric analogue modified the JH analysis by permitting the mean composition ahead of the \( \alpha \) and \( \beta \) lamellae to have different and unconstrained compositional variations [80]. Another constrained which have been assessed is the wholly planar characteristic of the interface with respect to the solute field. Sato and Sayama relaxed this for lamellar eutectics by assuming only a part of the interface ahead of \( \beta \), which is close to the trijunction among solid and liquid phases, is at the same temperature with
the entire $\alpha$/liquid interface [81]. Fisher and Kurz considered the effect of thermal gradient with a similar approach. This limits the length of the part of the $\beta$/liquid at the same temperature with $\alpha$/liquid interface [82, 83]. They modified JH treatment and used it to determine the critical spacing at which branching takes place in irregular eutectics and also explained the larger undercooling and spacing observed in irregular eutectics in comparison to regular eutectics.

Later, Magnin and Kurz based on previous work and JH analysis, proposed a new analysis in which with consideration of thermal gradient a non-isothermal coupling condition is proposed and showed that by adding a correction factor JH analysis could also be used to estimate the growth of irregular eutectics [83]. They also explained the deviation from the Eq. 12 at very low growth velocities as a result of the fact that correction factor is a function of growth velocity. The JH analysis was also modified for very high growth rates by including the effect of Péclet number and redistribution coefficient into account in the periodicity function. Another assumption relaxed is the almost equal density of solid and liquid phases [84]. When the density difference was taken into account the length of eutectic tie line is changed. Also, asymmetry in the phase diagrams with respect to partition coefficients are considered and used for modification of JH analysis and undercooling was rewritten with a structural part in addition to the material/phase dependent properties [85].

1.1.6 Operating point selection

Tiller suggested that the operating point or the spacing selected of the lamellar coupled growth structures is the one which requires the minimum undercooling [45]. Jackson and Hunt conveyed there is range of stable spacing for a given velocity by a qualitative stability analysis
The minimum of this band is the extremum spacing ($\lambda_m$). They stated the spacings below this value is not stable because the depression in the interface would cause the elimination of lamellae and increase the local spacing. The maximum limit is determined as the point where the interface becomes infinity ($\lambda_M$). Figure 5 shows this limits on an undercooling- spacing ($\Delta T$-$\lambda$) diagram.

After JH, there have been many attempts for determination of stability of the eutectic structures and operation point selections. Cline [86] and Hurle and Jakeman [87] treated the solid-phases as a single phase by averaging and by a perturbation analysis and determined the destabilization scale of the interface. Later analysis by Cline [88] and Strassler and Schneider [89] considered the stability with respect to variation in the eutectic spacing. Both of these studies confirmed the presence of a band of stable spacing as offered by JH [90] The shortcoming of these analysis was the fact that they did not consider the effect of trijunctions. This constrained was relaxed by Datye and Langer [17]. In the study where they coupled early analysis of lamellar growth with the motion of three phase junction, they also verified that the spacing lower than $\lambda_m$ is not stable due to lamellae eliminations. They also showed that an oscillatory instability with a wavelength of $2\lambda$ is present for sufficiently off-eutectic compositions. This was verified by other studies [91, 92]. Also, by Kassner and Misbah presence of tilted steady-states was discovered [52]. All of these studies, while confirming the lower limit, showed that $\lambda_M$ as it is offered by JH is only an upper limit for the $\lambda_{max}$ [77] and actually it is dictated by stability criterion that is different than what JH offered.

The presence of a range of spacings also confirmed experimentally [3, 77, 93-96]. One of the example of distribution of spacing for different velocities can be seen in Figure 6. The comparison of the experimental results with the Jackson-Hunt’s theoretical work showed that
the average spacing is almost 20% percent higher than $\lambda_{\text{ext}}$ and the smallest spacing corresponds to the extremum spacing. On the other hand, the maximum spacing is lower than the one theory implies. Experimental studies along with theoretical calculations caused a new trend in reporting eutectic spacings. The range of spacings has been given in terms of reduced spacing ($\phi = \lambda / \lambda_{\text{ext}}$), where $\phi$ found to be in a range of 0.7 -2.2 (where the upper limits larger than 1.2 is generally observed for thin samples) [35, 54-56, 58, 97]. A similar behavior has also been observed in irregular eutectic growth [64, 77, 98]. So, the equations 11 and 12 was modified as [98]:

$$< \Delta T > = (\phi + 1/\phi) \sqrt{K_C K_R}$$  \hspace{1cm} (15)

$$< \lambda >^2 V = \phi^2 (K_R/K_C)$$  \hspace{1cm} (16)

In these equation the values in brackets showing the average values. The value of $\phi$ is about 1.2 for regular eutectics amd found be higher than 2 for irregular eutectics [48, 64, 98, 99]

Another important point on dynamics of spacing selection is the mechanism. Several studies addressed this issue [100-102]. As a consensus of these studies, it can be said the general mechanism for spacing selection in lamellar eutectic growth is the motion of trijunction. Another point which was stated that the movement and interaction of fault lines are a competitive selection process in a way that the subgrains with lamellar spacings closest to the optimum would be the one selected [101].

1.2 Ternary Alloy Solidification

As it is given in the previous section, the binary eutectic solidification has been studied widely. However, the extension of this knowledge to ternary alloy solidification is limited. The
common trend for study of the ternary solidification is studying the ternary invariant solidification. During this extension, the effect of addition of the third element firstly shows itself in the more complex structure of the phase diagram. An example of a ternary eutectic phase diagram is given in Figure 7. The additional degree of freedom shows itself as turning equilibrium points to lines and lines to surfaces. In a simple diagram as the one given in Figure 7, univariant equilibrium lines from binary eutectic invariants meet at the ternary eutectic invariant point, where now 4 phases are in equilibrium. Due to complexity of the ternary eutectic phase diagrams, a general trend for determination phase equilibria is examining isothermal sections. Figure 8 shows the isothermal section of the ternary eutectic system Al-Cu-Ag at three different temperature below, at, and above ternary eutectic point.

In a ternary eutectic system, the possible phases and morphologies are far more complex than those can be formed in binary eutectic diagrams. However just as in determination of coupled zone in binary eutectics, it is possible to determine the microstructure, which can be described by phases, phase morphologies, distributions, arrangements, topology, and texture of the solidified material, by considering the solidification conditions and the thermophysical properties of the alloys.

1.2.1 Phase and morphology selection

The thermodynamics reflected in phase equilibria are not enough to answering previously stated question of phase and morphology selection due to importance of kinetics in determining the microstructure during solidification. In order to study the effect of both together, phase and microstructure selection maps have been widely used, which have generally been constructed using competitive growth models [5-8, 10, 12, 15, 22, 38, 103-105].
Competitive growth models normally accept extremum condition, which can be briefly defined as the selection of the phase and/or morphology, which has the highest interface temperature or the fastest growth kinetics. The origin and use of extremum growth criterion will be detailed below.

The first extensive study on microstructure selection of ternary eutectic systems was conducted by McCartney et al. [6]. As indicated in the general approach, they first determined the possible morphologies which could be observed: single phase planar and dendritic growth, two phase planar, cellular, and dendritic growth, and finally three phase eutectic growth (Figure 9). By extending the competitive growth conditions of binary systems to determine the growth velocity and thermal gradient dependence of binary and ternary eutectic ranges, the limits of the regions of different morphologies were predicted. They then tested their predictions experimentally and confirmed the existence of all predicted regions and at least a qualitative agreement as to the limits of said regions [7].

The same kind of analysis has also been applied for different alloy systems and growth conditions [8, 10, 11, 106]. By introducing interface response functions, which are the functions determining interface temperature as a function of composition, phases, growth velocity and temperature gradient, interface temperature on various conditions for all possible phases and morphologies have been calculated and by use of extremum criterion, maps are calculated.

**1.2.2 Ternary invariant eutectic growth model**

The studies on ternary eutectic morphologies were started with classification of morphologies. There have also been efforts to measure microstructural parameters aimed at a
better understanding of their complex evolution. Many of these studies [107-115] revealed that the ternary eutectic structures obey the scaling law, $\lambda^2 V = (K_R/K_C)$, presented by JH for binary eutectic previously [90]. This agreement of experimental results with the extremum criterion lead to the extension of the JH analysis [90] to TE systems. Delamore and Hill computed the solute redistribution by following JH and using the lamellar Pb-Sn-Cd eutectic [116]. They reached the conclusion that the solute distribution ahead of the lamellae can be asymmetrical with respect to the S/L interface, which can explain the occurrence of irregular phase boundaries.

Almost twenty years after that, Himemiya and Umeda [13, 14] studied mutual relationships among solidification front undercooling, eutectic spacing, and growth rate and expressed the analytical growth equations in terms of material properties for three different morphologies: lamellar, rod+hexagon, and semi-regular brick type (Figure 10). These are the simplified form of the morphologies observed experimentally. By following JH, they calculated the undercooling and extremum spacings for different velocities and applied their model to Sn-Pb-Cd and Al-Cu-Ag alloy systems.

The basic assumptions of this analysis are same with those of JH analysis [90]. Due to the local equilibrium at the interface, the total undercooling was given by the solutal undercooling and capillarity undercooling. For the calculation of solutal undercooling the interface assumed to be planar, so that the only curvature of the solid phase/ liquid interface was a result of capillarity. The problem was chosen to be a steady-state by accepting constant growth velocity for the growth of the solid phases. In addition to this, kinetic undercooling and the interaction between two solutes were ignored.
The difference between these three different growth modes changes the domain of the diffusion equation (Figure 12) and in result formulation of diffusion problem. In lamellar morphology, since each phase can be considered as thin films, diffusion is only considered along x- and z-directions. The relationship between lamellar spacing, \( \lambda \), and the phase fractions, given below determines the domain as \( 0 \leq x < S_\alpha + S_\beta + S_\gamma \) and \( 0 \leq z < \infty \), where \( S_\alpha \) and \( S_\gamma \) half width of \( \alpha \)- and \( \gamma \)- phases, and \( S_\beta \) is the width of one \( \beta \)-phase.

\[
2S_\alpha / \lambda = f_\alpha \tag{17}
\]

\[
2S_\beta / \lambda = f_\beta \tag{18}
\]

\[
2S_\gamma / \lambda = f_\gamma \tag{19}
\]

For rod+hexagon structure, where the phase fractions are connected with radius of the phases, the hexagon area was approximated by the circle

\[
\pi r_\alpha^2 = \frac{\sqrt{3}}{2} \lambda^2 \tag{20}
\]

The third case of the considered growth modes was semi-regular brick, in which \( \alpha \)- phases have thin film shapes, like phases in lamellar growth mode, and between \( \alpha \)-phases, \( \beta \)- and \( \gamma \)- phases form a lamellar structure. Due to the two-dimensional periodicity of this structure, the domain of the diffusion problem is three dimensional. The volume fraction of each phase are given as

\[
\frac{2S_\alpha}{\lambda_1} = f_\alpha, \tag{21}
\]

\[
\frac{2S_\beta}{\lambda_2} = \frac{f_\beta}{1-f_\alpha}, \tag{22}
\]

\[
\frac{2S_\gamma}{\lambda_2} = \frac{f_\gamma}{1-f_\alpha}. \tag{23}
\]

For all geometries the undercooling equation is expressed the same way in JH analysis. The difference is appeared in the material constants, since three phases are considered in this
case. Although, the relationship between growth velocity, characteristic spacing(s), and undercooling are subject to the limitations of constraining the geometry to three simple structures, the analytical model showed reasonable agreement with the experimental results for Al-Cu-Ag system. However, when the improvement in JH analysis with modifications considered, it is obvious that this model also ignores many important aspects of the eutectic solidification, such stability, operating point selection, and morphology selection [117].

1.2.3 Univariant growth

Univariant growth takes place along the tie-line combining the binary eutectic point and ternary eutectic point. Along this line, the liquid is in equilibrium between two solid phases as shown in a liquidus projection of Al-rich corner of Al-Cu-Si ternary eutectic diagram given in Figure 11 [118]. In contrast to the invariant reaction observed in the phase diagram, the eutectic solidification taking place at compositions along the tie line is univariant. At compositions on this line, it is possible to observe binary eutectic structures or two-phase eutectic cells. The morphology is decided by the stability of the solid liquid interface, which will be detailed below. However, before we move to interface stability, it is necessary to differentiate between transients of an advancing solid/liquid interface.

1.2.3.1 Transients in an advancing interface

As a common practice of directional solidification experiments, the melt stays at rest prior to start of growth and under the absence of radial convection the solid/liquid interface is planar. When the growth starts by pulling, the temperature at the position of interface decreases causing the front moves backward relative to the temperature gradient. To maintain local
thermodynamic equilibrium the solidification starts interface rejecting solute to the liquid and bringing the liquid at the interface to the composition at equilibrium with solid at the solidification temperature. The length along which sample needs to move until reaching equilibrium composition is called initial transient length. The first analytic calculations of initial transient was employed by Tiller et.al. [119] by considering the composition of solid as a function of growth distance as

\[
C_S = \frac{1}{2} C_\infty \left\{ 1 + \text{erf} \left( \sqrt{\frac{V}{2D}} z \right) + \left( 2k - 1 \right) \exp \left[ -k(1-k) \frac{V}{D} z \right] \text{erfc} \left( \frac{(2k-1)\sqrt{V}z}{2} \right) \right\}
\]

where
- \( C = \text{Solute concentration} \),
- \( C_\infty = \text{Alloy composition} \),
- \( k = \text{Partition coefficient} \),
- \( V = \text{Growth velocity of the interface} \),
- \( D = \text{Solute diffusion coefficient} \),
- \( z = \text{Interface position} \).

Later by Smith et.al [120] this was improved by considering time-dependent solution of the diffusion equation as

\[
C_S = \frac{1}{2} C_\infty \left\{ 1 + \text{erf} \left( \sqrt{\frac{V}{2D}} z \right) + (2k - 1)\exp \left[ -k(1-k) \frac{V}{D} z \right] \text{erfc} \left( \frac{(2k-1)\sqrt{V}z}{2} \right) \right\}
\]

After the solidification proceeds for a while, the steady-state growth starts [120]. At this stage the solid/liquid front advances at a constant rate, which mostly taken equal to the pulling velocity, and the solid composition becomes constant. So, the distribution of solute only takes place in liquid and forms a solute boundary layer, because of the equilibrium
dictated by phase diagram. Since the solid solidifies will be at the original alloy composition, the liquid in equilibrium with solid will be at $kC_\infty$ at the interface, where excess solute rejected into the liquid from forming solid phase. By considering diffusion as only transport mechanism, the distribution of solute during steady-state planar growth is given as

$$C = C_\infty + C_\infty \left( \frac{1-k}{k} \right) e^{-Vz/D}.$$  \hspace{1cm} (26)

A calculation of initial transient solid phase composition and steady-state solute distribution in liquid or different compositions along tie-line of Al-Cu-Ag alloy are given in Figure 12.

1.2.3.2 Interface stability

The univariant reaction does not necessarily create a different structure than its binary counterparts. If both phases grow in a non-faceted manner, the observed microstructures are either lamellar or rod-type regular eutectics [110, 121-123]. Although the growth takes place by exchange of solutes between solid phases similar to invariant binary eutectics, the third alloying element could segregate in the liquid if one of the phases has lower solubility of the ternary element, causing formation of a long range solute boundary layer. This solute boundary layer can cause an interface instability just like in two component single phase alloys [124]. Schematic representations of the steady-state instability problem was first addressed by Tiller et.al. [119] and they determined the planar interface stability by the balance between the thermal gradient and the solute boundary layer in front of the interface. The onset of instability is assumed to occur when the equilibrium temperature of the liquid decreases below the temperature dictated by thermal gradient at the interface. When this combined the steady-state distribution the critical growth velocity at which the planar interface destabilizes can be written
in terms of thermal gradient \( G \), liquidus slope \( m \), initial composition \( C_0 \), diffusion coefficient \( D \), and partition coefficient \( k \) \cite{111}:

\[
V_C = \frac{GD}{mC_0(1-k)}
\]  

\( (27) \)

The constitutional supercooling criterion is not a complete analysis of interfacial stability because it only considers diffusional effects and the thermal gradient in the liquid but it ignores the thermal gradient in the solid, the latent heat of fusion, and the stability of the solid/liquid interface energy. In order to fill those gaps, Mullins-Sekerka offered a linear perturbation analysis \cite{125}. They first perturbed interfaces and described the mathematical conditions for the growth of this perturbation. Their calculation took into account both thermal gradients in liquid and solid and the latent heat of fusion. By their perturbation analysis, the instability wavelength of a steady-state planar interface could be predicted.

