# Near-surface Microstructure of Cast Aluminum and Magnesium Alloys

### NEAR-SURFACE MICROSTRUCTURE OF CAST ALUMINUM AND MAGNESIUM ALLOYS

BY

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To my wife and parents

#### Abstract

Crystal growth has been recognized as a paradigm for non-equilibrium pattern formation for decades. Scientific interest in this field has focused on the growth rates and curvature of branches in snow flake-like structures patterned after a solid's crystallographic orientations. Similar patterns have been extensively identified in solidification of metals and organic metal analogues and are known as dendrites, which is originated from a Greek word *dendron* meaning tree.

Dendritic spacing and morphology established during casting often sets the final microstructure and second phase formation that develops during manufacturing of alloys. This is particularly true in emerging technologies such as twin belt casting of aluminum alloys, where a reduced amount of thermomechanical processing reduced the possibility of modifying microstructure from that determined at the time of solidification. Predicting and controlling these microstructure of cast alloys has thus been a driving force behind various studies on solidification of materials.

Mg-based alloys are another class of materials gaining importance due to the high demand for weight reduction in the transportation industry which accordingly reduces the gas consumption. While the solidified microstructure and its effect on the material properties have been the subject of intensive studies, little is known about the fundamental mechanisms that determine dendritic microstructure in Mg alloys and its evolution under directional growth conditions.

This thesis investigates the relationship between the microstructure and cooling conditions in unsteady state upward directional solidification of Al-Cu and Mg-Al alloys. The four-fold symmetry of Al-Cu alloys are used to study the dynamical spacing selection between dendrites, as the growth conditions vary dynamically, whereas, the Mg-Al system with a six-fold symmetry is used to study a competition between neighbouring, misoriented grains and the effect of this as the resulting microstructure. Mg-Al also presents a situation wherein the cooling conditions dynamically vary from the preferred crystallographic growth direction. Analysis of phase field simulations is used to shed some light on the morphological development of dendrite arms during solidification under transient conditions. Our numerical results are compared to new casting experiments.

Chapter three studies spacing selection in directional solidification of Al-Cu alloys under transient growth conditions. New experimental results are presented which reveal that the mean dendritic spacing versus solidification front speed exhibits plateaulike regions separated by regions of rapid change, consistent with previous experiments of Losert and co-workers. In fact, The primary spacing of a dendritic array grown under transient growth conditions displays a distribution of wavelengths. As the rate of change in solidification front velocity is decreased, the evolution of the spacing follows the prediction of the geometrical models within a band of spacing fluctuations. The width of the band is shown to highly depend on the rate of the solidification front velocity acceleration, such that the higher the rate, the wider the band of available spacings. Quantitative phase field simulations of directional solidification with dynamical growth conditions approximating those in the experiments confirm this behavior. The mechanism of this type of change in mean dendrite arm spacing is consistent with the notion that a driven periodically modulated interface must overcome an energy barrier before becoming unstable, in accord with a previous analytical stability analysis of Langer and co-workers.

In chapter four, it is demonstrated both computationally and experimentally that a material's surface tension anisotropy can compete with anisotropies present in processing conditions during solidification to produce a continuous transition from dendritic microstructure morphology to so-called seaweed and fractal-like solidification microstructures. The phase space of such morphologies is characterized and the selection principles of the various morphologies explored are explained. These results have direct relevance to the microstructure and second phase formation in commercial lightweight metal casting.

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### Chapter 1

# Introduction and Problem Statement

Continuous casting and subsequent rolling has been applied for many years to produce metal strips which are relatively surface finished. Conventional slab casting, thin slab casting, twin-roll casting, single-belt casting and twin-belt casting are the five different technologies being used for hot strip production as illustrated in figure 1.1 and 1.2.

In conventional and thin slab casting, casting is done in a stationary mold and the slab thickness is large. Therefore, more hot rolling is needed to obtain the final thickness and the casting rate is lower. In the other three processes, stationary molds have been replaced by traveling molds and the casting rate is much higher (Schwerdtfeger, 1998). However, the casting rate in two-roll process is still low and prohibits in-line rolling.

Twin-belt casting is an alternative for two-roll casting which provides a higher production rate compared to two-roll process. It was first employed commercially for aluminum in 1959. The twin-belt system consists of two carriages, each one having a steel or copper belt around. The molten metal is fed between the top and bottom belts and the mold heat extraction is done by water-jet cooling on the back side of each belt. The thickness of the strip can be controlled by the carriage spacers from 3/8" to 3" (Petry C.J., 1986; Gal, 1989). Figure 1.2 indicates a twin-belt system being used by Hazelett Company.

The major advantages of twin-belt casting are low maintenance, choice of continuous operation, possibility of in-line hot rolling and improved cross-section homogeneity and dimensional tolerance. However, since in twin-belt casting the slab is very thin, the possibility of utilizing two or more hot rolling stages for improving the microstructure decreases and thus the need of a very good as-cast microstructure production appreciably increases.