Although all the stability analysis methods mentioned above were first formulated for single phase alloys, they can be extended to the two phase structure. Gruzleski and Winegard did such an analysis to Sn-Cd binary system by adding Pb as impurity and used Tiller’s constitutional supercooling criterion to determine the interface breakdown velocity and composition \cite{126}. In their papers on microstructure selection maps, McCartney et al. extended JH analysis to univariant alloys in order to determine the planar growth limit by using the constitutional undercooling criterion \cite{6, 7}. By adopting the parameters to the univariant alloy, i.e., words by using slope of the univariant groove instead of liquidus slope, and phase fraction weighted equilibrium partition coefficient with respect to the third component as partition coefficient, the constitutional supercooling criterion given in Eq. 25 can be used. At this point, it should be stated that the composition of the phases at the solid/liquid interface is calculated by tie triangle at which the composition of the alloy is equal to that of the liquid \cite{22}. An
example is given for the alloys on the univariant groove connecting Al-Al$_2$Cu eutectic and ternary eutectic points of Al-Cu-Ag in Figure 13. Mullins-Sekerka’s perturbation analysis can also be applied to univariant alloys by using the weight fraction averaged properties for solid phases to treat them as a single solid. All of these stability analysis assumes steady-state growth. In addition to these, there are other analysis examining the instabilities during initial transient [127, 128].

1.2.3.3 Coupled growth

The recent effort on coupled growth in univariant alloys has been focused on investigation of the morphological pattern and the stability limit of the planar interface [129], thermodynamics and microstructure simulation [130], and the breakdown of the planar interface and cellular coupled growth and the characterization of the two-phase cells [131]. The studies on the morphology of the coupled growth, mostly focused on Al-Cu-Ag system, showed little difference than the binary Al-Cu eutectic alloy [129]. The structure consists of eutectic grains with a lamellar structure, the order of which is decreasing with decreasing velocity and increasing Ag content. A more fragmented lamellar structure with Ag contents suggests two different types of stability. The scaling law $\lambda^2 V = \frac{K_R}{K_C}$ has been verified and Ag has not been found to have an effect on eutectic spacing. On the other hand, due to segregation of Ag, competitive growth between different morphologies was observed. Also, an analytical approach for the binary coupled growth in ternary systems with lamellar structure has been presented [132] with the assumption that, at slow steady-state growth, the alloy composition will stay along the univariant line; this analysis showed good agreement with experimental results.
The cellular structure formed along the univariant path was also examined in the Al-Cu-Ag system. Two types of cells are differentiated; one being elongated and the precursor to the second type, which is radial. These two types of cells can be found in different grains of [131]. Also, these two different types of cells have different definite crystallographic orientations between the Al(fcc) and Al$_2$Cu phases, and the symmetry of the crystallography determines the cell structure. The onset of cellular structure formation has also been found to be related to the topologic order of the grains.

1.2.3.4 Effect of convection

One of the major objectives of the microgravity solidification studies is to understand the effects gravity-driven phenomena on solidification. The mass and heat transport during solidification can be influenced by the force of gravity due to buoyancy-driven convection, Stokes’ flow and hydrostatic pressure [133, 134]. This buoyancy stems from the difference in density between the components of liquid. This density can be a factor of thermal and/or solutal effects. The thermal buoyancy can be negated by orienting directional growth antiparallel to the gravity, since the less dense fluid will then float over the colder one which at the solid/liquid interface. Although there are contradictory reports in the literature on the effect of convection on coupled growth [135-144], due to very limited solute boundary layer, regular binary eutectics are not much affected from the effect of convection.

On the other hand, for off-eutectic alloys according to density of the primary phase the segregation or floatation is possible as a result of convectional effects [21]. The effect of fluid flow on off-eutectic alloys can also result in deviation of liquid composition at the interface from the equilibrium value. According to density difference between solute and liquid radial
or axial segregation could be observed [145]. Whenever the rejected solute is less than the liquid solutal convection will take place and affect purely diffusive solute boundary layer and cause axil segregation. On the other hand, the higher density solute change in the morphology of solid/liquid interface changes like from regular to dendritic or fibrous as a consequence of fluid flow [145]. With the presence of a ternary element, the solute boundary layer gets longer and possibility of being subjected to convectional effects is increased. The same results obtained for the off-eutectic alloys can be applied to univariant alloy form the aspect of the solute in the long-range solute boundary layer. However, no comprehensive report is present on this area.

1.3 Scope and Objectives

The present research is primarily concerned with microstructural evolution and interface dynamics in invariant and univariant eutectics in Al-Cu-Ag system. The major area of focus are summarized below by listing the principal questions considered, each with a description of some of the major issues involved.

What microstructural changes takes place in the solid-state behind the solidification front, and can we quantify/account for these?

A general method for understanding the evolution of microstructure in metallic materials is ex-situ examination of microstructures and correlation of the microstructural features with the conditions form these. However, the phase transformations taking place after solidification could obscure many aspects of the solidification morphology present at the growth front. So,
quantification of post-solidification effect is necessary for proper interpretation of the microstructures.

What can be defined as a descriptor of morphology in these complex microstructures?

The research on ternary invariant eutectic structures has been proceeded by considering them as an extension of binary eutectics. Although, this is a valid approach till a point, with regard to quantification and parameterization, the stereological methods used and the parameters chosen to define microstructure is not resembling overall properties of these complex structure with different periodicities. In order to improve our understanding by accepting further challenges on invariant ternary eutectic growth, firstly the problem of description of the microstructure should be overcome.

What microstructural features could be used to distinguishing different growth modes in ternary eutectic structure?

Although, there are many attempts on characterizing the ternary eutectic microstructures according to their morphology, it is still not possible to say that there is a complete consensus on selection of microstructural features. This is mostly related to the fact that the offered parameters are specific to the set of microstructures and are not general enough to be applicable to large variety of microstructures that can form. So, new generalized parameters for distinguishing between different morphologies are immediately needed.

What is reasoning and mechanism of morphology change with increased velocity in different ternary eutectic invariant systems?

In several ternary eutectic system, a change in morphology with changing growth velocity has been observed. The explanations of change in morphology in different systems are again system based and cannot be generalized to understand the dynamics causing this
morphological change. The present ternary eutectic growth models also does not explain this changes due to very simple geometries chosen and disregarded dynamics taking place during growth. So, ternary invariant eutectic microstructures grown at different velocities should be characterized in detail and reasoning for the morphology change should be based on the parameters which are changing with the morphology.

*What is the effect of radial thermal gradient induced natural convection on solutal configuration in liquid ahead of interface?*

The solutal boundary layer thickness in univariant alloys has been used to determine the transients in the vertical directional growth of univariant alloys against gravity by models considering purely diffusive flow. However, the radial thermal gradient has been shown to disturb the diffusive solute boundary layer by causing natural convection. So, in order to differentiate the effect of convection and determine transients correctly, the effect of radial thermal gradient should be clarified in a standard vertical directional solidification experiment. The effect of the direction of the gravity vector was also investigated.

*How does grain selection proceed, and what is the transient length for this selection process?*

Single grain production or in other words, choosing a definite texture is required for most of the advanced applications due to anisotropic reply of material to an external stimuli. One of the most widely used method for production of single phase material is directional growth from an alloy melt which is especially intensively used for single phase materials. However, the control over texture in multiphase much more limited and even the kinetics, which can answer
the questions necessary growth length to obtain single grain under different growth conditions is still unknown.

*What is the role of topological order on grain selection?*

Grain competition during eutectic solidification has been reported since early 1960s, even before the declaration of formal eutectic theory. Preferred grains were suggested to be the floating ones which can adjust themselves along the thermal gradient, and hence having the smallest projected spacing. However, another effective characteristic, topological order, which has suggested as a factor qualitatively multiple times, was never attempted to be quantified in order to understand its true effect.

*What is the effect of grain boundary configuration on grain selection kinetics?*

In single phase materials it has been explained lately that the orientation of two dendrites with respect to each other is an important criterion for the growth rate of one at the expense of the other. In binary eutectics where the many different boundary types and configurations are possible, the effect of grain boundaries are not revealed. This is important especially for the cases where growth from a single grain seed is not possible.

*What are the effects of the pre-growth holding period during directional growth of eutectics?*

The fundamental knowledge on formation of single-phase layers during stationary hold prior to directional growth of eutectics are limited two-phase thin transparent alloys which were examined in a thin slab geometry. Although, similar layers were observed to form in bulk metallic samples, a systematic study on characteristics of these layers is lacking. The characterization of these layers based on different experimental conditions are needed since they are effective on early stage dynamics of eutectic growth. Furthermore, pre-growth phenomena in ternary alloys may involve the formation of single-phase and/or two-phase layers.
1.4 Approach

In order to address the questions given in the goals and objective section, we employ a gradient stage directional solidification technique to produce univariant and invariant coupled growth scenarios over a range of growth conditions, several alloy compositions were used within the Al-Cu-Ag system. Coupled growth structures were analyzed using optical and electron-beam imaging, electron-beam microchemical analysis, and computer-aided image analysis schemes. Details of these are given below.

1.4.1 Preparation of test alloys for directional solidification

This study employed test samples from the TE Al-Cu-Ag system we will focus focusing on the portion of the phase diagram highlighted in Figure 14 below consisting of binary eutectic Al-Al₂Cu, the ternary eutectic point, and the monovariant line connecting them. The binary eutectic forms as a result of the reaction

\[ \text{L}(\text{Al} - 17.2 \text{ at}\% \text{Cu}) \rightarrow \alpha(\text{Al} - 3.7 \text{ at}\% \text{Cu}) + \theta(\text{Al} - 33.1 \text{ at}\% \text{Cu}) \]

Along the tie-line connecting the binary eutectic point to the ternary eutectic point, binary eutectic structure with three component forms as a result of solidification. The phases present in the univariant alloy are identical to those in the binary invariant reaction. The composition that we chose for univariant alloy was Al-16.55 at\%Cu-2.82at\%Ag. Finally, the ternary eutectic structures consisting of Al(fcc) (\(\alpha\)), Al₂Cu (\(\theta\)), and Ag₂Al (\(\gamma\)) are formed following the reaction

\[ \text{L}(\text{Al} - 12.8 \text{ at}\% \text{Cu} - 18.1 \text{ at}\% \text{Ag}) \rightarrow \alpha(\text{Al} - 4.51 \text{ at}\% \text{Cu} - 18.33 \text{ at}\% \text{Ag}) + \theta(\text{Al} - 32.29 \text{ at}\% \text{Cu} - 0.04 \text{ at}\% \text{Ag}) + \gamma(\text{Al} - 2.94 \text{ at}\% \text{Cu} - 58.46 \text{ at}\% \text{Ag}). \]
Test alloys were fabricated by melting high-purity elements (99.999 wt. % Al, 99.999 wt. % Cu, and 99.999 wt. % Ag) in a boron-nitride-coated (BNC) clay crucible in air and then cast in a BNC steel mold into rods of 5mm diameter and 260 mm length. In order to minimize impurities, the surface of the rods were lightly ground with SiC paper and cleaned with ethanol. The rods were then placed inside an alumina crucible with a 5.5 mm inner diameter and an 8 mm outer diameter for directional solidification experiments.

1.4.2 Directional Solidification

The alloys were pulled with different velocities through a thermal gradient anti-parallel to the gravity to decrease effect of convection. A schematic of gradient-stage furnace and thermal gradient are shown in Figure 15. Different growth conditions were employed for different alloys. However, in a general sense, the velocities employed were in the range of 0.0002 to 0.020 mm/s, and thermal gradients were 6 to 9 K/mm. No change in thermal gradients with velocity was observed and thermal gradient was varied by different furnace set temperatures. To quench, samples were plunged into a water-cooled bath containing Ga-In-Sn.

In order to examine the effect of tube diameter on interface stability in univariant growth, we have made several different thin tube experiments in which the tube diameters were varied between 1 mm to 0.8 mm. Furthermore, to investigate the effect of direction of gravity experiments with inverted configuration, growth parallel to the gravity, was conducted again with univariant composition.
1.4.3 Analysis of coupled growth structures

In order to examine the solidification structures, the samples were sectioned at different growth distance and with different increments. The imaging of the samples were imaged either with scanning electron microscopy or optical microscopy. The scanning electron microscopy was preferred for ternary alloys due to high back scatter contrast differences between phases, whereas optical microscopy was used for examination of longitudinal sections and also binary eutectic samples.

Different analyses were conducted on samples; however, stereology measurements can be classified into two major categories. Firstly, area measurements were done included the area and perimeter of each particle, as well as the major and minor axis caliper lengths for each particle Figure 16a. Secondly, line measurements were done using a centered radial pattern of eighteen evenly spaced lines (Figure 16b) and recording the length of each particle, δ, and the length between particles of the same phase from midpoint to midpoint, λ, on each line Figure 16. The measurements were averaged across all images of each respective velocity.

In addition to the stereology analysis detailed above, Fast Fourier Transform (FFT) patterns obtained from images were used to characterize topological features. By quantification of FFT patterns, radial and angular order distribution plots were obtained and two different order parameters were defined: radial and angular. The radial order parameter, $S_R \Phi$, quantifies the periodicity of each phase, whereas angular order, $S_A \Phi$, quantifies the orientation characteristics of the phases. Both parameters were calculated as peak intensity over half-maximum width for the peaks present in the distribution plots. In addition to these, by written image analysis scripts, boundary lengths, fractions, and orientations were measured.
1.5 Dissertation Organization

This dissertation is written in an alternate format based on five original manuscripts, subsequent to a general introduction. References cited in each manuscript are placed immediately after the manuscripts.

The first manuscript in Chapter 2, “Post-solidification effects on directionally solidified Al-Cu-Ag eutectics” was submitted to the Journal of Phase Equilibria and Diffusion and is currently in review. The changes in the microstructure as a result of solid-state phase transformation after solidification are quantified and compared to the coupled morphology at the solidification front. A cellular automaton method is proposed here to mimic either the forward or reverse solid-state changes, providing a means to estimate many features of the directional growth morphology based on sampling the structure at some known distance from the front.

The second manuscript in Chapter 3, is “Quantitative analysis of directionally solidified eutectic Al-Cu-Ag alloy”. A subjective set up of parameters to quantify these complex microstructure are introduced and suggested to be used for distinguishing different morphologies. The change in morphology with increasing velocity is explained by considering phase and morphology selection based on undercooling calculations, diffusion cell triangles, and spacing correlation as a scaling optimization process.

The third manuscript in Chapter 4 is “The effect of convection on solutal configuration during univariant eutectic growth in Al-Cu-Ag system”. The effect of radial gradient induced natural convection on the solutal profile and morphology is examined and shown to be effective on altering the solutal configuration and in result formed structures, and growth morphology. Also, increased convection by changing pulling direction from anti-parallel to
parallel (with respect to gravity) was shown to delay the transition to a cellular front, overcome radial gradient and homogenize the front composition, whereas smaller sample size was not completely effective for the latter during vertical growth in the anti-parallel configuration.

The fourth manuscript in Chapter 5 is “Eutectic grain competition in a directionally solidified binary Al-Cu alloy”. The kinetics of grain selection are investigated here, taking growth distance as the main parameter. In addition to this, a better understanding of microstructure evolution in directionally solidified eutectic alloys is achieved by explanation of mutual relationship between interlamellar spacing, order and growth distance and their overall effect on grain selection.

The fifth manuscript in Chapter 6 is “Effects of the pre-growth holding period during directional solidification of eutectics”. The single-phase layers formed at different growth conditions with different alloy compositions are characterized with respect to thickness and content. The composition of the single-phase layer was observed to be only dependent on alloy composition, whereas morphology and thickness were found to be dependent on composition, holding period, pre-growth velocity, and thermal gradient. The processes forming single phase layers are explained and shown to vary in the presence two different solutes, although for both cases, one or two types of solutes, the processes are controlled by dynamics of solute boundary layer

In Chapter 7, a brief summary is provided, describing the connection between the different parts of the study, summarizing the overall contributions, and highlighting areas for further investigation.
References


K.A. Jackson, J.D. Hunt. Lamellar and rod eutectic growth, Transactions of the Metallurgical Society of AIME 236 (1966) 1129-.


Table 1. Classification of eutectics according to different criteria

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Possibilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth Mechanism</td>
<td>Coupled, divorced, symbiotic</td>
</tr>
<tr>
<td>Stability of solid/liquid interface</td>
<td>Planar, Cellular, Dendritic</td>
</tr>
<tr>
<td>Interface Structure</td>
<td>Faceted, Non-faceted</td>
</tr>
<tr>
<td></td>
<td>Regular, Irregular</td>
</tr>
</tbody>
</table>
Figure 1. Typical microstructures observed in a) Binary Al-Cu eutectic, b) Ternary Al-Cu-Ag eutectic structures showing three scale of features as grains, subgrains, and eutectic mixtures.

Figure 2. Schematic binary eutectic phase diagrams illustrating a) Symmetrical and b) Skewed coupled zones [77].
Figure 3. Schematic representation of (a) Lamellar, and (b) Rod-like eutectic as given in JH. In the rod eutectic the $z$-direction is out of the page [90].

Figure 4. Optimization of the eutectic spacing. Minimum undercooling for directional solidification and maximum growth for constant undercooling [64].
Figure 5. Schematic representation of stable and unstable spacing according to JH analysis [90].

Figure 6. Eutectic spacing distribution curves of Pb-Pd eutectic at growth velocities [96].
Figure 7. Simple ternary eutectic phase diagram [146].