Dendritic solidification has been a well accepted paradigm for many non-equilibrium interface pattern formation phenomena (Burden M.H., 1974; Hunt, 1979; Langer, 1980; Ben-Jacob E., 1990; Losert W., 1996; Trivedi R., 2002; Granasy L., 2003, 2004; Haxhimali T., 2006; Amoorezaei M., 2010; Gurevich S., 2010b). Dendritic microstructures are formed in most alloys during processes such as casting and welding. The complex patterns created by the dendritic network leave their signature on the distribution of secondary phases that form in the inter-dendritic spaces that contain supersaturated liquid pools due to solute rejection in the late stages of solidification. As a result, understanding the mechanisms for morphological selection of dendritic structures will be key in the development of next-generation lightweight alloys of aluminum and Magnesium used in automotive and aerospace applications. The word dendrite is originated from the Greek word dendron meaning tree, which is owing to the tree-shape of dendrites. It is very important to know how these structures develop



Figure 1.1: Different technologies applied to manufacture hot strip products (Schwerdtfeger, 1998).



Figure 1.2: A typical twin belt caster (www.hazelett.com).

and how different length scales of a cell or dendrite affect the properties of a solidified alloy. These length scales are dendrite tip radius ( $\rho$ ), primary arm spacing ( $\lambda_1$ ) and secondary arm spacing ( $\lambda_2$ ). Many attempts have been made to correlate these length scales with characteristic lengths of different physical processes. These physical processes are thermal and solute diffusion, liquid convection, interfacial energy and also interface attachment kinetics.

Solidification microstructures are controlled by the aforementioned physical processes. These physical processes have characteristic lengths associated with them being the solute diffusion length  $(l_D = \frac{2D}{V})$ , the thermal length  $(l_T = \frac{2\alpha}{V} \text{ for an un$  $dercooled melt and } l_T = \frac{\Delta T_0}{G}$  for directional solidification) and the capillary length  $(d_0 = \frac{\Gamma c_p}{L_f} \text{ for a pure material and } d_0 = \frac{\Gamma}{\Delta T_0} \text{ for an alloy})$  where  $\Gamma$  is the Gibbs-Thomson coefficient,  $\Delta T_0$  is the equilibrium solidification range  $(T_L - T_S)$ ,  $c_p$  is the specific heat,  $L_f$  is the latent heat of fusion,  $\alpha$  is the thermal diffusivity, V is the growth velocity and G is the thermal gradient. Typical values of different scales in directional solidification are given in figure 1.3.

In isolated dendritic growth, the controlling parameters are undercooling and surface energy anisotropy (see below). In directional solidification, V and G are the controlling parameters; the former affects only the solute diffusion length and the latter influences the thermal length only. Figure 1.4 shows the dependence of the different characteristic lengths on growth rate (Trivedi R., 1994b).

It has been conjectured (largely empirically) that all microstructural length scales such as primary and secondary dendrite arm spacing, dendrite tip radius and also dendritic transition conditions can be written as:  $L = A[l_D]^a[l_T]^b[d_0]^c$  where a, b and c are constants whose sum equals unity (to satisfy the dimensions) (Trivedi R., 1994a).



Figure 1.3: Typical values of different scales in directional solidification (Gurevich, 2006). Note that  $\Lambda$  corresponds to the primary spacing ( $\lambda_1$ ) in this thesis.



Figure 1.4: Dependence of the different characteristic lengths on growth rate.(Trivedi R., 1994b)

For instance, in case of dendrite tip radius and primary spacing at high velocities it has been found that a = c = 0.5 and b = 0. Moreover, near the limit of planar growth at low growth rates the solute diffusion length is twice the thermal length. This limit at high velocities satisfies  $l_D = 2kd_0$ , where k is equilibrium distribution coefficient. Many of the experiments and theories in solidification microstructure research focus on the developments of models related to the equation above. To date a unified and self-consistent understanding of dendritic growth, dendritic spacing selection and growth rates still eludes us.

#### 1.1 Single dendrites: modelling and experiment

Theoretically, the time evolution of dendrites can be determined by solving the solute and thermal diffusion equations for both solid and liquid phases considering the appropriate initial and boundary conditions. Different assumptions are usually included to simplify the equations and take a specific aspect of the growth rate into account. One of these assumptions is that the dendrite grows at a constant velocity and the shape of the dendrite is preserved during growth. This model is known as quasisteady-state model which only considers a branchless dendrite, i.e. this model neglects the interaction between the side branches and the dendrite tip. If this interaction is sufficiently small, a quasisteady-state model can provide a reasonable approximation of the dendrite tip shape ( $\rho$ ) and growth rate (V).

The Ivantsov equation (Ivantsov, 1947) was the first attempt to model a single dendrite of a pure material. It arises from the solution of the diffusion equation solved for an isothermal parabolic needle growing under steady state condition (It should be noted that for a pure material a steady-state solution of the diffusion equation for a planar or spherical front growing into an undercooled melt is lacking). This equation can be written as:

$$\Delta T = \left(\frac{L_f}{C_p}\right) Iv(p_t) + \frac{k\Delta T_0 Iv(p)}{1 - (1 - k)Iv(p)}$$
(1.1)

where the function  $Iv(p) = p \exp(p)E_1(p)$  and  $E_1(p) = \int_p^{\infty} \frac{e^{-y}}{y} dy$ ,  $p = \frac{V\rho}{2D}$  is the solutal Peclet number and  $p_t = \frac{V\rho}{2\alpha}$  is the thermal peclet number. Adding the capillarity to equation 1.1, a modified Ivantsov equation can be obtained:

$$\Delta T = \left(\frac{L_f}{C_p}\right) Iv(p_t) + \frac{k\Delta T_0 Iv(p)}{1 - (1 - k)Iv(p)} + \frac{2\Gamma}{\rho}$$
(1.2)

The first two terms in equation 1.2 are undercooling due to thermal and solute diffusion processes respectively and the third term is the undercooling due to capillarity.

Since the Ivantsov equation is a steady state solution for an isothermal interface and the capillary term causes the interface not to be isothermal, the capillary modification in equation 1.2 is not a rigorous solution. Furthermore, this equation correlates tip undercooling with solute and thermal peclet numbers, i.e. tip undercooling vs.  $\rho V$  product, rather than individual  $\rho$  and V. Similar to any other isothermal models, this model is not able to predict both dendrite tip radius and velocity as a function of undercooling.

More accurate but still approximate solutions that account for a non-isothermal dendritic interface have been offered by Trivedi (Trivedi, 1970, 1969), Temkin (Temkin,

1960) and Nash and Glicksman (Nash G.E., 1974). The main difficulty involved in the non-isothermal interface models is that unlike the isothermal interface problem, the interface shape is only determined by a highly non-linear integral equation that has no analytical closed form solution. Moreover, the solution of the non-isothermal steady state problem also does not give a unique value for V and  $\rho$ , as evidenced by experimental findings, and instead it only introduces a family of solutions,  $V = f(\rho)$ . As a result, researchers have sought another criterion to uniquely identify V and  $\rho$  as a function of process parameters (undercooling) and materials parameter (surface energy anisotropy or interface attachment kinetics). One such criterion is called the "maximum growth rate criterion", which in conjunction with the above model provides unique values for the dendrite tip radius and growth rate.

Oldfield (Oldfield, 1973) proposed that the conventionally used maximum growth rate criterion be replaced more generally by a stability criterion " $V\rho^2 = constant$ " based on the balance between the stabilizing effect of capillarity and destabilizing effect of solute diffusion (or heat conduction). Oldfield's result was verified both experimentally (Somboonsuk K., 1984) and analytically (Langer J.S., 1977, 1978b; Langer, 1980).

Langer and Muller-Krumbhaar offered a similar stability criterion which was first motivated by a linear stability analysis on a planar interface perturbed by sinusoidal ripples of infinitesimal amplitude, known as Mullins and Sekerka analysis (Mullins W.W., 1964). This analysis gives rise to the following equation:

$$\frac{wl_D^2}{2D} = -2k + \left(-1 + 2k + \sqrt{1 + q^2 l_D^2 + \frac{wl_D^2}{D}}\right) \left(1 - \frac{d_0(1-\varepsilon)}{2l_D}q^2 l_D^2 - \frac{l_D}{2l_T}\right)$$
(1.3)

where k is the partition coefficient,  $\varepsilon$  is the surface energy anisotropy strength,  $q = \frac{2\pi}{\lambda}$ is the wavelength of the perturbations and w(q) is the growth rate of the perturbations. All the wavelengths which result in a negative w(q) will shrink to a planar interface, whereas the ones giving rise to a positive w(q) are unstable and ultimately form cells or dendritic branches. The shortest wavelength for planar instability can then be obtained as  $\lambda_s = 2\pi \sqrt{l_D d_0}$  in which  $l_D$  is the diffusion length and  $d_0$  is the capillary length. It was then suggested that the tip radius can be scaled with  $\lambda_s$  such that  $\rho \simeq \lambda_s$ . Under this "marginal stability criterion", the dimensionless stability parameter  $\sigma$  was defined as  $\sigma = \frac{l_D d_0}{\rho^2}$ , which provides a second equation relating the tip velocity to the tip curvature. The parameter  $\sigma$  equals  $(\frac{1}{2\pi})^2$ , which is in good agreement with the direct calculated value of  $\sigma^* = 0.025 \pm 0.005$  based on linear stability analysis of the steady state solutions (Langer J.S., 1977). However, there are still some uncertainties in determining the exact value of  $\sigma^*$ . It was found that very fast and sharp dendrites  $(\sigma > \sigma^*)$  tend to broaden and slow down to reach the value of  $\sigma = \sigma^*$  due to side branching effects whereas the broad and slow dendrites  $(\sigma < \sigma^*)$  undergo tip splitting instabilities to form the sharper dendrites (Langer J.S., 1978b). That means the dendrite tip is merely marginally stable against dendrite tip radius and velocity changes. Also, the stability criterion,  $\rho \simeq \lambda_s$ , is only valid for small peclet numbers, i.e.  $\rho \ll 1$ .