Figure 8. Isothermal sections of ternary eutectic Al-Cu-Ag system a) Above, b) At, c) Below eutectic temperature.
Figure 9. a) Schematic phase and morphology stability regions and b) Microstructures as suggested by McCartney et.al. according to minimum undercooling criterion. 1: single phase with planar interface; 2: Two component eutectic with planar interface; 3: three component eutectic cell or dendrites; 4: three phase eutectic; 5: single phase cells or dendrites. A: two phase eutectic, b:two phase cells and ternary eutectic; c: three phase eutectic; d: single phase cells and ternary eutectic; e:single phase cells, two phase cells, and ternary eutectic; f: single phase cells and ternary eutectic [6].

Figure 10. The growth models proposed by Himemiya and Umeda. Left: lamellar, middle: rod-hexagon, and right: semi-regular brick [13, 14].
Figure 11. Liquidus projection in Al-rich corner of Al-Cu-Si system [118]

Figure 12. a) The initial transient and b) Steady-state profiles of different alloys on univariant groove at $v=0.0015$ mm/s.
Figure 13. Tie triangle of the Al-16.55at%Cu-2.82 at%Ag alloy composition on eutectic groove in Al-Cu-Ag system.

Figure 14. Projection of the liquidus surface of ternary eutectic Al-Cu-Ag at eutectic temperature (adapted from [22]).
**Figure 15.** The directional solidification unit a) Schematic of the furnace, b) Thermal gradient profile in the furnace during pulling.

**Figure 16.** Schematic representations of microstructure measurements a) Area measurements: area and perimeter (L); caliper length and width (W); b) Line measurements: delta ($\delta$); lambda ($\lambda$).
Figure 17. Schematic drawing of line intercept method with centered and evenly spaced radial lines shown on an ideal one lamellar and two fibrous phase morphology.
CHAPTER 2. POST-SOLIDIFICATION EFFECTS IN DIRECTIONALLY SOLIDIFIED AL-CU-AG EUTECTICS

A paper submitted to the Journal of Phase Equilibria and Diffusion

Irmak Sargin, A. L. Genau, and R. E. Napolitano

Abstract

The post-solidification reactions that take place behind the growth front in directionally solidified ternary eutectic Al-Cu-Ag alloys have a marked influence on the observed room temperature microstructure, obscuring many aspects of the solidification morphology present at the growth front. Quantifying these solid-state processes is necessary for proper interpretation of ex-situ microstructure as an indicator of growth dynamics and operating point selection. In this study, the directional growth structure and phase compositions are quantified as a function of distance from the quenched interface to describe microstructural changes that occur during cooling in the solid state behind the growth front. The solubility of Ag in the Al(fcc) phase decreases rapidly below the eutectic point, and the excess Ag is accommodated by growth of the Ag\textsubscript{2}Al phase, mainly by motion of the Al(fcc)-Ag\textsubscript{2}Al interface. These structural changes are quantified, and compared to the coupled morphology at the solidification front. A cellular automaton method is proposed here to mimic either the forward or reverse solid-state changes, providing a means to estimate many features of the directional growth morphology based on sampling the structure at some known distance from the front.

2.1 Introduction

Periodic multi-phase structures offer great promise toward realizing new functionality in materials, where unusual optical, electrical, magnetic, and mechanical properties may arise
from the interplay between various elements of multi-scale hierarchy. Beyond the properties offered by conventional multiphase composite structures, examples of remarkable behavior such as artificial magnetism, negative refraction, and optical cloaking have been reported for the class of hierarchical multiphase structures known as metamaterials [1-3]. Such discoveries and advancements place new value on understanding and controlling various types of multiphase growth, including solidification from the melt.

The understanding of two-phase coupled solidification is reasonably well developed, based largely on the Jackson-Hunt [4] analysis, where both rod and lamellar morphologies are treated explicitly and where the structure is defined by a single characteristic length that provides an operational descriptor of both solid-liquid interface curvature and diffusion length. Modifications of the general approach have been shown be useful for describing the basic scaling behavior for irregular eutectics and other symmetry-breaking structures where the geometry and interfacial properties do not permit such a simple one-parameter description of the structure [5-8]. In addition, operating point selection during eutectic growth has also been shown to depend on the properties of the solid phase boundaries and the orientation between the solid phases, giving rise to "floating" or "locked" boundary behaviors [8-12]. For the case of coupled growth structures involving three phases and multiple possible geometries with more complexity, even the simple characterization of diffusional and capillary related contributions becomes more challenging. Considering these issues, Himemiya and Umeda (HU) extended the Jackson-Hunt analysis to three-phase coupled growth by assuming three simple geometries [13-15], permitting analytical solution of the diffusion field and, with a suitable operating point selection criterion, prediction of the expected scaling behavior (V-C-
T relationship). Of course, these predictions are subject to the limitations of constraining the geometry to three simple structures.

Assessing the validity and utility of the HU treatment (or any other model) requires careful and systematic comparison with experiment. The method of gradient-stage directional solidification provides a means for carefully controlling the growth conditions [15-17], but quantification of morphological response requires ex-situ sampling and analysis of the microstructure. The Al-Ag-Cu ternary system provides an excellent test alloy for examining critically the HU extension of the Jackson-Hunt analysis, with three non-faceted phases, a relatively low eutectic point, low reactivity with air, and well described binary and ternary thermodynamics [18-20]. Indeed, reports of several different growth morphologies have been reported for this system [20-23], with the most notable structure being the "semi-regular brick" (SRB) structure, which is one of the structures included in the HU analysis. The SRB structure has been observed to be dominant in the Al-Cu-Ag eutectic at velocities below approximately 0.001 mm/s [22]. However, the solid-state reactions that occur upon cooling below the eutectic [22] serve to obscure the solidification morphology, making systematic investigation difficult. We address this issue here by examining the nature of these reactions, quantifying the characteristic microstructural features, and offering a means to estimate the expected morphological changes.

2.2 Experiments

Experiments include gradient-stage directional solidification of Al-Cu-Ag alloys of eutectic composition (Al-12.8 at%Cu-18.1 at%Ag) and characterization of coupled growth structures arising from a range of growth conditions. Specimens were fabricated by casting the
test alloy into 5 mm diameter rods using a steel mold coated with boron nitride. For directional solidification, specimens were placed in an alumina crucible with a 5.5 mm inner diameter and an 8 mm outer diameter. After a 1-hour melting/holding period in a stationary gradient of about 6 K/mm in solid and 11 K/mm in liquid, specimens were solidified by translating the gradient field at a selected pulling velocity ($V_p$) over a distance of 80 to 100 mm. The growth period was followed immediately by a quench step, involving rapid translation ($V_p = 20$ mm/s) into a water-cooled liquid-metal bath (Ga-In-Sn). Selected pulling velocities include 0.0002, 0.0005, 0.001, 0.002, 0.004, and 0.008 mm/s.

All experiments produced a three-phase coupled growth structure, comprised of the Al(fcc), Ag$_2$Al, and Al$_2$Cu phases, as shown in (Figure 18). The dominant morphology observed for velocities up to 0.002 mm/s is known as the 'semi-regular brick' (SRB) structure [13, 14] consisting of two fibrous phases and one lamellar phase [24, 25]. Other less ordered structures are observed in the early stages of the directional growth sequence, but these are extinguished by the dominant structure during a grain selection transient, occurring nominally over the first 40-50 mm of growth, beyond which only a small number of favorably oriented grains persist. At velocities greater than 0.002 mm/s, less regular three-phase structures are favored, and the SRB structure is not observed.

The effects of solid-state processes operating behind the growth front are clearly evident in Figure 19, showing how the three-phase morphology varies with distance from the quench, for $V_p = 0.001$ mm/s. Figure 19 also reveals a significant variation in phase composition with distance from the growth front. Owing to an increased Ag content, the Al(fcc) phase appears in light gray contrast at the growth front, becoming increasingly dark with axial
distance. The variation in average composition of the Al(fcc) phase was measured using EDS analysis, as shown in (Figure 20a).

To examine the change in structure behind the growth front, the microstructure was analyzed on a series of transverse sections taken at 5 mm increments, using a total of 20 images (0.2 μm resolution) at each axial location. Several parameters related to features of isolated phase regions (on each test plane) were measured, including area, perimeter, and major/minor caliper lengths. Corresponding average phase fractions and caliper lengths are plotted in Figure 21.

Several microstructural measurements were made using a randomly placed test-line pattern. A radial test-line pattern was used, consisting of eighteen line segments of equal length, arranged in 10 degree increments, mutually bisecting each other at their midpoints with a uniform angular distribution. The parameters measured include internal chord length (δ), defined here as the length of line segment that lies within a given phase region or particle, and phase spacing (λ), defined here as the distance along a sampling line between midpoints of chords through consecutive particles of a particular phase. Local average values of λ and δ were measured and averaged broadly over all test lines on all 20 images for each axial location, as plotted in Figure 22. Finally, the total phase boundary lengths and boundary length fractions were measured for each of the three two-phase interface types. These structural measurements are summarized in Figure 23 and Figure 24.

2.3 Analysis and Discussion

Inspection of Figure 18-Figure 24 reveals that the effects of post-solidification reactions give rise to dramatic structural and compositional variation over the region within approximately 15 mm of the growth front, corresponding roughly to the temperature range within 90 K of the eutectic temperature of 773.4 K, based on the thermal gradient of 6 K/mm.
Examining this variation more closely, we compare in (Figure 19) the measured axial profile of local compositions in the Al(fcc) phase with the compositions given by the equilibrium tie-triangles associated with the local temperatures along the axial profile at the time of quenching. The comparison clearly shows that the composition of the Al(fcc) phase follows the equilibrium solvus curve during cooling. Over the same axial range, the Al(fcc) phase fraction decreases dramatically, while the fraction of the Ag₂Al phase increases, as shown in Figure 21a. These two observations together indicate that a precipitation process is occurring during cooling, with the Ag₂Al phase growing at the expense of the Al(fcc) phase.

Lateral composition profiles across phase boundaries are shown in Figure 25. All of the measured profiles exhibit sharp variation between equilibrium values, with no detectable evidence of composition profiles that would accompany diffusion-limited growth. We conclude that, for the low velocity investigated here, the solid state reactions that control structural changes, while certainly diffusional, are not diffusion-limited in a practical sense. Accordingly, the observed phase compositions correspond roughly with the equilibrium values associated with the local temperature at the time of quench, and the general variation in phase fractions follows the equilibrium temperature dependence, as shown in Figure 20.

Considering the nature of the solid-state reactions and the structural effects clearly evident in Figure 18, we now revisit the microstructure measurements. Figure 21b shows that the major caliper length for Ag₂Al increases significantly over the first 5 mm behind the quenched interface while its phase fraction increases. Over this same axial distance, the phase fraction and minor caliper length of Al(fcc) both decrease. These are consistent with Figure 20, which reveals that the Ag₂Al phase tends to lengthen into the Al(fcc) phase, developing a 'dog-bone' type of morphology. We expect that the solid-state changes are influenced to some
degree by phase crystallographic orientation relationships between the three phases. Our observations are limited to two strongly selected (favorable) phase orientations, and two distinct types of structural changes were observed, as shown in Figure 26.

Quantitative measurements of caliper lengths, eutectic spacings, and phase fractions reveal no measurable difference between these two grains with increasing distance from the interface. A marked difference in the relative phase boundary lengths, however, was observed to develop as the solid-state reaction proceeds behind the growth front. This effect is clearly shown in Figure 23 and Figure 24, revealing that the relative boundary lengths are not only changing substantially with solid-state processes, but that the changes are different for the two grains. The important point to make here is that, while the structures at the solid-liquid interface are very similar, they evolve to become very different at locations behind the growth front. Considering the importance of the configuration of boundaries and triple-junction lines in the competition and description of operating point selection [8, 25-30], it is clear that sampling the structure at a location far from the growth front will confound interpretation with respect to solidification dynamics. This effectively constrains experimental investigation mainly to the analysis of the near-front microstructure and limits, in a practical way, the amount of information that can be obtained from a given growth experiment. To facilitate more comprehensive study, it is desirable to correlate the far-from-front structure with the near-front growth morphology. We have done this using a simple cellular automaton (CA).

The simple CA method used here is an image processing tool and is not a physical model for phase evolution. Phases are discretized (i.e. black, white, grey), and no direct consideration is given to composition, diffusion, or the energetics of phase boundaries, triple-lines, and quadrijunctions. Evolution occurs by boundary motion, with no allowance for
formation of new phase regions (i.e. nucleation). Rules for evolution in two dimensions are based on the von Neumann (4 nearest neighbors) and Moore (8 nearest neighbors) neighborhoods, as summarized in Table 2. To mimic solid-state effects behind the front, the near-front structure is treated by executing process steps until the equilibrium phase fraction is reached, associated with a given axial location and temperature. Using a reverse process, the method can be used to mimic the expected growth-front morphology from a structure measured behind the front by targeting the expected phase fractions just below the eutectic temperature. Structures produced with this way are shown in Figure 27 and compared with observed near-front images for two grains. A comparison of microstructural parameters measured from the CA-generated structure and the observed structure is provided in Table 3. A similar comparison is made in Table 4 for several growth velocities, estimating near-interface structure from microstructures sampled from an axial location 20 mm behind the growth front. The comparison between estimated structure and those observed at a distance of 2 mm from the front shows reasonable accuracy for different velocities. The major discrepancy is observed in the boundary fractions for the pulling velocity of 0.004 mm/s. This is related to the fact that the observed morphology at this velocity is different than the semi-regular brick structure with different boundary orientations. So, we can conclude, this simple method is suitable for a range of velocities where the semi-regular brick structure is observed.

**Table 2.** A summary of the rules used in the cellular automaton processing scheme.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Condition</th>
<th>Action</th>
<th>Structure Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>von Neuman</td>
<td>3 black neighbors</td>
<td>3→1</td>
<td>front</td>
</tr>
<tr>
<td></td>
<td>3 gray neighbors</td>
<td>1→3</td>
<td>beyond front</td>
</tr>
<tr>
<td>Moore</td>
<td>3 black neighbors</td>
<td>2→1</td>
<td>front</td>
</tr>
<tr>
<td></td>
<td>3 white neighbors</td>
<td>1→2</td>
<td>beyond front</td>
</tr>
</tbody>
</table>

Notes: 1= Al(fcc); 2= AgAl; 3=AlCu
Table 3. Comparison of microstructural parameters measured at quench in the real and simulated structures for Grain 1 in Figure 27 ($V_p=0.001$ mm/s).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Experimental</th>
<th>Simulated</th>
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<tbody>
<tr>
<td>Al(fcc)</td>
<td>0.52</td>
<td>0.51</td>
</tr>
<tr>
<td>Ag$_2$Al</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>Al$_2$Cu</td>
<td>0.28</td>
<td>0.29</td>
</tr>
<tr>
<td>Al(fcc)</td>
<td>30.45</td>
<td>32.61</td>
</tr>
<tr>
<td>Ag$_2$Al</td>
<td>5.94</td>
<td>5.87</td>
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<td>Al$_2$Cu</td>
<td>6.98</td>
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<td>9.81</td>
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<td>2.99</td>
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<tr>
<td>Al$_2$Cu</td>
<td>4.64</td>
<td>4.14</td>
</tr>
<tr>
<td>Al(fcc)</td>
<td>11.37</td>
<td>10.95</td>
</tr>
<tr>
<td>Ag$_2$Al</td>
<td>12.50</td>
<td>11.95</td>
</tr>
<tr>
<td>Al$_2$Cu</td>
<td>8.13</td>
<td>9.69</td>
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<td>Al(fcc)-Ag$_2$Al</td>
<td>0.19</td>
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<tr>
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<td>0.50</td>
<td>0.58</td>
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<tr>
<td>Al$_2$Cu-Al(fcc)</td>
<td>0.31</td>
<td>0.25</td>
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Table 4. Comparison of microstructural parameters measured at a location 2mm from the quench in the real and simulated structures, for different velocities.

<table>
<thead>
<tr>
<th>$v=0.0005$ mm/s</th>
<th>Phase</th>
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<th>Simulated</th>
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<tbody>
<tr>
<td>Al(fcc)</td>
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<td>0.47</td>
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</tr>
<tr>
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<td>0.30</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Al$_2$Cu</td>
<td>0.28</td>
<td>0.33</td>
<td></td>
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<tr>
<td>Al(fcc)</td>
<td>37.13</td>
<td>30.66</td>
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</tr>
<tr>
<td>Ag$_2$Al</td>
<td>8.58</td>
<td>8.12</td>
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<tr>
<td>Al$_2$Cu</td>
<td>9.74</td>
<td>9.61</td>
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Table 4 continued.

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</tr>
<tr>
<td>Al$_2$Cu</td>
<td>6.37</td>
<td>5.83</td>
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<td>Al(fcc)</td>
<td>14.70</td>
<td>12.95</td>
<td></td>
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<tr>
<td>Ag$_2$Al</td>
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<td>15.05</td>
<td></td>
</tr>
<tr>
<td>Al$_2$Cu</td>
<td>9.75</td>
<td>11.12</td>
<td></td>
</tr>
<tr>
<td>Al(fcc)-Ag$_2$Al</td>
<td>0.15</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Al-Al$_2$Cu</td>
<td>0.55</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Al$_2$Cu-Al(fcc)</td>
<td>0.31</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Al(fcc)</td>
<td>0.45</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Al</td>
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<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Al$_2$Cu</td>
<td>0.26</td>
<td>0.33</td>
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</table>
2.4 Summary and Conclusions

For directional solidification of the Al-Cu-Ag three-phase eutectic structures, solid-state reactions behind the growth front give rise to significant microstructural changes. For pulling velocities up to 0.002 mm/s, composition and phase fraction variation is reasonably described by the equilibrium solvus surface and associated tie-lines. For these low velocities, a small number of grains are selected over a transient length of approximately 50 mm, and the surviving grains exhibit a semi-regular brick morphology, for which regularity and order decrease with growth velocity. Because of the solid state effects, the growth morphology can
be effectively observed only within a few millimeters of the quenched growth front. For \( V_p=0.001 \) mm/s and \( G=6 \) K/mm, measured parameters such as phase composition, phase fraction, and relative phase boundary length exhibit substantial variation with distance from the interface, with the most dramatic changes observed over the first 15 mm. A cellular automaton was shown to be an effective tool for analyzing growth structure, enabling reasonable estimation of the structure at the growth front based on the structure measured at some known distance behind the front.

Acknowledgement

The research reported here was supported by the National Aeronautic and Space Administration (NASA), through the Marshall Space Flight Center Microgravity Research Program, under Grant Number NNX10AT61G.

References


Figure 18. Transverse (left) and longitudinal (right) sections for $V_p=0.0005$ mm/s, showing characteristic three-phase coupled solidification structures in Al-12.8at%Cu-18.1at%Ag. For the transverse view taken 25 mm being the growth front (left), the Al(fcc) phase appears black,
Al$_2$Cu appears grey, and Ag$_2$Al appears white. The contrast is different for the longitudinal view showing the solid-liquid interface, where Al(fcc) appears grey, Al$_2$Cu appears black, and Ag$_2$Al appears white, under backscattered electron contrast.

**Figure 19.** Representative images of the microstructures observed at a) Quench, b) 5 mm, and c) 10 mm from quench. At quench, grey phase is Al(fcc), and black phase is Al$_2$Cu. This was reversed at later sections. The white phase is Ag$_2$Al for all sections.
**Figure 20.** a) Average composition of the Al(fcc) phase as a function of distance from the quenched interface. b) Tie triangles of the solid phases below eutectic point, inlet shows the dependence of Ag solubility in Al(fcc) on temperature.

**Figure 21.** Variation in a) Phase fractions, and b) Caliper lengths as a function of distance from quenched interface, for \( V_p = 0.001 \) mm/s.
Figure 22. Variation in a) $\lambda$ and b) $\delta$, as a function of distance from quenched interface, for $V_p=0.001$ mm/s.
Figure 23. Variation in relative phase boundary length as a function of distance from quenched interface, for $v_p=0.001$ mm/s.
Figure 24. Fractions of boundary length (area) for each of the two-phase boundary types, a) Grain 1 and b) Grain 2. The closed symbols shows the boundary fraction at solidification front and open symbols shows the boundary fraction at 45 mm away from the interface.
Figure 25. Qualitative line analysis of different phase couples a) At the quench b) 5 mm before quench, showing uniform composition across the entire width of each phase region.
Figure 26. Microstructures of the two different grain structures a) & b) At quench and c) & d) At 45 mm away from quench. The arrows indicate the Al(fcc)/Ag\textsubscript{2}Al boundaries.

Figure 27. Front structures obtained from images taken from 45 mm away from solidification front, and true front structures.
CHAPTER 3. QUANTITATIVE ANALYSIS of DIRECTIONALLY SOLIDIFIED TERNARY EUTECTIC AL-CU-AG ALLOY
Irmak Sargin and R.E Napolitano

Abstract

Research on ternary eutectic solidification has come to a point that a comprehensive understanding of ternary eutectic growth is only possible with a better and detailed parameterization of the structures. In this study, Al-Cu-Ag ternary eutectic alloys are directionally solidified at velocity range of 0.0002 mm/s-0.020 mm/s. Quantitative examination of microstructure is conducted using a set of objective parameters. In the velocity range examined, two different general morphologies are observed. The change in morphology with increasing velocity is shown to be a result of scaling optimization by use of diffusion cell triangles and spacing correlations. Among the parameters investigated, angular order and boundary orientation with respect to angle are suggested as new and important descriptors of eutectic structure. These suggestions are based on the changes in the microstructure and undercooling calculations.

3.1 Introduction

The solidification process of higher-order eutectic systems are far less understood in comparison to their binary counterparts. These systems often give rise to a host of complex structures, which are difficult to describe with existent geometric models and parameters. Ternary eutectic alloys can be considered as the simplest case of higher-order eutectics. However, the formation of the ternary eutectic microstructures are still complex enough to form the basis of our understanding on higher-order eutectic solidification. In other words, a quantified and comprehensive understanding of the solidification process of ternary eutectic
(TE) alloys is of great worth as an initiation to better understanding of multiphase microstructure evolution by answering challenging questions about their complex microstructures and dynamics forming these.

Starting from 1960s, there have been many attempts to classify the ternary eutectic microstructures, however a standardized classification has yet to be agreed upon. The first attempts were conducted by Kerr et al. who studied the directional solidification of Cd-Sn-Pb and Zn-Sn-Pb alloy systems [1,2]. In these studies, they characterized the eutectic structure and the solid/liquid interface. The later advances on classification of the ternary eutectic structures have been based on the idea that ternary eutectics are extensions of binary ones. Cooksey and Hellawell examined microstructures of several directionally solidified alloys including Cd-Sn-(Pb, In, Tl), Al-Cu-(Mg, Zn, Ag), and Zn-Sn-Pb and the first classification of the ternary microstructures were given as those exhibiting two binary lamellar arrangements, one binary lamellar arrangement, and finally those without a lamellar arrangement by comparing the morphology of the ternary eutectics to the binary eutectic ones [3]. Following these, numerous studies presented different growth morphologies in different alloy systems [4-8]. Ruggiero and Rutter proposed five possible TE morphologies by considering diffusion distances and surface energies using eutectic structure formed at 332 K in Bi-In-Sn system [9]. The proposed morphologies are three lamellar, one fibrous two lamellar, two fibrous one lamellar, two fibrous in a continuous matrix, and three fibrous. Also, transition from three fibrous morphology to lamellar morphology in In-Bi-Sn and Pb-Sn-Cd with increasing velocity has been explained by consideration of diffusion requirements. Another study classified the morphologies in the Al-Cu-Si system as regular, lamellar, meshy, fishbone, forked and anomalous [10].
In addition to these, there have been studies which used constitutional super cooling criteria and explained phase and morphology selection in ternary eutectic systems. Holder and Oliver used the Pb-Sn-Cd TE system to build a map of the phase morphologies. They showed that it was possible to form steady-state TE microstructures over a range of solidification parameters [11]. They were also the first to show that different morphologies might form as a result of different growth rates for the same alloy system. McCartney, Jordan, and Hunt divided the ternary phase diagram into five regions and determined the stability limits of each [12, 13]. The first one of the possible regions were stated as single phase region, which was close to pure component corners. Another region was planar two phase eutectic region which were formed close to two component eutectic compositions. Another region was determined according to the stability of solid/liquid interface. At compositions near binary eutectic valleys and at temperatures close to ternary eutectic, the third region which was consisted of binary eutectic cells and dendrites were reported to be expected. The fourth region was accepted as ternary eutectic growth region with a planar interface. The fifth structure was single phase dendrites and cell region which formed away from eutectic valleys and pure components. They also divided these region into three parts according to phases and morphologies which could form along with single phase dendrites and cells: two phase planar eutectic, binary eutectic cells and ternary eutectic, and finally single phase dendrites and ternary eutectic.

There have also been efforts to measure microstructural parameters aimed at a better understanding of their complex evolution. Many of these studies [2, 7, 8, 14-18] revealed that the ternary eutectic structures obey the scaling law, $\lambda^2 V = (K_R/K_C)$, presented by Jackson and Hunt (JH) for regular binary lamellar and rod eutectics previously [19]. This agreement of experimental results with the extremum criterion lead to the extension of the JH analysis to the
Delamore and Hill computed the solute redistribution at the solid/liquid interface by following JH and using the lamellar Pb-Sn-Cd eutectic [20]. Almost twenty years after that, Himemiya and Umeda studied mutual relationships among solidification front undercooling, eutectic spacing, and growth rate and expressed the analytical growth equations in terms of material properties for three different morphologies: lamellar, rod+hexagon, and semi-regular brick type [21, 22]. By following Jackson and Hunt analysis [19], they calculated the undercooling and extremum spacings for different velocities and applied their model to Sn-Pb-Cd and Al-Cu-Ag alloy systems. Their extension of the well-known analysis involved the addition of the third element to the solution of the solute profile and also material properties of the third phase to the analytic constants. When the models applied on real systems, the undercooling values of different growth modes were found to be very close to each other and showed some agreement with the experiments. However, the simple geometries chosen could only be representative of a small fraction of the morphologies observed in ternary eutectic alloys. Much more complex actual structures require additional parameters to be defined.

Alternative microstructural parameters have been claimed to overcome the mentioned problems. Dennstedt and Ratke presented shape factor and specific area as possible microstructural parameters and suggested that shape of probability factor curve could be used as a parameter for discrimination between different morphologies [23]. Another proposed microstructural parameter was the number of adjacent phases [24]. Although these parameters were objective, their use was limited to a set of microstructures because the correlation of the microstructural parameters to the growth conditions did not depend on the changes taking place on growth front dynamics with changing growth velocity.
These previous studies have shown the need for a detailed parameterization of structures for a complete understanding of ternary eutectic solidification. In the present study, we construct a set of objective parameters for quantifying steady-state three phase eutectic microstructures in directionally solidified Al-Cu-Ag TE alloys. Through the use of these parameters, we also aim to differentiate between different growth modes. Additionally, we are explaining the driving force and mechanism of morphology change.

3.2 Experimental Procedure

The scope of experiments included directional solidification of Al-Cu-Ag ternary eutectic alloys (Al-12.8 at% Cu-18.1 at% Ag) at different growth velocities by use of a computer controlled vertical Bridgman-type furnace equipped with a water cooled liquid metal quench chamber. Test alloys were fabricated by melting high-purity elements (99.999 wt% Al, 99.999 wt% Cu, and 99.999 wt% Ag) in a boron-nitride-coated (BNC) clay crucible in air and then cast in a BNC steel mold into rods of 5 mm diameter and 260 mm length. In order to minimize impurities, the surface of the rods were lightly ground with SiC paper and cleaned with ethanol. The rods were then placed inside an alumina crucible with a 5.5 mm inner diameter and an 8 mm outer diameter. Sixteen different alloys were pulled with different velocities in the range of 0.0002 mm/s - 0.02 mm/s, through a thermal gradient of approximately 9 K/mm stayed constant in the studied velocity range. To quench, samples were dipped into a Ga-In-Sn bath at a velocity of 20 mm/s for a further growth of 60 mm. The samples were sectioned 2 mm before the quenched front to examine microstructures, which were not exposed to post-solidification effects [24]. 25 backscatter scanning electron microscope images were taken on each of the 16 samples and the microstructural parameters were measured. The stereological
analysis can be classified into two major categories. Firstly, line measurements were done using a centered radial pattern of eighteen evenly spaced lines and recording the length of each particle, \( \delta \), and the length between particles of the same phase from midpoint to midpoint, \( \lambda \), on each line. The measurements were averaged across all images of each respective velocity. Instead of conventional line method we preferred this fully objective method to cover and average the periodicities along different directions. Secondly, area measurements were done included the area and perimeter of each particle, as well as the major and minor axis caliper lengths for each particle.

In addition to the stereology analysis detailed above, Fast Fourier Transform (FFT) patterns obtained from images masked to reveal just one phase were used to characterize topological features. Subsequently, the FFT patterns of the same grains were batched. From these batched FFTs, radial and angular order distribution plots were obtained and two different order parameters were defined: radial and angular. The radial order parameter, \( S_R \Phi \), quantifies the periodicity of each phase, whereas angular order \( S_A \Phi \) quantifies the orientation characteristics of the phases. Both parameters were calculated as peak intensity over half-maximum width for the peaks present in the distribution plots. The parameters were averaged according to the number of grains. Also, orientation of phase boundaries were measured as a function of angle and averaged over the 12 images of a grain in the structure.

3.3 Results and Discussion

3.3.1 Stereology of the ternary eutectic structures

Qualitative inspection of the microstructures revealed three different velocity ranges and the representative microstructures in these ranges are shown in Figure 28. In the slow
velocity range (0.0002 mm/s-0.001 mm/s), the microstructures can be classified as semi-
regular brick type, which is one of the growth patterns examined by Himemiya and Umeda [21, 22] or two-fibrous one lamellar structure [9]. The change in the microstructure with increasing velocity could be explained by elongation of Al2Cu and Ag2Al rods transforming into a morphology which was defined as half-lamellar [23].

In order to scale the microstructure, the stereology analyses described above were implemented. Figure 29a shows the distribution of eutectic spacing with respect to the measurement angles. Figure 29b shows the eutectic spacing calculated by radial line-intercept (RLI) method, whereas Figure 29c shows the spacing calculated from FFT patterns by obtaining radial distribution function (RDF).

The eutectic spacing depends on the growth velocity linearly in logarithmic scale as it can be seen in Figure 29. The spacings measured by RDF is close to but smaller than the spacings measured by RLI method because of the fact that in the latter one at some angles the line is not perpendicular to the major axis of the phases and as a result of this the measured spacing are slightly larger than the actual value. Table 5 shows the exponential coefficient and scaling factor of each phase. The exponential coefficient is very close to -0.5 for each phase Ag2Al having relatively a smaller one, so we confirmed that \( \lambda^2 V = (K_R/K_C) \). In order to see the scaling of each phase with velocity, the scaling factor \( K_R/K_C \) [19] was calculated by linear regression. By considering the scaling factors from RDF, we can see that there is a strong coupling between the intermetallic phases. However, the scaling factor of the Al(fcc) is much different than those of Ag2Al, and Al2Cu. This proves different scaling of phases with velocity.
Table 5. Exponential coefficient and scaling factor of each phase

<table>
<thead>
<tr>
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<th>Al(fcc)</th>
<th>Ag2Al</th>
<th>Al2Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (Kv^n)</td>
<td>RLI</td>
<td>RDF</td>
<td>RLI</td>
</tr>
<tr>
<td>0.435</td>
<td>0.494</td>
<td>0.402</td>
<td>0.387</td>
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<table>
<thead>
<tr>
<th></th>
<th>K_r/K_c (µm³/s)</th>
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<tbody>
<tr>
<td></td>
<td>RLI</td>
</tr>
<tr>
<td>Al(fcc)</td>
<td>128.891</td>
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</table>

In order to compare our experimental results with the analytical models. We revisited the Himemiya-Umeda (HU) model [21, 22] and using more recent and accurate thermophysical parameters given in Table 6, we calculated scaling ratio for the proposed growth models. The comparison of scaling factors calculated from the model and obtained from the experiments showed that the scaling factor of Al(fcc), which was 91.497 µm³/s is in relatively good agreement with that of lamellar growth morphology (106 µm³/s) calculated from HU model. On the other hand, the scaling factors of the intermetallics, were closer to scaling factor calculated for the semi-regular brick morphology of the model, which was 28.1 µm³/s. The ratio calculated for lamellar morphology and measured for Al(fcc) is very close to measured value, 92 µm³/s, of univariant Al-Cu-Ag by DeWilde et.al. [25].

The dependence of other microstructural parameters on growth velocity was also examined. The phase thickness, δ, had a similar dependence to the velocity with similar
exponential coefficients for each phase. The length and width of the phases showed linear dependency to growth velocity however their exponential coefficient was lower than those of the eutectic spacing and phase width. The changes in the mentioned parameters could be seen in Figure 30. From the analysis so far we can conclude that all different parameters in the structure are dependent on velocity in a similar manner by showing differences among phases.

Different dependence of the microstructural parameters of the phases on velocity was previously reported by Ruggiero and Rutter for Bi-Cd-Sn and Bi-Cd-Pb eutectics in terms of eutectic spacing, \( \lambda \), [9, 26]. This behavior was attributed to different faceting characteristics resulting in varying branching of the phases. Although, none of the phases are faceted in Al-Cu-Ag system different scaling behavior with velocity were reported before the present study [18]. Divergent behavior can be related to the different liquidus slopes of the univariants. When the liquidus slopes, given in Table 6, are examined, it is seen that the change in the equilibrium temperature with solute amount at Al(fcc)/liquid shows a stronger dependence on growth velocity for Al(fcc). This also explains the very similar \( K_R/K_C \) for unvariant Al-Cu-Ag alloy and Al(fcc) phase in invariant ternary eutectic.
Table 6. Thermophysical properties of TE Al-Cu-Ag.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Al(fcc)</th>
<th>Al$_2$Cu</th>
<th>Ag$_2$Al</th>
<th>Source</th>
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<td>0.51</td>
<td>0.31</td>
<td>0.13</td>
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</tr>
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<td>2.94</td>
<td>ThermoCalc</td>
</tr>
<tr>
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<td>58.46</td>
<td>ThermoCalc</td>
</tr>
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<td>-6.38</td>
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<tr>
<td>Slope of Liquidus Plane (Cu)</td>
<td>K/at%</td>
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<td>-</td>
<td>-4.83</td>
<td>ThermoCalc</td>
</tr>
<tr>
<td>Slope of Liquidus Plane (Ag)</td>
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<td>-5.87</td>
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<tr>
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<td>52/52</td>
<td>24.76</td>
<td>[28]</td>
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</table>

We also examined the regularity of the structure by batched Fast Fourier Transform (FFT) images. An example of the masked image, FFT pattern, radial, and angular distribution functions are shown in Figure 31. Here, Ag$_2$Al masked image belongs to the sample grown at 0.0006 mm/s. FFT patterns were batched over 20 images belonging to same grain. The order parameters were calculated as intensity over half-max-width of the peaks in the radial distribution function (RDF) and angular distribution function (ADF). After the ratios were calculated for each orientation, the angular order parameter, $S_A\Phi$, and the radial order parameter, $S_R\Phi$ values were acquired as grain number weighted averages.