Later on, the theory of *microscopic solvability* offered a self-consistent method to obtain the parameter  $\sigma$ . This theory introduces capillarity into the sharp interface model for pure materials and shows that nontrivial steady state solutions exist only when a finite anisotropy of surface energy or interface kinetics is considered (Brower R.C., 1983; Ben-Jacob E., 1983, 1984). It also shows that the only linearly stable dendrite solution is the one with the fastest velocity (Kessler D.A., 1989; Brener E., 1991). Considering the aforementioned findings, for a pure dendrite growing into an undercooled melt the following approximation for V and  $\rho$  is obtained, which indicates that the parameter  $\sigma$  is only dependent on the surface energy anisotropy.

$$\rho = \frac{d_0}{\sigma_0} \frac{\varepsilon_4^{-7/4}}{p(\Delta)} \sim d_0 \frac{\pi}{\sigma_0} \Delta^{-2} \varepsilon_4^{-7/4}$$
(1.4)

$$V = \frac{2\alpha\sigma_0}{d_0}p^2(\Delta)\varepsilon_4^{7/4} \sim \frac{2\alpha\sigma_0}{\pi^2 d_0}\Delta^4 \varepsilon_4^{7/4}$$
(1.5)

where  $\sigma_0$  is a constant. The parameter  $\sigma$  at high values of undercooling depends also on the anisotropy strength of interface attachment kinetics. Figure 1.5 represents the effect of anisotropy on  $\sigma^*$ .



Figure 1.5: Effect of anisotropy on  $\sigma^*$  for  $\Delta = 0.45$ . (Karma A., 1998)

Different methods have been applied to measure the solid-liquid interface energy such as measurement of the maximum undercooling required for the onset of nucleation, the grain boundary groove method and also characterization of the equilibrium shape of liquid droplets in a solid or solid particles in a liquid. The first two methods are not applicable to measure the anisotropy of the interface energy. Liu et al. (Liu S., 2001) applied the last method by measuring the diameter of Al - 4wt%Culiquid droplets solidified on a single crystal single phase solid normal to < 001 >direction and determined the anisotropy to be 0.98%.

Figure 1.6 shows the growth rate as a function of dendrite tip radius for the three different steady state dendritic growth theories: Ivantsov equation (Ivantsov, 1947; Horvay G., 1961), modified Ivantsov equation, and the Temkin theory. The solid circle indicates the maximum growth rate criterion and the shaded rectangle is the approximate data obtained by different workers. The dashed line is the stability criterion offered by Langer and Muller-Krumbhaar and the open circle which is the intersection between the steady state curve and the constant  $\sigma$  curve for  $\sigma = 0.025$  is their theoretical prediction for V and  $\rho$ . As can be seen, the L-MK stability criterion is in a better agreement with experiments than the maximum velocity criterion which overestimates observed dendrite tip velocity by nearly an order of magnitude. The possible sources of errors can be the maximum velocity criterion itself, neglecting the effect of side branches and also neglecting the effect of anisotropy in growth kinetics (Langer J.S., 1977).



Figure 1.6: Dimensionless growth rate as a function of dimensionless tip radius for different steady state theories (Langer J.S., 1977). Note that solvability theory gives a line close to that obtained by the marginal stability theory.

### 1.2 Directional solidification: modeling and experiment

A significant number of experimental (McCartney D.G., 1981; Bell J.A.E, 1963; Bolling G.F., 1974; Seetharaman V., 1988; Eshelman M.A., 1988; Kirkaldy J.S., 1989; Bouchard D., 1996) and theoretical (Hunt, 1979; Kurz W., 1981; Trivedi, 1984; Makkonen, 1991, 2000; Spencer B.J., 1997, 1998, 1999) studies of directional solidification of alloys have been devoted to predict the relationship between primary arm spacing,  $\lambda_1$ , and growth rate. Many of them have claimed that the spacing as a function of velocity is reproducible or at least the change is very small. From the theoretical point of view, most studies have been based on the consideration of a steady state geometry for a dendrite array and have tried to relate the interdendritic spacing to the geometry and the fundamental length scales of the extended dendrite array. Kurz and Fisher (Kurz W., 1981) and Hunt (Hunt, 1979) offered similar equations that correlated  $\lambda_1$  with velocity, temperature gradient and solute concentration. These are reviewed next.

Kurz and Fisher (Kurz W., 1981) considered the cells and dendrites as an array of ellipsoids in which:

$$\rho = \frac{b^2}{a} = \frac{\lambda_1^2 G}{3\Delta T'} \tag{1.6}$$

where a and b are the radii of the ellipsoid, a being larger than b. They approximate a and b as,  $a = \frac{\Delta T'}{G}$  and  $b = \frac{\lambda_1}{\sqrt{3}}$ . Finally, by substituting for  $\rho$  from the marginal stability criterion (for alloys) they obtained the final result for two different velocity regimes. For low velocities  $\left(V_{tr} < \frac{V_{CS}}{k}, V_{CS} = \text{constitutional supercooling velocity}\right)$ they obtained:

$$\lambda_1 = \left[\frac{6\Delta T'}{G(1-k)}\right]^{\frac{1}{2}} \left[\frac{D}{V} - \frac{k\Delta T_0}{G}\right]^{\frac{1}{2}}$$
(1.7)

and for high velocities  $\left(V_{tr} > \frac{V_{CS}}{k}\right)$  they obtained:

$$\lambda_1 = 4.3\Delta T'^{\frac{1}{2}} \left[ \frac{\gamma D}{\Delta S k \Delta T_0} \right]^{\frac{1}{4}} V^{\frac{-1}{4}} G^{\frac{-1}{2}}$$
(1.8)

where  $\Delta T_0 = T_L - T_S$  and  $\Delta T'$  is the difference between tip temperature and the

temperature of the base of the dendrite.