The radial order showed no regular trend while the angular order, which is shown in Figure 32, of Ag$_2$Al and Al$_2$Cu phases had peaks at 0.001 mm/s, the velocity associated with the morphology change as a result of the elongation of these phases. Subsequently, angular order started to decrease due to fragmented form of the half-lamellar structure.
Operating point selection in ternary eutectic structures

Different scaling of each phase with velocity shows that an overall parameter covering all phases' scaling should be introduced as an operative point of the ternary eutectic structures. This parameter could be found by considering the coupling among phases. The coupling is shown in Figure 33. The yellow triangle shows diffusion cell in ternary eutectic structure. The altitudes of the triangle are the effective diffusion distances, since in these structure each phase is communicating with a mixture of the other phases. The red lines are the eutectic spacing of each phase by definition, since the each edge of the diffusion cell triangle is a symmetry boundary the effective spacing would be an average of these. The meaningful average is suggested as the geometric mean of the eutectic spacings. Figure 33b shows the geometric mean of eutectic spacing calculated by both line-intercept and radial distribution function. It is also linear with velocity at the logarithmic scale with coefficients of -0.428 and -0.437, and scaling factors of 70.824 and 47.213 μm³/s for the mean calculated from RLI and RDF, respectively.

In order to see the effect of velocity on phase coupling we have also examined how the shape of the diffusion triangles changed with velocity. Figure 34 shows the diffusion cells at the velocity range of 0.0002 mm/s to 0.008 mm/s. The shape of the triangles show almost no change with velocity when the distances are calculated from spacing obtained by line-intercept method. For the triangles coming from RDF there is a slight change with velocity. However, the spacings showed strong linear correlation providing a constant ratio as it can be seen from the spacing correlations (Figure 35). This slight changes in the symmetry of diffusion cells can be associated with the change in the order of the structure through 0.0002 mm/s to 0.008 mm/s. which did not change the scaling of structure with velocity.
3.3.2 Change in morphology with growth velocity

Although, the change in morphology was visually obvious, none of the microstructural parameters could truly showed it. So, in order to see if the transition in morphology was a crystallographic effect, a two-velocity experiment was designed. During this experiment, the velocity increased slowly from 0.0007 mm/s to 0.004 mm/s with an acceleration of 0.0015 mm/s² after 80 mm of growth. When the microstructural changes in the same grain were examined, it was seen that the first change in the microstructure was the elongation of Al₂Cu particles resulting in the connection of the neighboring same phase particles (Figure 36c). In the further growth distances, the orientation completely changed and the lamellar structure between Al(fcc) and Al₂Cu phase became clear (Figure 36d). Also, Ag₂Al phase also started to change orientation and became more elongated, however it could never complete the process because of very slow diffusion coefficient of Ag, which is 0.89E-9 m²/s, in liquid in comparison to four times faster diffusion coefficient of Cu 3.5E-9 m²/s [28] and caused the formation of half-lamellar morphology. The change in morphology of the same grain with increasing velocity suggested that it is not a crystallographic effect.

The changes in the microstructure suggest a change in coupling among three phases as the Al₂Cu phase transition toward a more lamellar morphology. In order to test this hypotheses, we performed a morphology selection study by calculating the undercooling of possible coupling which can be computing at solid/liquid interface. At the compositions very close to ternary eutectic composition, the possible couplings are three univariant coupling formed between Al(fcc)-Al₂Cu, Al(FCC)-Ag₂Al, and Al₂Cu-Ag₂Al and the ternary eutectic coupling. For calculation of univariant undercoolings De Wilde et al.’s analytical approach [28] was
applied. The undercoolings of the compositions of the liquid in equilibrium between two solids in the univariant undercoolings were calculated at right above ternary eutectic temperature 774.43 K by use of ThermoCalc. Due to definition of the slope of liquidus plane in ternary eutectic systems [21, 22], the same slopes calculated for the ternary system were used. Also, the Gibbs-Thomson coefficient and the contact angles accepted same as the ternary eutectic, since solids are in equilibrium between liquid at eutectic composition. Although De Wilde et.al's analysis only included lamellar geometry, we modified it by changing the periodicity function from Fourier to Besser and enabled it to analyze the rod-like growth based on JH analysis. Figure 37 through a to c shows the comparison of measured phase fraction weighted average univariant undercooling to the ternary eutectic structures at 3 different velocities. The vertical lines shows the geometrics mean spacings measured at the given velocities. As it can be seen from the plots, the undercooling of the ternary semi-regular brick structure starts to be higher at spacings close to the measured ones. However, the change in coupling can be suggested based on a more clear evidence by minimum undercooling versus velocity plot given in Figure 38. The crossover between the average lamellar curves of univariants and ternary semi-regular brick below 0.001 mm/s shows a change in the coupling at solid/liquid interface suggesting the ternary coupling between Al(fcc)-AgAl2Al2Cu is broken into three univariant couplings in lamellar morphology. This shows the morphological change can be clarified by approaching structures as mixture of three univariants.

When the basic morphological differences between the lamellar and the semi-regular brick structure were considered, it is seen that a clear difference would be the orientation of the phases. This could be easily visualized by comparing the perfect lamellar and semi-regular brick structures and FFT patterns obtained from these images as shown in Figure 39. In the
lamellar morphology, it is obvious that all three phases are orientated along the same direction, whereas for the semi-regular brick morphology, the orientation of Al(fcc) is perpendicular to those of Al\(_2\)Cu and Ag\(_2\)Al. This can also be compared to our real structures FFTs. Figure 40 shows the masked images of our structures at velocities where regular semi-regular brick structure, and half-lamellar structure. Images are from the samples at different velocities of 0.0005 mm/s and 0.004 mm/s. As it can be seen from the figure, the phase orientations represent that of semi-regular brick, whereas at 0.004 mm/s, the phase orientations are similar to that of lamellar structure. So, the relative orientation of phases are good candidates for differentiating between morphologies, as it is given above by use of change in angular order of the intermetallic phases. The change in angular order (Figure 32) is related to the diffuse transition between morphologies from semi-regular brick to half-lamellar.

Another way of differentiating morphologies is the use of orientation of interphase boundaries based on the same consideration. In order to test this, we have measured the distribution of boundaries with respect to angle. For these measurements, a single grain from each sample grown at different velocity was chosen and boundary fraction measurements with respect to angle were conducted over 12 images of the same grain. Figure 41 shows these distribution at four different velocities. It is seen that at low velocity, the Al(fcc)/Al\(_2\)Cu and Al(fcc)/Ag\(_2\)Al had peaks which were almost at 90° to the peak of Al\(_2\)Cu/Ag\(_2\)Al. As velocity increases, the angle difference between the peaks of solid solution/intermetallic couple to two-intermetallic couple gets closer to each other and at 0.004 mm/s and 0.01 mm/s, they are at almost the same angle as dictated by lamellar geometry. This change in the boundary orientation along with the previously explained change in couplings showed the morphological
change from semi-regular brick to lamellar structure took place with increasing velocity and it was driven by lower undercooling of univariant couples.

The change in morphology can be showed by phase orientations however, when the scaling of average spacing, spacing correlations, change in diffusion cell shapes with velocity are considered, it is seen that the change in morphology more of scaling optimization than a growth mode change. Our approach of considering ternary eutectic as mixture of univariant couplings also showed that such a change in morphology is required for diffusion distances and boundary energies consideration since these are the variables for different growth modes examined.

3.4 Conclusion

Using directionally solidified ternary eutectic Al-Cu-Ag, we have investigated the three-phase eutectic structures and different morphologies in the velocity range of 0.0002 \text{mm/s} - 0.020 \text{ mm/s}. The different scaling of phases with velocity showed that another scaling parameter for the structure is required. By considering coupling among three phases, we suggested geometric mean of the three phase spacings as a new characteristic scaling descriptor of the structure.

The change in morphology with velocity, appearing as elongation of intermetallics at small velocities and then formation of a more fragmented structure at higher velocities, was explained by considering the ternary eutectic structures as univariant mixtures and can be estimated by the transition of the Al(fcc)-Al$_2$Cu and Al(fcc)-Ag$_2$Al univariants. However, a completely regular lamellar structure could never be observed because of the very slow diffusion of Ag.
Among the objective set of measurements developed to quantify the eutectic scale and morphology; angular order, quantified by FFT, may be suggested as new descriptor and indicator of different growth type. However, the clear image is only possible by examination of orientation of interphase boundaries.

When all of the measured parameters are examined, it is revealed that the change in morphology is a result of optimization process for scaling of structure with velocity instead of a growth mode change.
References


Figure 28. Representative microstructures of three phase invariant eutectic Al-Cu-Ag for various velocities at 2 mm before quench. The light gray phase is Al(fcc), the black phase is Al$_2$Cu, and the white phase is Ag$_2$Al.
Figure 29. a) Normal distribution of eutectic spacing at v=0.0005 mm/s, error bars show the standard deviation for each angle, the average eutectic spacing as a function of velocity for each phase. b) Eutectic spacings obtained by line-intercept method, and c) Obtained by radial distribution function. The minimum and maximum values are given by extension bars for line intercept measurement. Error bars in the eutectics pacing are RDF shows the variation among different grains.
Figure 30. The scaling of different microstructural parameters with growth velocity in logarithmic scale a) Length, b) Width, and c) Phase thickness of the phases. For each parameter the error bars show the standard deviation.
Figure 31. a) An example for the masked image of Ag2Al at 0.0006 mm/s, b) FFT pattern of 20 images form the same grain with image in a), c) RDF, and d) ADF patterns.

Figure 32. Change in angular order parameter with velocity.
Figure 33. a) Coupling among three phases, b) Geometric mean of eutectic spacings as a function of velocity.

Figure 34. Diffusion cells calculated from phase spacings a) Radial line intercept b) Radial distribution.
Figure 35. Spacing correlations of a) Radial line intercept, b) Radial distribution function.

Figure 36. The microstructures observed at a) 80 mm, b) 85 mm, c) 95 mm, d) 105 mm in the two-velocity experiment.
Figure 37. The comparison of calculated undercoolings with respect to eutectic spacing at a) 0.0002 mm/s, b) 0.0005 mm/s, c) 0.002 mm/s.
Figure 38. Undercooling of averaged univariants for different morphologies in comparison to those of ternary eutectic for different morphologies as a function of velocity.
Figure 39. The perfect structure, single phase masks, and FFT patterns for a) Lamellar, and b) Semi-regular brick morphology.
Figure 40. The masked images, single phase masks, and FFT patterns of structures at a) 0.0005 mm/s, and b) 0.004 mm/s.
Figure 41. Interphase boundary distribution with respect to angle at (a) 0.0005 mm/s, (b) 0.001 mm/s, (c) 0.004 mm/s, (d) 0.01 mm/s.
CHAPTER 4. THE EFFECT OF CONVECTION AND GRAVITY ON SOLUTAL CONFIGURATION DURING UNIVARIANT EUTECTIC GROWTH IN AL-CU-AG SYSTEM

Irmak Sargin and R.E. Napolitano

Abstract

The convective flows that arise during directional solidification of an alloy can substantially alter the solutal profile in the liquid ahead of the solid/liquid interface. For the case of a ternary alloy, convection effects may influence the stability of the planar univariant (two-phase) coupled growth front by altering the transport of the partitioning component and the associated liquid composition profile. The approach for characterization of morphological and solutal transitions in these systems has been based on models regarding only diffusive regions, which cannot be maintained in terrestrial experimental studies. So, a detailed examination of effect of convection during a standard vertical directional growth of univariant alloys is necessary. In this study, we have studied the effect of convection on solutal configuration and morphology of solidification front in univariant Al-Cu-Ag alloy under different experimental condition with different pulling velocity, sample diameter, and direction of pulling. We have shown that radial gradient and natural convection stemming from this gradient change the solutal profile and morphology immensely. Increased convection by changing the growth direction from anti-parallel to parallel (with respect to gravity) was shown to suppress the transition to a cellular front, by producing a more homogenize the front composition, whereas smaller sample size was not completely effective for the latter during vertical growth against gravity.
4.1 Introduction

The fundamental knowledge on solidification of alloys has been developed mainly for one or two component single phase materials or coupled two phase growth of invariant eutectic or peritectic reactions. However, microstructural evolution in high order systems, which often give rise to a host of complex multiphase structures, is less understood and has many open question regarding the phase and morphology selection and solidification front dynamics [1, 2]. Ternary eutectic alloys serve as a good example for multiphase solidification. Their extension from a binary eutectic with increased degree of freedom brings many important aspect, which can be disregarded for the simpler cases.

Univariant eutectic coupled growth of two non-faceted solid phases from a three component liquid results in a regular lamellar or rod-like arrangement of phases as in their boundary counterparts [3-13]. Although, these two phases grow by exchanging of solute species also segregation of the third component into the solid/liquid interface takes place. This segregation results in formation a long-range solute boundary layer in the liquid ahead of solid/liquid interface similar to single phase growth from a two component liquid. The structure of the ternary two-phase eutectics was shown to scale with velocity according to $\lambda^2V=constant$ relationship by experimental studies [6, 12, 14] and by an analytical model [9]. However, the planar interface of a univariant eutectic is prone to morphological instabilities due to presence of long range solute boundary layer.

The stability of the interface has been mostly approached [4-6, 14-19] by use of theoretical models developed for purely diffusive regime [19-21] and tried to be estimated by either constitutional supercooling [20] or linear perturbation analysis [22]. The assessment of these models with experimental studies requires completely convective-free growth
conditions. Vertical directional solidification with pulling direction anti-parallel to the gravity can serve as a method for convection-free growth. This configuration avoids the buoyancy flow driven natural convection, since the hotter and less dense liquid overlays the colder and denser one. However, a radial thermal gradient is inevitable due to the heat extraction from side walls [23, 24] and convection effects were shown to be dominant for the systems with denser solutes in comparison to the solvent [25, 26].

A remedy for avoiding convective flow in terrestrial experiments is using narrower tubes than the generally used ones with diameter 3-7 mm for binary alloys [27]. However, there is no report providing that this is also applicable to ternary alloys.

In this study, firstly we examined the convection dependent phenomena observed during vertical directional solidification of univariant Al-Cu-Ag, which forms a eutectic between Al(fcc) and Al₂Cu. We also address the solutal configuration in liquid and solid phases with different growth condition which suppress or aids convective flow to clarify and explain the observed phenomena by varying growth velocity, sample size, and direction of pulling as parallel or anti-parallel to gravity.

4.2 Experimental

The scope of this study includes gradient-stage directional solidification of univariant Al-Cu-Ag alloys of composition (Al-16.55 at% Cu- 2.82 at% Ag) by use of different velocities and tube diameters. The thermophysical properties of the alloy given in Table 7. Specimens were fabricated by casting the test alloy into 5 mm diameter rods using a steel mold coated with boron nitride.
### Table 7. Thermophysical properties of Al-16.5 at%Cu-2.82 at%Ag

<table>
<thead>
<tr>
<th>Thermophysical Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag content</td>
<td>at%</td>
<td>2.82</td>
</tr>
<tr>
<td>Solidus Temperature (K)</td>
<td>K</td>
<td>785.2</td>
</tr>
<tr>
<td>Liquid composition (at.%)</td>
<td>at%</td>
<td>12.61</td>
</tr>
<tr>
<td>Phase Fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(fcc)</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>Partition Coefficient ((C_s/C_l=k))</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>Melting Temperature (K)</td>
<td>K</td>
<td>815</td>
</tr>
<tr>
<td>Thermal Conductivity Al(fcc)</td>
<td>W/mK</td>
<td>152.99 [181]</td>
</tr>
<tr>
<td>Thermal Conductivity Al₂Cu</td>
<td>W/mK</td>
<td>110.64 [181]</td>
</tr>
<tr>
<td>Phase Fraction Weighted Average Thermal Conductivity</td>
<td>W/mK</td>
<td>132.24</td>
</tr>
<tr>
<td>Thermal Conductivity of Liquid</td>
<td>W/mK</td>
<td>55 [181]</td>
</tr>
<tr>
<td>Gibbs Thomson Coefficient Al(fcc)</td>
<td>Km</td>
<td>4.8E10-8 [132]</td>
</tr>
<tr>
<td>Gibbs Thomson Coefficient Al₂Cu</td>
<td>Km</td>
<td>5.9E10-8 [132]</td>
</tr>
<tr>
<td>Phase Fraction Weighted Average Gibbs Thomson-Coeficient</td>
<td>Km</td>
<td>5.33E10-8</td>
</tr>
</tbody>
</table>

These samples are used to investigate the initial transient, instability, non-planar growth modes, and effect of convection and segregation. The first set of samples involved 6 different velocities employed as coupled to one directional solidification sample. The growth was started at slow rates, namely, 0.0001, 0.0002, and 0.0005 mm/s. After 50 mm of growth without any quench higher velocities, 0.001, 0.002, and 0.005 mm/s, were started.
In order to examine the effect of tube diameter on radial convection and solutal configuration at solid/liquid interface, thin tube experiments were conducted. The tube diameters studied are 1, 0.8, and 0.5 mm. In the sample, there were 4 thin tubes having two 1 mm. Thin tube samples were pulled at 0005 mm/s.

Furthermore, to investigate the effect of direction of gravity experiments with inverted configuration, growth parallel to the gravity, was conducted. For this experiment, two different steps were involved. First, the samples were held for 4 hours followed by a quench with 20 mm/s for 30 mm. After that, in order to provide homogenization sample was held stationary for an hour and grown for 30 mm at 0.002 mm/s, and then quenched again for 30 mm. This procedure was replicated for standard configuration, anti-parallel to gravity. For all these experiments, the thermal gradients was measured to be 11 K/mm in liquid and 6 K/mm in solid.

The samples were examined both in transverse and longitudinal sections by use of scanning electron microscopy equipped with Energy Dispersive Spectroscopy (EDS). In order to measure the solutal profiles in liquid along longitudinal sections and in solid in transverse section, compositional area analysis was done by EDS.

4.3 Results and Discussion

The microstructures in the thick tube samples grown at different velocities, shown in Figure 42 showed that slow velocities show lamellar/maze-like structures. The transition to non-planar growth modes took place between 0.0005 and 0.001 mm/s. The cells observed at relatively lower velocities were elongated, whereas radial cells were present in the sample grown at the highest velocity of this set. The presence of elongated cells were associated with the anisotropy of the solid phase boundaries [16, 29]. Due to this anisotropy, the lamellar
structure forced formation of elongated cells which are eventually expected to transform to regular radial cells. Formation of radial cells at the same growth distance at higher velocities showed that the decrease in $G/v$, overcame the anisotropy at shorter growth distances. Figure 43 shows the initial transient in our samples. The symbols belong to measurements whereas solid lines showed the calculated profile during initial transient. Due to the solute-rich boundary layer formed in liquid during growth at low velocities, when the growth was accelerated, the composition of the initially formed solid was higher than expected. The inconsistency between the calculated and measured profiles at low velocities could be attributed to the effect of natural convection as it will be explained below with solid/liquid interface examinations. So, in summary our compositions was not consistent with purely diffusional Smith-Tiller-Rutter model. However stability analysis showed that the critical velocity calculated according to constitutional supercooling criterion was consisted with what was observed at thick tube samples. The calculated velocity was 0.00054 mm/s and the microstructure changed from lamellar to the cellular at a velocity between 0.0005 and 0.001 mm/s. Also, we have observed that topological transient occurred more quickly than the solutal transient.

Further investigation of higher velocity microstructures (0.001 mm/s, 0.002 mm/s, and 0.005 mm/s) showed that as a result segregation the periphery of the samples were circled by as circling (Figure 44) This layer’s thickness was decreasing with growth distance. As the composition reaches to the equilibrium value, Al(fcc) phase chunks appeared in the central region of the sample. The presence of this region continued until the end of the sample resembling the tree-like structure observed in peritectic alloys as a result of convection [23, 30]. Compositional analysis given in Figure 45, showed that radial segregation was present in
samples which were grown at 0.002 mm/s and 0.005 mm/s. The low Ag amount at the center brought the composition to the hypoeutectic range and caused formation of chunk-like Al\(\text{fcc}\) regions at growth velocities of 0.002, and 0.005 mm/s.

In all of the thick tube samples, the quenched solid/liquid interface was observed to be convex and in accordance solute profile in the liquid was affected from segregation. Although, the analyses were made on tangential flat, the distribution was showing major changes with the distance from the center of the sample. The solute content aligned according to position of interface such that the lowest content was observed at the highest position of the interface. The difference between the position and solute content along lines x1, x2, and x3 shows the presence and effect of natural convection on fluid flow [31]. The driving force for natural convection is the presence of horizontal gradient which cannot be eliminated in thick tube samples. The origin of this gradient is the difference between thermal conductivities of solid phases and alumina crucible. By using the concentration difference along the interface, the horizontal temperature gradient can be estimated roughly by using

\[
\Delta C = c_{x1} - c_{x3} = \Delta T/m
\]

\[
\Delta T = G_x \Delta x + G_y \Delta y [31]
\]

By using values at the interface the horizontal gradient for three velocities calculated and found to be 0.61±0.11 K/mm with no direct correlation with the velocity. Due to this horizontal gradient, none of the profiles were in accordance with steady-state distribution based on purely diffusional models [20].

Another effect of convection was observed at the solid/liquid interface of 0.001 mm/sample (Figure 46a). The single phase Al\(\text{fcc}\) chunks was observed to float to higher
temperatures in the liquid during growth. This showed also the effect of buoyancy and appeared as the second convection related phenomena after the shape of solid/liquid interface.

In order to examine the effect of sample diameter, we conducted thin tube experiments. The tube diameters studied were 1, 0.8, and 0.5 mm. In the sample, there were 4 thin tubes having two 1 mm. The growth velocity was 0.0005 mm/s. Tubes were named according to decreasing tube size. There was a long holding period prior to start of growth and as a result of this, high solute piled up was observed at the beginning of growth affecting morphology (Figure 47) and solute redistribution (Figure 48). It was possible to observe cellular structures at initial sections. As the high solute content decreased with increasing growth distance and composition got closer to the original composition after 10 mm of growth, the microstructure was observed to be lamellar/maze-like as expected at this pulling rate.

The solid/liquid interfaces shown in Figure 49 were curved similar to ones in the thick tube experiments. This caused a slight difference between compositions of center and corners for the outer tube whereas it caused no difference at thin tube in longitudinal sections (Figure 50). However, the radial profile in the solid at 25 mm of growth showed that the horizontal gradient was homogenized lately during growth, since a compositional gradient was present at these section in thin tube samples. Also, the distributions were not consisted with calculated ones. So, we can deduce that although, the interface shape is not changed with natural convection, convection was effective on fluid flow disturbing the purely diffusional solute boundary layer.

In order to quantify the effect of the direction of the gravity, we have conducted experiments in which we reversed our growth direction and called them inverted setup experiments. The transverse microstructures shown in Figure 51 at 2 mm before quench
showed that although the velocity was above the constitutional supercooling criterion, at the sample grown with inverted configuration complete evolution of cells were not complete. The radial segregation from sample center to periphery region was also measured on transverse sections. For the same experiments, no segregation at the 2 mm before quench was observed at the inverted one, whereas axial segregation was present at the same section of the standard one.

We have also examined the solid/liquid interface after growth and measured the solute profile in the liquid following to growth and quench (Figure 52). The morphology of the solid/liquid interface for both case were cellular-like, however the cells were deeper in the standard setup sample in accordance with transverse section. The intercellular distance also showed large differences between samples such as the distance was 220±17 μm in the inverted setup sample, whereas it was 73±18 μm. According to Mullins-Sekerka analysis [22], the onset of stability corresponds to a wavelength of 400 μm in this alloy under the growth conditions employed, so shorter wavelength showed that both interfaces were unstable, however the transition from planar to cellular interface proceeded faster in the standard sample. When we considered both transverse (Figure 51) and longitudinal sections (Figure 52), two major results of increased effect of gravity could be stated. Firstly, the horizontal gradient was overcome by the increased convection and secondly, the planar to cellular transition of the interface was delayed.

The solute profile in the liquid, given in Figure 52, explains the why the planar to cellular transition was delayed. The profile was almost linear for the inverted setup sample with a very limited solute boundary layer with high segregation of Ag away from solid/liquid interface. On the other hand, the solute profile in the standard sample the thickness of the solute boundary
layer was same with the diffusional model except that it was less enriched, which could be related to the radial thermal gradient and/or cellular interface. In order to quantify the level of contribution of convection to flow, we visited the phenomenal study of Burton et.al [32]. By assuming the Nerst’s stagnant film model [33], they defined a solute boundary layer, in which only diffusional transport takes place, whereas outside this layer the composition is homogenized due to effective mixing by convection. They also defined a parameter for scaling the contribution of convection. The parameter, effective partition coefficient \( k_{\text{eff}} \), is the ratio of solid composition at the interface to the bulk liquid composition. For complete mixing \( k_{\text{eff}} \) is equal equilibrium partition coefficient \( k \) and solute boundary layer thickness is 0. The other extreme, no convection, has a \( k_{\text{eff}} \) equal to 1 and solute boundary layer thickness going to infinity. Any value in between corresponds to partial mixing of diffusion and convection. In our samples \( k_{\text{eff}} \) of inverted set up is 0.45, and that of standard setup is 0.76. So for both setup, \( k < k_{\text{eff}} < 1 \) showing the partial mixing of convection and diffusion. However \( k_{\text{eff}} \) was much closer to \( k \) in the inverted setup and it was closer to 1 in the standard setup. As a result homogenization in solidifying melt during growth parallel to the gravity, the compositional boundary layer and in result constitutionally supercooled layer was diminished and cellular growth was delayed.

4.4 Summary and Conclusions

By directional solidification of univariant Al-Cu-Ag alloy with composition Al-16.55 at%Cu-2.82 at%Ag varying pulling velocity, sample diameter, and direction of pulling, effect of convective flow on solutal configuration in solid and in liquid ahead of solid/liquid interface was studied. The conclusions are listed here:
• The thick tube samples grown at relatively low velocities of 0.0001 mm/s, 0.0002 mm/s, and 0.005 mm/s exhibit lamellar/maze-like morphologies. The transition from planar to non-planar growth modes took place between 0.0005 mm/s to 0.001 mm/s, which is in agreement with the constitutional supercooling criterion [20].

• The solute profiles during initial transient were not in accordance with purely diffusive Smith-Tiller-Rutter model [21] for higher or lower velocities. This is related to the presence of radial thermal gradient, which also caused solid/liquid interfaces to have a convex shape. The steady-state solute profiles associated with the convex shape was different at different locations of the interface. The highest solute content was at the lower point. As a result, it has a slower advancing rate.

• As an effect of the radial thermal gradient, the outward segregation of Ag to the periphery of the sample was observed in sections near the start of growth, leading to initiation of ternary eutectic structure at these outer regions. Also, with the concomitant depletion of Ag, single-phase Al(fcc) particles were observed along the central axis of the specimen. These were observed to migrate upward in the liquid, toward higher temperature regions assisted by buoyancy driven convection.

• Thin tube experiments with different tube diameters showed that the radial convection can be suppressed but not eliminated by decreasing sample diameter to 0.6 mm. Also, the stability of the planar morphology was shown to be highly dependent on Ag content.

• The growth direction was shown to strongly influence solutal configuration in liquid ahead solid/liquid interface, the radial profile in solid, the transition to cellular growth and the length scale of the cells. The solute profile in the liquid in the inverted setup sample was almost linear with a very thin solute boundary layer resulting in delay of
fully grown cell development. The scale of the cells were also very different for two different setups due to the delay in cellular formation in the inverted one.

• The increasing effect of convection with growth parallel to gravity also stabilizes interface and overcomes the radial thermal gradient. The transverse sections in standard samples were shown to have segregation of solute through periphery, whereas radial profile was linear in the inverted setup sample.
References


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Figure 42. Representative steady-state microstructures of the univariant alloys at growth velocities of the lowest (top) to the highest (bottom).

Figure 43. The initial transient of the samples with velocities 0.0002, 0.0005, 0.002, and 0.005 mm/s. Symbols show experimental data whereas solid lines shows the initial transient by diffusive model [34].
Figure 44. Microstructure observed at) 15 mm, and b) 20 mm of growth showing the tree-like structure and ternary eutectic. $v_p=0.002$ mm/s.

Figure 45. The radial composition profiles of the transverse sections at 30 mm for growth velocities a) 0.002 mm/s and b) 0.005 mm/s. Inlets show the Ag distribution separately.
Figure 46. Solid/liquid interface and corresponding solute distribution in liquid for a) 0.001 mm/s, b) 0.002 mm/s, and c) 0.005 mm/s.

Figure 47. Microstructures observed at the first thin tube experiment.
Figure 48. a) The solute profile in the solid as a function of growth distance. The solid curve shows the calculated initial transient. Tubes are numbered according to decreasing diameter. b) The first 10 mm is disregarded in order to show that, after 10 mm, the effect of solute pile up is somewhat eliminated and except tube 4, it is possible to see consistency with the calculated initial transient.

Figure 49. Solid/liquid interfaces observed in the first thin tube sample. (a) The outer (thick) tube showing a slight curvature. (b) The first thin tube with Ø=1 mm, (c) The first thin tube with Ø=1 mm at a smaller scale of the interface showing resembling cellular front.
Figure 50. Solute profile in liquid of the first thin tube experiment (a) Outer tube, (b) Thin Tube-1 (Ø=1 mm), c) Transverse section of thin tubes at 25 mm of growth.

Figure 51. Observed microstructures and radial segregation profile in the (a) Inverted, (b) Standard configuration at 2 mm before quench following 30 mm of growth.
Figure 52. The solid/liquid interface of the (a) Inverted, (b) Standard sample, and c) Corresponding solute profile in the liquid after growth and quench.
CHAPTER 5. EUTECTIC GRAIN COMPETITION IN DIRECTIONALLY SOLIDIFIED AL-CU ALLOY

Abstract

The knowledge and control of the texture in multiphase materials are limited in comparison to single-phase materials; although it is widely required to acquire the properties for advanced functions. In this study, the morphological transients, spacing optimization, and topological evolution, and their effect on texture selection in directionally solidified binary eutectic Al-Cu were studied. The grain selection transient and spacing optimization transient were found to coincide, whereas spacing of the competing grains did not show any difference. By quantification of the Fast Fourier Transform patterns, topological order was quantified and shown to be an important parameter in grain selection. Also, degree of periodicity was found to be much higher in eliminated grains than in preferred or selected grains. This may be an indication that these grains are less responsive to the dynamic requirements of the advancing solid/liquid interface. In addition to this, by examination of the grain boundaries we are suggesting that the selected grains are growing at the expense of others by the perturbations on the lamellae of the shrinking grain on the grain boundary aligned the direction of the growing grains’ lamellae.

5.1 Introduction

The industrial demand has changed the material scientists’ approach from discovery to design of materials to achieve desired properties for advanced functions, which requires understanding of dynamic spatiotemporal hierarchy at different length scales. Among this different scales, texture of the microstructure holds an important place, since the unique
properties expected are affected by crystal orientation involving an anisotropic response to external stimuli [1-3]. Furthermore, observation of anisotropic effects on properties like superconductivity and electrical properties is not possible with sintered polycrystals or even with small single crystals [2-5]. Accordingly, not only for realizing new and enhanced functionality but also being able to understand these, optimization of single crystal production methods is required.

Starting from first offering by Tammann [6] and following realization by Bridgman directional solidification have been the most widely used mass production method for producing single-crystals with desired texture [7]. Although control of crystallographic texture during growth-from-melt is well-understood and has been applied successfully in single phase materials [8-11]; the information and control on orientation selection and texture evolution in multiphase growth structures are limited. This is mainly because of non-linear dynamics taking place during the microstructure evolution in multiphase material and many different possible arrangement of phases [12-14]. In addition to these, the continuous effect of epitaxial properties from nucleation to growth can be counted as an additional difficulty for control of texture in multiphase material [15-18].

The microstructure evolution in directionally solidified binary lamellar eutectics serves as good initiation of understanding the texture selection and control of it in multiphase materials. The final microstructure of directionally solidified lamellar eutectics consist of several grains within many subgrains. In a eutectic grain, crystallographic orientation of each phases and their microscopic angular orientation is fixed [19-24]. The preferred epitaxial orientation between phases was reported to occur during the nucleation process [15, 16, 18]. Although the crystallographic orientation is fixed within a grain, subgrains, which are separated from each
other by eutectic fault lines, are formed by several degrees of deviation from the mean crystallographic orientations [20]. In weakly anisotropic eutectic systems, there are locked and floating grains. In locked grains solid/solid interface is strongly locked to an epitaxial orientation and as a result of this they can only grow at a direction parallel to a certain crystallographic plane in a rectilinear orientation to the solid/liquid interface. On the other hand, in floating grains, such an epitaxial condition cannot be satisfied. Floating grains bend smoothly about their stationary orientation showing tilt instability and aligned themselves parallel to the solidification direction as growth proceeds [25-28].

Although there are many grains, which may or may not have a fixed orientation relationship, at the beginning of a directionally solidified sample, as the growth proceeds, number of grains decreases to one or several grains. The rate of decrease in number of grains was dependent on steady-state growth rate, whereas the initial number of grains increases with increasing growth velocity [15, 29, 30].