Another theoretical model was developed by Hunt (Hunt, 1979) to characterize the primary spacing. Hunt made the assumption that the temperature and liquid concentration in the direction perpendicular to the growth direction of the primary stalk are constant which is valid only for the regions far behind the tip. The following relationship between the dendrite tip radius and the primary arm spacing was developed by Hunt based on this assumption:

$$\frac{G\lambda_1^2}{\rho} = -4\sqrt{2} \left[ mC_t(1-k) + \frac{DG}{V} \right]$$
(1.9)

where  $C_t$  corresponds to the solute concentration at the tip and G is the temperature gradient in the liquid.

Another assumption made by Hunt was that dendrites grow at the minimum undercooling for a given velocity. Based on this assumption, Hunt obtained a second expression for the primary dendritic spacing given by:

$$VG^{2}\lambda_{1}^{4} = -\left(\frac{64\gamma D}{\Delta S}\right) \left[mC_{0}(1-k) + \frac{kDG}{V}\right]$$
(1.10)

where  $\gamma$  is the interfacial energy,  $\Delta S$  is the entropy of fusion per unit volume. For velocities much higher than the critical velocity of planar instability,  $V \gg V_{CS}$ , equation 1.10 can be simplified to:

$$VG^2\lambda_1^4 = -\left(\frac{64\gamma D}{\Delta S}\right) \left[mC_0(1-k)\right]$$
(1.11)

The equation of Kurz and Fisher equation is very similar at high velocities to that by Hunt in that they both predict a same slope for  $\lambda_1 - V$  curve. However, the results are very different at low velocities, where based on the Kurz and Fisher model a sharp increase in  $\lambda_1$  with decreasing velocity occurs at  $V_{tr}$ , which was attributed to the dendrite-to-cell transition (Figure 1.7).



Figure 1.7: Primary spacing as a function of velocity for two theoretical models.(Burden M.H., 1974)

Figure 1.8 illustrates the comparison between the theoretical models by Hunt and Kurz and Fisher (only the high velocity regime) with experimental data in a succinonitrile-acetone system. As can be seen, the slope of the experimental line
is slightly higher than those of the theoretical lines. Furthermore, the Hunt model predicts a velocity for dendrite-to-cell transition that is around an order of magnitude lower than that observed experimentally.



Figure 1.8: A comparison between experimental data (points) and Hunt and K-F models (lines) for dendrite arm spacing.(Trivedi, 1984)

Another theoretical model was developed by Trivedi (Trivedi, 1984; Somboonsuk K., 1984) to correlate dendrite tip radius and primary arm spacing to the growth rate. This work first obtained an equation correlating the dendrite tip radius to the solute Peclet number ( $p = \frac{V\rho}{2D}$ ) by applying Burden and Hunt's approach (for a single dendrite). Then, to find a unique tip radius, he utilized the marginal stability criterion developed by Trivedi (Trivedi, 1980) and Kurz and Fisher (Kurz W., 1981), which can be expressed as:

$$-G + mG_c\xi_c = \left(\frac{2\gamma}{\Delta S\rho^2}\right)L\tag{1.12}$$

where L is determined for different crystallographic systems.  $G_c$  is the concentration gradient at the tip and  $\xi_c$  is a function of the Peclet number which for very small Peclet numbers equals unity. For regions where the effect of temperature gradient and capillarity is negligible, Trivedi's result can be simplified as:

$$V\rho^2 = \frac{(2\gamma DL)}{\Delta Sk\Delta T_0},\tag{1.13}$$

valid for  $p \ll 1$ . However, Trivedi's general equation indicates that at low velocities the effect of temperature gradient is important, whereas at high velocities capillarity plays a significant role. Trivedi's results showed a qualitative agreement with experimental data (Somboonsuk K., 1984) (Figure 1.9 and 1.10).



Figure 1.9: Variation of Peclet number with velocity. (Somboonsuk K., 1984)

It should be noted that the minimum in the Peclet number-Velocity curve was



Figure 1.10: Variation of tip radius with velocity. (Somboonsuk K., 1984)

attributed to the dendrite-cell transition by the author.

To find a unique relation between primary arm spacing as a function of velocity, Trivedi defined two dimensionless parameters  $\Lambda$  and A as  $\Lambda = \left(\frac{\lambda_1}{\rho}\right)\left(\frac{\lambda_1}{l_T}\right)$  and  $A = \frac{l_C}{l_S}$ where  $l_T = \frac{k\Delta T_0}{G}$ ,  $l_S = \frac{2D}{V}$ ,  $l_C = \frac{\gamma}{\Delta S k \Delta T_0}$ . Applying equation 1.9 and substituting the marginal stability criterion, Trivedi obtained the following equation which relates primary arm spacing to the tip radius for a given  $C_0$ , V and G:

$$\Lambda = \frac{4\sqrt{2}\,AL}{p^2} \tag{1.14}$$

Another relationship relating the tip radius to  $C_0$ , V and G was developed earlier by Trivedi (Trivedi, 1980) which can be expressed as follows:

$$\frac{1}{2}\varphi\Big[1-F_1(p)\Big] + \Big(\frac{AL}{p^2}\Big)\Big[1-F_2(p)\Big] = \Big[1-\phi(1-k)\Big]^{-1}$$
(1.15)

where  $\varphi = \frac{l_S}{l_T} = \frac{2GD}{Vk\Delta T_0}, F_1(p) = \left\{\frac{\phi(1-k)}{1-\phi(1-k)}\right\} \left\{ \left[\frac{(1-\phi)}{\phi-p+p\phi}\right] - \left(\frac{1}{\phi}\right) \right\}, F_2(p) = \left[\frac{2}{L}\right] \left\{\frac{\phi(1-k)}{1-\phi(1-k)}\right\} \left[1 + p - \left(\frac{p}{\phi}\right)\right]$  and  $\phi = pexp(P)E_1(p).$ 

Solving the equations 1.14 and 1.15 simultaneously enables us to find the variation of  $\lambda_1$  with velocity. The calculated curve and the experimental results are given in Figure 1.11. The theoretical curve predicts the maximum in  $\lambda_1$  whose position is very close to that observed experimentally in SCN - Aceton system. However, the slope of the experimental line in both low velocity and high velocity regimes is higher than that related to the theoretical calculations. Moreover, this curve has only been tested for one organic system.



Figure 1.11: calculated curve and the experimental results for primary arm spacing (Trivedi, 1984).

Such a maximum has also been observed in organic (Bechhoefer J., 1987; Kirkaldy J.S., 1995; Somboonsuk K., 1984; Eshelman M.A., 1988) and metallic systems (Klaren C.M., 1980; Mason J.T., 1984; Min Q., 2009) (in Pb-Sn, Pb-Au systems by Klaren et al., in Pb-Pd system by Mason et al., and in Al-Cu system by Min et al.). However, because the density difference in Pb-Sn and Pb-Au systems is large, which could cause convection within the liquid, the validity of Klarens results is under doubt. This maximum in  $\lambda_1$  corresponds to the minimum in solute Peclet number which indicates that the dendrite-cell transition velocity,  $V_{tr}$ , depends on the temperature gradient such that it increases with increasing gradient.

Makkonen (Makkonen, 1991, 2000) also performed a simple thermal balance on a moving interface considering an isotropic material with dendrite tip following a paraboloid of revolution (figure 1.12), and concluded that the primary spacing in steady state constrained solidification (Bridgman solidification, where the velocity and temperature gradient are imposed) is mainly determined by the heat balance and solute diffusion only indirectly influences the spacing through the tip radius selection. He recast the thermal balance in a moving reference frame:



Figure 1.12: Unit volume of a cubic dendrite array at the tip region (Makkonen, 2000).

$$L\frac{\partial f}{\partial x} = C_p \frac{\partial T}{\partial x} \tag{1.16}$$

where the solid fraction is obtained as

$$f = \frac{\int_0^{-x} \pi g^2(x) dx}{-x\lambda^2}$$
(1.17)

where  $g(x) = \sqrt{2Rx}$  for a paraboloid and R is the radius of the curvature. It was also shown that neglecting surface energy effects, the only possible steady state shape for an array of axisymmetric dendrites having a *unique* spacing is a paraboloid of revolution. Very close to the tip, this shape was shown to be quite accurate, even in the presence of the surface tension anisotropy, which causes some deviation from the parabolic shape away from the tip (Glicksman, 1984). Inserting eq. 1.17 into eq. 1.16 gives rise to the analytical solution of the spacing as:

$$\lambda = \left(\frac{\pi \Delta TR}{G}\right)^{1/2} \tag{1.18}$$

where  $\Delta T = L/C_p$  and  $G = \partial T/\partial x$ . A similar equation was suggested by Hunt (Hunt, 1979) and Kurz and Fisher (Kurz W., 1981) which offer the dependency of the spacing on the tip radius. The one suggested by Kurz et al. is very similar to eq. 1.18, the only difference is that  $\pi \Delta T$  has been replaced by  $3\Delta T_0$  in which  $\Delta T_0$  is the solidification range. This indicates that Kurz's model for constrained growth attributes the spacing selection to the transfer of solute atoms while Makkonen's model considers the thermal diffusion determining the steady state spacing establishment. Note that considering the empirically obtained criterion for a single dendrite  $V\rho^2 = constant$ , eq. 1.18 will yield the usual form of the well-known geometrical models, i.e.  $\lambda = aG^{-1/2}V^{-1/4}$ , where *a* is a constant which depends on the concentration. For directional casting where the heat is extracted from a chilling surface and the velocity and thermal gradient are not directly imposed, Makkonen obtained the following relationship for the spacing:

$$\lambda = \left(\frac{\pi \Delta TR}{G + \dot{q}/(C_p V)}\right)^{1/2} \tag{1.19}$$

where  $\dot{q}$  is the heat extraction rate per velume.