The selected grains observed to be aligned parallel to the growth distance many time in experimental studies [31-33]. Many studies were aimed to explain this phenomenon, grain selection, in coupled growth eutectics taking interlamellar spacing and crystallographic orientation as the basis [19, 31, 32, 34, 35]. By determining the preferred grain as the one with smallest interlamellar spacing, Tiller [34] claimed that the reason behind the grain selection is the faster growth rate of this grain due to smaller diffusion distance at solid/liquid interface providing steps on grain boundaries as a proof, whereas the same finding related to preferred grain was interpreted as an orientation dependent phenomenon by Chilton and Winegard [31]. Authors followed Chalmer’s suggestion [36] which can be summarized as different characteristic equilibrium temperature of different planes with liquid metal and concluded that
the grain growing ahead of others is the one with the lowest characteristic equilibrium temperature with molten metal. A few years later Chadwick [37], examining the decanting surfaces and explaining the reason for step formation on grain boundaries as remaining liquid layer attached to the solid\liquid interface, proposed that the grain selection is dominated by local competitive processes taking place at grain boundaries. Other explanations were based on crystallographic orientation, suggesting some grains have a more favorable orientation relationship than the others and as a result of this, the most favorable orientated grain in the beginning of growth tend to grow at the expense of those poorly oriented ones [17-19]. This explanation was based on the presence of degenerate/maze-like structures in the beginning and their elimination from the sample with increasing growth distance by growth of more ordered grains at the expense of them or faster transition rate of maze-like to lamellar transition in more ordered grains [29, 30, 35].

Despite much work on grain selection in binary eutectics, a systematic study testing the qualitative hypotheses is lacking and mechanism of the grain selection is still not clear. In the work presented here the morphological transients, grain selection, spacing optimization, and topological evolution, were characterized and their mutual effect was explained during directional growth of binary eutectic Al-Cu alloys. Firstly, the kinetics of grain selection was studied. In addition to this, effect of microstructural characteristics on the grain selection was presented by comparison of different grains with respect to eutectic spacing and topological order. Finally, by examination of different boundary types and their propagation velocities a mechanism for growth of one grain at the expense of others are explained.
5.2 Experimental Procedure

The scope of this study includes gradient-stage directional solidification of binary eutectic Al-Cu alloys of composition (Al-17at%Cu) at different pulling velocities. Specimens were fabricated by casting the test alloy into 5 mm diameter rods using a steel mold coated with boron nitride.

The samples were pulled at 0.0012, 0.0025, 0.005, and 0.01 mm/s for 50 and 90 mm and then quenched at 20 mm/s for 90 mm and 50 mm, respectively. Following, the samples were sectioned with 2 mm increments until 10 mm of growth, with 5 mm of increments from 10 mm to 40 mm, and finally with increments of 10 mm from 40 mm to 60 mm. By optical microscopy low magnification images were taken to form stitched images showing all grains and grain maps were constructed. An example of such a map is shown in Figure 53. By use of the maps, grain size and distances taken by grain boundaries were measured by image processing software. In order to understand the forces determining the preferred grain in this study, the attributes of the surviving grains after transient length (namely 25 mm) were examined for the pulling velocity 0.005 mm/s. For the pulling velocity 0.0012 mm/s all grains present at each section were examined. Three to eight images were taken by optical microscope according to grain size. For the interlamellar spacing and order quantification, the FFT patterns of the same grain images were obtained. From these FFTs, radial and angular order distribution plots were obtained and two different order parameters were defined: radial and angular. The radial order parameter, $S_R\Phi$, quantifies the periodicity of each phase, whereas angular order $S_A\Phi$ quantifies the orientation characteristics of the phases. Both parameters were calculated as peak intensity over half-maximum width for the peaks present in the distribution plots and then averaged for the images of the same grain.
5.3 Results and Discussion

The studies showed that the grain selection took place over a distance. Figure 54 shows sequential grain maps of the sample grown at v=0.005 mm/s and Figure 55 shows the change in number of grains with growth distance for different velocities. As it is seen in the figures, most of the poorly oriented grains were eliminated until growth distance of 20 mm. Kinetics of grain elimination was similar for all velocities such that it was faster at the earlier growth distances in comparison to later distances; although the initial number of grain shows significant differences according to pulling velocity. Accordingly, the grain size distribution at the initial sections were different for the slow and faster velocities (Figure 56). For the slow velocities, several large grains were accompanied by much smaller ones, whereas for the faster velocities all of the grains had smaller and similar sizes. In order to see if this was related to nucleation rate or if the grain selection also continued following to solidification, we also looked at the effect of growth distance on the number of initial grains. Figure 57 shows the grain maps of the samples pulled at velocity of 0.0012 mm/s with different total growth distances of 90 mm and 50 mm. The sample pulled until 50 mm had much more initial grain in comparison to the one grown for 90 mm, showing that elimination of some grains took place after solidification.

The change in grain size of the surviving grains, grains stayed in the structure of the grain selection transient length (~25 mm) was reached, showed that grain selection had a similar behavior for all different velocities (Figure 58). One of the grains (the selected one) was growing continuously whereas others exhibited a maximum in their sizes. The rate of grain selection was determined from the rate of growth of the first grain and the result was presented
in Figure 59. The exponential coefficients for the grain growth were 0.2281, 0.5264, 0.8217, and 0.8983 for growth velocities of 0.0012 mm/s, 0.0025 mm/s, 0.005 mm/s, and 0.010 mm/s, respectively. The exponent of slower growth rate showed similarity to the exponent of abnormal grain growth in the solid state, showing that solid-state grain growth was effective for this velocity, whereas for faster growth rates there was no time for solid-state growth. This also explains the large difference of the grains present in the initial sections of the slower velocities, the larger grains were the more thermally stable ones, the ones with the equilibrium orientation [22], and they grew at the expense of the less stable ones.

Another difference between high and low velocity initial structures was the presence of maze-like grains, which later either wiped out or transformed into lamellar structure, in the slower velocities. On the other hand, no maze-like structure was observed in the initial growth distances at faster growth velocities. This is an expected result since the degenerate structure were observed velocities lower or around 0.001 mm/s [32]. Some of the maze-like structures which survived till they were wiped off were shown in Figure 60. These structures were representatives of the different kind of transient structures observed in the lower velocity samples. The ones exemplified from the sample pulled at 0.0012 mm/s consisted of short lamellar segments at different angles, whereas the others had fragmented but aligned [33, 38]. Actually, the later type grains had a tendency to transform into maze-like structure if they could survive in the sample long enough to complete the transition. The examples of this transition were given in Figure 61. The transition was completed at 4 mm for both velocities. So, we can conclude that the topological transition completed earlier than the grain selection.

In order to understand the forces determining the preferred grain, the order of the surviving grains in the sample grown at 0.005 mm/s after transient length (namely 25 mm) and
order of all grains for pulling velocity of 0.0012 mm/s were quantified by fast fourier transform (FFT).

Figure 63 shows the microstructure, and Figure 63 shows Fast Fourier Transform (FFT), radial distribution function (RDF), and angular distribution function (ADF) plots for the grains present at 25 mm of growth for the sample grown with 0.005 mm/s. The change in radial and angular order with growth velocity for pulling velocities of 0.0012 mm/s and 0.005 mm/s are given in Figure 64. The radial order of the lamellar structure and/or preferred grains was lower than that of maze-like grains. Considering the radial order’s dependence on faults and scaling optimization; the higher radial order of the maze-like structure suggested that they were incapable of activating mechanisms for adjusting dynamic requirements of solid/liquid interface equilibrium. A reverse situation was valid for the angular order. The preferred grain had the highest angular almost for all sections for both velocities. Elimination of the grains with lower angular order and the selected grains’ higher order showed that the angular order was the determinant characteristic of the grain competition, although the angular order difference among the lamellar grains was small.

In the literature grain selection was mostly associated with the smaller undercooling of the selected grain and eutectic spacing, in order to assess this hypothesis, we measured the eutectic spacing [31]. The eutectic spacings were calculated from the peak positions in the radial distribution function plots. Eutectic spacings did not show any difference in different grains. So, we cannot concluded that the eutectic spacing was effective on grain selection behavior or the preferred grain had a lower undercooling than the others. In both samples, there was a minima in the eutectic spacing at the growth distance where the grain selection transient completed. Although, the eutectic spacing was not effective on competition among grains, the
two transients of spacing optimization and grain selection, coincided. This supports the idea that the grains eliminated most rapidly were not capable of spacing arrangements.

We have also examined grain boundaries to understand the propagation of the grain growth. The different types of grain boundaries observed in the sample pulled at 0.0012 mm/s are given in Figure 66. The boundaries between the grains the lamellae of which were converging formed a boundary with a slightly disordered region. In the occasion where the two converging grains meet along a fault line a perfect matching boundary forms. The same-type lamellae at different sides of boundary could meet end to end or can alternate. If the alignment of the two grains were almost perpendicular a stepped boundary was observed. If the angular difference between the two grains were high, the grain boundary became highly disordered. Also, it was possible to observe different type of boundaries for the same grain according how lamellae at the boundary according to orientation of neighboring lamellae. An example for this is given in Figure 67. The distance traveled by different boundary types showed that as the disorder at the boundary increased the distance traveled by the boundary decreased. An example of this situation is shown in Figure 68. Between 2 mm and 8 mm, the shown boundary was immobile. However, as the disordered region thickness decreased the boundary started to move. The change in the boundary was stemmed from the decrease in the topological order of the two grains as the grain on the right hand side transformed from maze-like to lamellar. On the other hand, when the boundary between a stable maze-like grain (Figure 60a) and a lamellar grain was examined it was seen that at the boundary among the different lamellar segments just one was present and the boundary was growing with motion of this segment. If the lamellae were converging along the boundary, the matching boundaries was observed to be the slowest one. So, the fastest boundaries were the boundaries where the boundary was formed by
continuous lamellae of the one of the grains. The mechanism of boundary motion between lamellar grains was observed to be perturbations on the boundary lamellae along the alignment of the neighboring one. Examples showing perturbations were shown in Figure 69.

5.4 Conclusions and Summary

In this study, the morphological transients, grain selection, spacing optimization, and topological evolution, and their mutual effect were studied in directionally solidified binary eutectic Al-Cu were studied. In the velocity range studied, 0.0012-0.010 mm/s, the grain selection was completed around 20 mm. The eutectic spacing measurements showed that although, spacing is not parameter on competition among grains, scaling optimization and grain selection transient coincided. This finding along with the higher radial order of the eliminated grains than the preferred ones suggested that the eliminated grains are irresponsible to changes in the solid/liquid interface since the range of spacings coming from eutectic faults and adjustment mechanism would cause a decrease in the radial order. The highest angular order of the preferred grains and the elimination of the grains with the lowest angular order showed that also angular order is one of the main criteria in grain selection. In addition to this, by cataloguing of the grain boundaries we showed that the boundary type and how fast they would advance into a shrinking grain is determined by how the lamellae in two grains were aligned with respect to each other and how big was the difference in their angular order. Also, we are suggesting that the perturbations on the boundary lamellae of the shrinking grain aligned parallel to the growing grains are responsible for the movement of grain boundary.
References


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Figure 53. The grain map on a stitched image. V=0.0025 mm/s. Growth Distance= 15 mm.

Figure 54. Sequential grain maps of the sample grown at v=0.005 mm/s.
Figure 55. The total number of grains as a function of growth distance for different grains.

Figure 56. Grain size distribution at 2 mm of the samples pulled with 0.0012 mm/s (top) and 0.01 mm/s (bottom).
**Figure 57.** Grain maps of the 2 mm section of the samples with pulling velocity of 0.0012 mm/s with different total growth distances a) 90 mm, b) 50 mm.

**Figure 58.** Change in grain size of the grains present in 25 mm of growth with respect to growth distance for pulling velocities of a) 0.0012, b) 0.0025, c) 0.005 mm/s, d) 0.01 mm/s. Grains are named according to their survival distance. Grain 1 stands for the grain with the preferred orientation.
Figure 59. Growth rate of the selected grain at different velocities showing that the grain growth kinetics propagate according to conventional grain growth kinetics (Grain Diameter=$kt^n$).
Figure 60. Maze-like structures observed at lower growth rates. a) $v=0.0012$ mm/s - 2 mm b) $v=0.0012$ mm/s-4mm, c) $v=0.0025$ mm/s-2 mm, d) $v=0.002$ mm/s-4 mm. The same scale bars are valid for the images belong to same velocity.
Figure 61. Transition structures observed at lower growth rates. a) $v=0.0012 \text{ mm/s} - 2 \text{ mm}$ b) $v=0.0012 \text{ mm/s} - 4 \text{ mm}$, and c) $v=0.0025 \text{ mm/s} - 2 \text{ mm}$, d) $v=0.0025 \text{ mm/s} - 4 \text{ mm}$. The same scale bars are valid for the images belong to same velocity. The maze-like to lamellar transition took place at 4 mm.
**Figure 62.** The grain structures present at 25 mm of growth for the sample grown with $v=0.005$ mm/s. a) Grain 1, b) Grain 2, c) Grain 3, d) Grain 4, e) Grain 5.
Figure 63. Fast Fourier Transform (FFT), radial distribution function (RDF), and angular distribution function (ADF) are shown for the grains present at 25mm of growth for the sample grown with v=0.005 mm/s corresponding to microstructures in Figure 62.
Figure 64. Growth distance dependence of a) & c) Radial order and b) & d) Angular order of grains present in a & b) $v=0.005$ mm/s, and c & d) $v=0.0012$ mm/s.
Figure 65. Eutectic spacings of the grains in a) 0.005 mm/s and b) 0.0012 mm/s.
Figure 66. Different boundary types observed in the sample pulled at 0.012 mm/s. a) Converging, b) Stepped, c) Matching, d) Disordered. Scale bar applies all the images.

Figure 67. Same grains meeting at different boundaries.
Figure 68. Change in boundary structure between two grains as the angular order difference between decreases with growth distance a) 2 mm, b) 6 mm, c) 8 mm, and d) 10 mm.
Figure 69. The perturbations on the lamellae of the shrinking grain with same alignment of the propagating grain.
CHAPTER 6. EFFECTS OF THE PRE-GROWTH HOLDING PERIOD DURING DIRECTIONAL SOLIDIFICATION OF EUTECTICS

Irmak Sargin, James Acton, and R.E. Napolitano

Abstract

Formation of single-phase layers, which are frequently observed following to a stationary hold during a directional growth experiment, were examined in directionally solidified bulk eutectics in Al-Cu-Ag systems. By employing periodic pulling, hold, and quench periods, effect of different growth conditions on formation of single-phase layers were studied. The composition of the single-phase layer was observed to be only dependent on alloy composition, whereas morphology and thickness were found to be dependent on composition, holding period, pre-growth velocity, and thermal gradient. The processes occurring during the formation of single phase layers are explained and shown to vary in the presence two different solutes, although for both cases the processes are controlled by dynamics of the solute boundary layer.

6.1 Introduction

Designing materials for a specific application requires the control of the resultant microstructure in crystalline material. In addition to phase distribution, size, and morphology, crystal orientation also plays a crucial role in determining the behavior of the material since the response to an external stimuli is mostly anisotropic. So, it is desired to have large single crystal with desired texture in many technological areas.

Among many different methods, crystal growth from an alloy melt in an ampoule has been dominantly used for producing single crystals since it was offered by Tammann in 1925 [1], applied by Bridgman [2], and improved by Stockbarger [3]. This
method is long established because it can be applied to nearly all of the elemental materials, and congruently melting compounds and also because of relatively easier control of solidification conditions [4, 5]. However, texture selection by directional growth of crystal from an alloy melt requires a control over the nucleation of the crystal. Using a pre-grown crystal with desired texture as a seed is frequently applied method in crystal growth from an alloy melt. Seeding is mostly not required for Bridgeman-Stockbarger method because along the thermal gradient one specific crystalline orientation is selected over the others [6]. Still, it can be necessary for slow velocities where the texture selection transient may require longer lengths than the finite length of the directional solidification furnace.

Early-stage dynamics and initial conditions, which may have crucial effect on final solidification microstructure [7-11], becomes much more important for the seeding process to achieve targeted texture. One of the main issues that can be faced is the single-phase layer formation at the seed/liquid interface during stationary holding period for thermal and compositional homogenization of the melt prior to the pulling [7,8, 10-13]. Characteristics of this layer can change the early growth of the eutectic by changing the undercooling [11]. The presence of single phase (SP) layer has been reported in many experimental studies, mostly attributing its presence to off-eutectic composition or change in growth velocity [11]. These explanations are based on the assumption on stability of the stationary solid/liquid interface in a thermal gradient. However, when the compositional and surface energy requirements of the interface stability are considered, it can be said that this is an oversimplification of the interface dynamics that could take place during a stationary hold [11].

The knowledge on this aspect of directional solidification is limited to thin samples in binary alloys. In these studies, it has been shown that the single phase layer starts to form
immediately upon cessation of pulling by coarsening of the prior structure, coalescence of like-phase features, and formation of a continues single phase layer. Also, the thickness of this layer is shown to be dependent on holding time monotonically, in addition to the fact that its growth continues upon pulling until it is interrupted by eutectic growth [11].