The aforementioned theoretical models neglect the effect of the surface energy anisotropy and the solutal interaction of neighbouring stalks in establishing the interdendritic spacing. Steinbach (Steinbach, 2008) showed that the spacing is affected by the strength of the anisotropy owing to the tip curvature dependence on the anisotropy and the spacing dependence on the tip radius, as suggested in the literature(Hunt, 1979; Kurz W., 1981; Makkonen, 1991, 2000). He plotted the tip radius and the critical spacing (the spacing at which the effects of the surface energy anisotropy and the neighbouring solute interactions balance, leading to the tip destabilization and a spacing readjustment mechanism such as cell elimination) as a function of the anisotropy strength and found that as the anisotropy is raised, both the tip radius and the critical spacing decrease, as depicted in figure 1.13. Extending the model in 3D, he also showed that the dependency of the spacing on the tip curvature is larger in 3D by a factor of  $\sim 1.87$ .



Figure 1.13: Effect of anisotropy strength on the critical spacing and tip radius of an array of dendrites modelled by the phase field method (Steinbach, 2008).

Experimental studies have also been done by different workers (McCartney D.G., 1981; Bell J.A.E, 1963; Bolling G.F., 1974; Kirkaldy J.S., 1989; Bouchard D., 1996) to find an appropriate correlation between primary spacing and velocity, temperature gradient and composition. McCartney and Hunt (McCartney D.G., 1981) offered the following empirical equation relating steady state primary spacing to pulling velocity:

$$\lambda_1 = 272 \, G_L^{-0.55} V^{-0.28} C_\infty^{0.31} \tag{1.20}$$

To make sure that the coarsening effect does not jeopardize the validity of their results, McCartney and Hunt quenched their samples before coarsening and then measured the primary spacing. To obtain the above equation, they plotted  $\lambda_1$  as a function of G,  $GV^{\frac{1}{2}}$  and  $C_{\infty}$  for different metallic systems and calculated the slopes

of the lines and finally fitted the data into their equation by fitting the constant coefficient.

Another experimental work was done by Kirkaldy (Kirkaldy J.S., 1989; Bouchard D., 1996) on binary organic alloys and under steady state condition. For high velocities, he offered the following equation which is a semi-empirical relationship obtained for succinonitrile-salol system:

$$\lambda_1 = a_1 \left( \frac{24 T_m(\varepsilon \sigma) D}{(1-K) H \rho V G C_0^{\frac{1}{2}}} \right)^{\frac{1}{3}}$$
(1.21)

where  $\sigma$  is the surface tension, H is the latent heat of fusion,  $\varepsilon \approx 6$  and  $a_1 \geq 1$  is a fitting parameter. Figure 1.14 plots the primary spacing as a function of velocity for two different compositions. The maximum in the curve was found to be ten times that of the Mullins-Sekerka instability.

Kirkaldy et al. also measured the secondary arm spacing and tip radius (Kirkaldy J.S., 1995) (Figure 1.15) as a function of velocity for the same organic system. Their results can be expressed as:

$$\lambda_2 = 2a_2\pi \left(\frac{4d_0}{C_0(1-k)^2} (\frac{D}{V})^2\right)^{\frac{1}{3}}$$
(1.22)

where  $d_0 = \frac{\sigma}{\rho H}$  and  $a_2 \ge 1$ .

Huang and Glicksman (Huang S.C., 1981a,b) have also pointed out that there is another scaling relationship between the initial secondary spacing and the dendrite tip radius of the form  $\frac{\lambda_2}{\rho} = 3.0$ , while Somboonsuk et al. (Somboonsuk K., 1984)



Figure 1.14: Primary spacing as a function of velocity for an organic system for two different compositions .(Bouchard D., 1996)



Figure 1.15: Secondary spacing and tip radius as a function of velocity .(Bouchard D., 1996)

reported the value 2.2 for this ratio which is very close to the value 2.1 obtained theoretically by LM-K (Langer J.S., 1978c). Since the secondary dendrites tend to coarsen with time (or distance away from the tip), only the initial spacing,  $\lambda_2$ , forming close to the tip can be related to the tip radius.

In a study done by M. Greenwood, M. Haataja and N. Provatas (Greenwood M., 2004) was attempted to generate the scaling relationship for primary arm spacing of the form  $\lambda_1 = A l_T^{\alpha} l_D^{\beta} d_0^{\gamma}$  into a so-called crossover scaling function, which can achieve different power-law limits in different dendritic regimes (dendritic and cellular). Their spacing also abandoned, for the first time, the notion of a steady state and unique spacing in favour of a statistical description of length scales. They obtained the following scaling function:

$$\frac{\lambda_1}{\lambda_C} = \frac{l_T}{l_D} f\left(\frac{l_T}{l_D} - \frac{l_T}{l_{D^*}}\right) \tag{1.23}$$

where  $l_{D^*} \equiv \frac{2D}{V_C}$  and  $\lambda_C$  and  $V_C$  are the steady state wavelength and velocity at planar-to-cellular transition respectively. Figure 1.16 illustrates the computed data and the inset indicates the experimental data obtained by Kirkaldy et al. (Liu L.X., 1995). The scaled  $\lambda_1$  versus the scaled function  $\frac{l_T}{l_D} - \frac{l_T}{l_{D^*}}$  is given in Figure 1.17.