In the current study, the first systematic study on formation of single phase layers in a metallic bulk sample is presented. By controlling solidification parameters, pulling velocity and thermal gradient, and varying holding times, the characteristics and formation mechanisms of single phase layers are investigated.

6.2 Experiments

We have investigated the single-phase formation during a stationary hold in a thermal gradient with multiple alloy compositions in the Al-Cu-Ag system. The alloys used are binary eutectic (BE) Al-Cu with the composition of Al-17at% Cu, binary eutectic (BE) Al-Ag with the composition Al-35at%Ag, ternary eutectic (TE) Al-12.8at%Cu-18.1%Ag, and univariant Al-16.55at%Cu, 2.82at%Ag. Alloys with different compositions were pulled along a thermal gradient at constant velocities with intermediate annealing periods, which are followed by quench, by use of a vertical directional Bridgeman-type furnace equipped with a liquid-metal-cooling chamber. Rods which would be directionally solidified were melted from high-purity elements in a boron-nitride-coated (BNC) clay crucible in air and then cast in a steel mold into rods of 5 mm diameter and 260 mm length. For directional solidification an alumina crucible with a 5.5 mm inner diameter and an 8 mm outer diameter was used.

The procedure of experiments with invariant eutectic composition were pulling of samples with a constant velocity for 10 mm, and holding for a period of time, and quenching for 15 mm, and repeating the procedure with different annealing times. For a DS run the pulling
and quench velocity were constant, whereas four different hold times, resulting in four different single phase layers were employed. The different pulling velocities used were 0.002, 0.005, 0.012 mm/s, whereas quench velocity was 20 mm/s. Holding times were varied from 5 to 60 minutes. By changing the furnace set temperature, two different thermal gradients in the melt was achieved. For the univariant eutectic (UA), we held the sample stationary for 4 hours, quenched and then pulled with a constant velocity of 0.002 mm/s both parallel and anti-parallel to the gravity. List of DS-runs with experimental parameters are summarized in Table 8.

**Table 8.** Summary of experimental conditions for the test alloys used in the study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thermal Gradient (K/mm)</th>
<th>Pulling Velocity (mm/s)</th>
<th>Hold Times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE Al-Cu</td>
<td>11</td>
<td>0.002</td>
<td>10, 20, 40, 60</td>
</tr>
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<td>BE Al-Cu</td>
<td>11</td>
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<td>BE Al-Cu</td>
<td>11</td>
<td>0.002</td>
<td>10, 20, 40, 60</td>
</tr>
<tr>
<td>BE Al-Cu</td>
<td>11</td>
<td>0.002</td>
<td>5, 15, 30, 50</td>
</tr>
<tr>
<td>TE Al-Cu-Ag</td>
<td>11</td>
<td>0.002</td>
<td>5, 15, 30, 50</td>
</tr>
<tr>
<td>TE Al-Cu-Ag</td>
<td>11</td>
<td>0.005</td>
<td>10, 20, 40, 60</td>
</tr>
<tr>
<td>TE Al-Cu-Ag</td>
<td>11</td>
<td>0.012</td>
<td>10, 20, 40, 60</td>
</tr>
<tr>
<td>TE Al-Cu-Ag</td>
<td>7</td>
<td>0.002</td>
<td>10, 20, 40, 60</td>
</tr>
<tr>
<td>BE Al-Ag</td>
<td>11</td>
<td>0.002</td>
<td>10, 20, 40, 60</td>
</tr>
<tr>
<td>BE Al-Ag</td>
<td>11</td>
<td>0.002</td>
<td>5, 15, 30, 50</td>
</tr>
<tr>
<td>UA Al-Cu-Ag</td>
<td>11</td>
<td>0.002</td>
<td>240</td>
</tr>
</tbody>
</table>
In early trials, the samples were fractured while they were taken out from the alumina crucible because of the high brittleness of single-phase layers. As a remedy, the samples were sectioned and mounted with crucible. In order to observe the longitudinal section of the samples, alumina crucibles were ground through until directionally solidified rods were reached. Following to this, the longitudinal sections were metallographically prepared without etching and optical images were taken for determination of thickness of the single phase layers. In detection of single phase layers’ thickness, an image analysis code using the contrast difference between eutectic mixtures and single phase layers used.

6.3 Results and Discussion

The longitudinal and transversal examination showed that single-phase layers were roughly homogeneous in the transverse direction and heterogeneous in the growth direction. The compositional characterization of the single phase layers were revealed that they formed of intermetallic compounds in the phase diagram. In binary Al-Cu eutectic, the single phase layer was Al$_2$Cu, in the binary Al-Ag eutectic, it was Ag$_2$Al, and in ternary eutectic it was a mixture of Al$_2$Cu and Ag$_2$Al.

By examining different holding times, we revealed that as a single-phase layer grows, it is possible to observe three different regimes: a non-continuous regime, a banded regime, and a continuous regime. However, it should be stated all of the regimes were not observed at all compositions. Namely, in BE Al-Ag a non-discrete layer was never observed, whereas in TE a banded regime was not observed between non-continuous and continuous layers. Examples for different regimes were shown in Figure 70.

In addition to changing characteristics of the layer, different holding times results in very different layer thicknesses (Figure 71). The thickness of the single-phase layers increased
linearly with holding time for all compositions. It is also possible to see the effect of composition on layer formation from Figure 71. The compositional dependence showed that for short holding times, namely holding times less than 30 minutes, the type of alloy had no major effect on thickness of single phase layer. This is related to the fact that the single phase layers formed after short holding times are results of solute boundary layer which is expected to be very small for any eutectic composition. When holding times increased, TE alloy started to form a relatively thicker layer. The thicker single-phase layer in ternary eutectic can be explained by the formation of this layer as combination of these two intermetallic compounds. The solute solubilities of Ag in Al$_2$Cu and Cu in Ag$_2$Al are much smaller than those in Al(fcc) which is the common phase in all three systems. So, as the composition reached at a point where one of these compounds formed, there was a high rejection of the solute, Ag for Al$_2$Cu and Cu for Ag$_2$Al, which ends in formation of other compound easier.

The pre-growth velocity dependence studies were performed at TE composition for further understanding of the effects of pre-existing structure and solute boundary layer on formation of single phase layers. Lower growth velocity created a longer solute boundary layer and a coarser structure, whereas high growth velocities ended up giving a shorter boundary layer and finer structure. The length of solute boundary layer and scale of structure had inverse effects on thickness of single phase layer. For faster growth velocity, the extend of solute boundary layer was shorter than that of slower growth velocity at any distance from solid/liquid interface, however it is more enriched with respect to solute. The dependence of single-phase layer thickness on pre-growth velocities (Figure 72) showed that for shorter holding times the more solute-rich boundary layer resulted in a higher thickness. However, for intermediate and long holding times, the solute boundary layer thickness happened to be a much more effective
factor than the content of the solute boundary layer. As holding times increased the lighter solute, Cu in this case, floated through the thermal gradient leaving the liquid at the front enriched with second solute and this caused formation of Ag$_2$Al at the front resulting rejection of more Cu and initiating formation of Al$_2$Cu on top of it. Figure 5 shows the almost periodic characteristic of Al$_2$Cu and Ag$_2$Al phases in single-phase layer after short annealing times, and how they stacked over each other after long annealing for pre-growth velocity of 0.002 mm/s. Since this would not be possible with shorter but more-solute-rich boundary layers, an almost reverse relationship between boundary layer thickness and pre-growth velocity was established for longer annealing times.

This hypothesis was assessed by examining the effect of thermal gradient on solute boundary layer thickness with TE alloys again as it is shown in Figure 73. Thermal gradient, which was controlled by furnace set temperature, had a strong influence on the growth of single-phase layers. The furnace set temperature of 900$^\circ$C corresponded to a gradient in the liquid around 11 K/mm, whereas 700$^\circ$C created a gradient of 7 K/mm in liquid. The thermal gradient seemed to affect the incubation time strongly which is again related to presence of solute boundary layer. The lower thermal gradient would dictate a lower increase in temperature along the solute boundary layer, longer times were required for formation of single-phase layers. Also, decreased thermal gradient resulted in less buoyance convection driven float of lighter solute and results in slower single-phase layer formation kinetics.

Also, the examination of quench front following to four hour hold in univariant alloys showed the importance of solutal configuration on the formation of single phase layers. Figure 75 shows the solid/liquid interface after 4 hour hold for both against and parallel gravity pulling. No single phase formation even after four hour hold was observed in the sample pulled
against gravity was observed. The alloys at this composition forms Al(fcc) and Al\textsubscript{2}Cu eutectic in a coupled manner by exchanging species and also rejecting Ag to the liquid at the front. So, the solute boundary layer was rich with respect to Ag, which avoided the formation single-phase layers for short holding times, since the liquid was not enriched with the solute which could form a solid phase in equilibrium with the liquid. Also, with increasing time, no floatation of the solute could take place since it was heavier than the liquid. As a result of this, no single phase layer could form. Again no single phase formed at the quench front was examined whereas in the solid due to coarsening and dissolution a non-continuous single phase layer was observed when the sample pulled parallel the gravity.

6.4 Summary and Conclusion

Single phase layer formation in metallic bulk directionally solidified samples were investigated by using different alloy compositions in Al-Cu-Ag ternary system having different number and species of solutes. The thickness of SP layers was measured following different stationary hold periods in different alloys, which were solidified using different growth velocities and thermal gradients. The single-phase layers formed characterized as Al\textsubscript{2}Cu in BE Al-Cu, Ag\textsubscript{2}Al in BE Al-Ag, and a mixture of Al\textsubscript{2}Cu and Ag\textsubscript{2}Al in TE Al-Cu-Ag. Three different regimes during formation of single phase layers are observed. These are (i) a non-continuous layer associated with short annealing times, (ii) a banded layer consisting of two single phase layers divided by eutectic structure formed after intermediate annealing times, and (iii) a continuous layer which covers the complete solid/liquid interface and formed as a result of long annealing times. The dependence of single-phase layers on composition, annealing time, pre-growth velocity, and thermal gradient showed that the single-phase layer
formation was controlled by solute boundary layer in the liquid ahead of solid/liquid interface. We have shown that the solute boundary layer should be rich with respect to solute which can a form solid in equilibrium with the liquid. Also, the thickness of the single phase layers was shown to be dependent on the parameters the same way the solute boundary layer depends on them showing that single-phase layer formation is controlled by solute boundary layer dynamics.
References


Figure 70. Regimes observed during SPL growth in different eutectics for different times. a) Non-continuous in TE 10 minutes hold, b) Banded in Al-Cu BE 30 minutes hold, c) Continuous Al-Ag$_2$Al binary grown 60 minutes hold.

Figure 71. Effect of holding time on thickness of single phase layer for different alloy compositions.
Figure 72. Single-phase layer thickness variation with holding time for TE alloy for varying pre-growth velocity.

Figure 73. Effect of thermal gradient on SPL thickness with time. Pre-growth velocity was 0.002 mm/s.
Figure 74. Single phase layers observed in ternary eutectic Al-Cu-Ag (a) 40 minutes (b) 60 minutes. Pre-growth velocity is 0.002 mm/s.

Figure 75. Solid/liquid interfaces observed in univariant samples after four hour hold and subsequent quench with pulling direction a) Anti-parallel, b) Parallel to the gravity.
CHAPTER 7. SUMMARY AND CONCLUSIONS

Directional solidification structures are good candidates for advanced function which require homogeneous and directional properties, whereas they continue to be used expansively for conventional applications. Our fundamental understanding on solidification structures has been mostly built on single phase formation or coupled growth in peritectic or eutectic alloys, whereas the understanding on multiphase solidification is very limited and there are many open questions regarding spatiotemporal evolution of these complex structure. The present research is primarily concerned with microstructural evolution and interface dynamics in directionally solidified invariant and univariant eutectics in Al-Cu-Ag system.

One of the focus of this dissertation is quantification and parameterization of ternary invariant eutectic structures. Due to substantial changes in these structures due to solid-state reactions taking place after solidification with these alloy composition due to steep solvus of Al(fcc) phase, we first quantified these post-solidification effects and built a correlation between the near-front and far-away-front structures. The quantification of the changes in the microstructures showed that because of these solid state effects, the growth morphology can be only maintained within a few millimeters of the quenched growth front. For the experimental conditions employed, microstructural parameters such as phase composition, phase fraction, and relative phase boundary length showed strong deviation from the true growth structure with distance from the interface, with the most dramatic changes observed over the first 15 mm. In order to correlate between solid-state affected structures and front structures, a cellular automaton was developed providing reasonable estimation of the structure at the growth front based on the structure measured at some known distance behind the front.
The examination of ternary eutectic structures in the velocity range of 0.0002 mm/s to 0.020 mm/s showed that two different morphologies, semi-regular brick and half-lamellar, were present on this range and the transition between morphologies took place gradually starting around 0.001 mm/s. The quantification of the microstructural parameters, namely spacings, thicknesses, and caliper lengths, showed a linear relationship with velocity in the logarithmic scales, whereas different phases had different dependencies. This point revealed that a scaling parameter covering all phases was necessary to truly characterize the structure. We suggested geometric mean of phase spacing as the new scaling descriptor of the structure. None of the above mentioned parameters was observed to show a discontinuity on their dependence to velocity with the morphology change. So, by considering the changes in the morphology of phases we suggested angular order and angular orientation of two-phase boundaries with respect to each other as the parameters to distinguish between different morphologies. Finally, the change in morphology with increasing velocity was shown to be a result of scaling optimization by use of diffusion cell triangles and spacing correlations.

Another focus of the current work is effect of gravity and convection on solutal configuration of univariant eutectics during directional growth. Firstly, the radial thermal gradient was shown to be very effective on solute profile in the liquid along solid/liquid interface by causing natural convection and disturbing the diffusive solute boundary layer. The steady-state solute profiles in liquid was different at different locations of the interface being in accordance with the convex shape of it. This positional dependence of composition was reflected on the morphologies. The
periphery of the samples were subjected to segregation of Ag and formation of ternary eutectic structures were observed, whereas the central regions shifted to hypoeutectic compositions and caused formation of single phase. These single phases also floated to the higher temperatures as a result of buoyancy driven convection. While these were the convection-related effects observed in a standard vertical directional solidification, the increased convection by changing pulling direction from against to parallel to gravity delayed transition to cellular front, overcame radial gradient and homogenized the front composition, whereas smaller sample size was not completely effective for the latter during vertical growth against gravity.

We have also studied on the texture selection in binary eutectic alloys by focusing on the grain competition during directional solidification, in which morphological transient like grain selection, spacing optimization, and topological evolution were characterized. The grain selection transient was found to be completed with the spacing, whereas spacing was effective on the grain competition among different grains. The topological order quantification showed that the preferred grains have higher angular order and lower radial order in comparison to the eliminated ones. Higher radial order of the grains other than preferred ones showed that they are less responsible to dynamic requirements of advancing solid/liquid interface. In addition to this, examination of the grain boundaries revealed that type and velocity of a boundary were determined by how the lamellae in two grains were aligned with respect to each other and how large was the difference in their angular order. As a mechanism for grain boundary motion, we suggested that the selected grains were growing at the expense of others by the perturbations on the lamellae of the shrinking grain on the grain boundary aligned the direction of the growing grains’ lamellae.
Finally, we have focused on the effect of pre-growth holding period during directional growth of eutectics, since this can change the early-stage dynamics during directional growth. The holding period was resulted in formation of single phase layers, the characteristics of which depends on composition, annealing time, pre-growth velocity, and thermal gradient. The single-phase layers formed characterized as $\text{Al}_2\text{Cu}$ in BE Al-Cu, $\text{Ag}_2\text{Al}$ in BE Al-Ag, and a mixture of $\text{Al}_2\text{Cu}$ and $\text{Ag}_2\text{Al}$ in TE Al-Cu-Ag. Three different regimes of single phase layers were observed during formation: non-continuous, banded, and continuous. The single-phase layer formation was controlled by solute boundary layer in the liquid ahead of solid/liquid interface and in order to form a single-phase layer, the solute boundary layer should be rich with respect to solute which can a form solid in equilibrium with the liquid.

7.1 Remaining Important Questions

What can be a more effective way of characterization of complex multiphase structures? Is it possible group them by using statistical tools like principal component analysis?

What is stability regions of different phases and morphologies in ternary eutectic Al-Cu-Ag system?

What are the contact angles of Al(fcc), Ag2Al, Al2Cu at the solidification front for semi-regular brick structure and half-lamellar structure?

What is the effect of crystallographic orientation on ternary eutectic morphologies?
What are the responsible mechanisms for a transition from planar to cellular front in univariant eutectics? How is this different from the same transition observed in single-phase materials? How are the topologic order effective on the transition?

What is the actual flow characteristics during a directional solidification experiments? How can it be quantified and used in understanding its effect on univariant growth?

What is the mechanism for transition from maze-like to lamellar growth in the early stages of directional binary eutectic growth?

How are the lamellar faults effective on grain selection?

How can the characteristics of single phase layers changes the initial-stage dynamics of the eutectic growth in 3-dimensions?