For the selected  $\lambda_C$ , surprisingly, both experimental and computed data collapse onto the scaling function. This plot can predict a relationship between primary arm spacing and growth rate over an extensive range of pulling velocities, temperature gradients and alloy compositions, under steady growth conditions. This function covers both cellular and dendritic regimes. It was the first time that phase field was validated for directional solidification. Later on, Provatas et al. (Provatas N., 2005)



Figure 1.16: Computed primary spacing as a function of pulling speed. The inset represents the experimental data by Kirkaldy et al. (Liu L.X., 1995).(Greenwood M., 2004)



Figure 1.17: Computed and experimental data on *SCN* and *PVA* lying on the single scaling function.(Greenwood M., 2004)

also showed this scaling analysis to hold true in three dimensions, over a small range of pulling speeds near the maximum.

It is noteworthy that a similar approach to find a universal law of relationship between dendritic growth rate and dendrite tip undercooling has also been developed by Langer, Sekerka and Fujioka (Langer J.S., 1978a). They suggested that the velocity of a single dendrite growing in a pure melt be given by:

$$v = \left(\frac{2\alpha}{d_0}\right) V(\Delta) \tag{1.24}$$

Which for small peclet numbers becomes

$$V(\Delta) = \sigma^* p^2 \tag{1.25}$$

where V is a dimensionless function of the dimensionless undercooling  $\Delta = \frac{T_m - T_{\infty}}{\Delta T}$ and p is the thermal peclet number. Molecular attachment kinetics has not been included in this equation. Experimental data of ice and succinonitrile dendrites in Figure 1.18 indicates a good evidence for existence of such a universality of V. Since the data for different systems and different growth conditions lie on the same curve, it can be concluded that such a universal function exists. However, this universality can be obtained only when the molecular attachment effects, liquid convection and heat flow in the solid are negligible.



Figure 1.18: Dimensionless velocity as a function of dimensionless undercooling in SCN and ice (theory and experiment).(Langer J.S., 1978a)

### **1.3** History dependence of dendrite spacing

Warren and Langer (Warren J.A., 1990, 1993) believed that it is not possible to find a unique primary spacing as a function of growth conditions, because the branch spacing is sensitive to the history of evolution. They argued that no unique primary dendrite spacing exists at fixed growth conditions and instead, a continuous range of allowable states may exist. They pointed out that the selected state is determined by the sequence of events that provides the unique conditions for a particular system. In other words, pattern selection is history dependent and the final  $\lambda_1$  selected by the system is determined by the initial preparation of the systems and the sequence of pulling speeds imposed on the system after and before reaching steady state conditions.

Subsequently, Huang et al. (Huang W., 1993) experimentally showed that if directional solidification is carried out under the pulling speed of  $V'_p$  until the steady state array of dendrites develops and then the pulling speed is changed to a different value  $V_p$ , different values of primary spacing are obtained, depending on the selection of  $V'_p$ . Han and Trivedi (Trivedi R., 1994b) also observed that once the steady state array of dendrites is established, the pulling speed can be increased appreciably without significantly changing  $\lambda_1$ .

Other experiments done by Losert et al. (Losert W., 1996, 1998) were consistent with the two previous studies, demonstrating that there is no unique dynamical selection mechanism for  $\lambda_1$ . They showed that as  $V_p$  decreases from the steady state velocity, i.e.  $V_p \rightarrow V'_p$ ,  $\lambda_1$  remains constant until the velocity reaches a critical value,  $V_{p_{Cr}}$ , at which point the array becomes unstable such that every other stalk falls back, thus doubling the primary spacing. Figure 1.19 portrays a dendritic array before, during and after the period-doubling instability and Figure 1.20 indicates the step-wise decreasing of the pulling velocity and rms spread of the primary spacing vs. time.



Figure 1.19: dendritic array before, during and after the period-doubling instability.(Losert W., 1996)

Makkonen (Makkonen, 2000) claimed that because of the anisotropy in the surface energy, dendrite tips are slightly non-axisymmetric and deviate from a parabolic shape. Considering the fact that the paraboloid of revolution is the only possible steady state shape leading to a unique spacing selection (i.e. constant spacing between any two dendrites), this indicates that in directional solidification, no stable steady state dendritic array with a unique spacing is possible. However, he mentioned that since these deviations from a parabola are not large, the available spacing range is narrow. Moreover, he attributed the existence of a range of available spacing and history dependence of the spacing in the presence of the incremental changes of Vand G to the thermal hysteresis occurred in the system.



Figure 1.20: pulling velocity decrease steps (a) and rms spread of primary spacing vs. time (b).(Losert W., 1996)

For an array of dendrites, the parabolic shape is no longer retained at some distance down the tip and the diffusion fields of the neighbouring dendrites squeezes them inward. There are a few studies taking into account the influence of the neighbouring dendrites (Lu S-Z, 1992; Spencer B.J., 1997, 1998, 1999). Spencer et al. (Spencer B.J., 1997, 1998, 1999) performed an integral analysis on slender needle crystals at the limit where  $\rho \ll l_D$  and found that for an array of interacting dendrites or for a dendrite confined in a small system, even in the absence of surface energy, the neighbouring interaction or small system size effect is enough to uniquely determine the dendrite tip curvature at a given solidification condition. In other words, the interaction between neighbouring dendrites is as relevant as the surface energy in establishing dendrite characteristics. In the absence of surface energy, for an isolated dendrite they recovered the Ivantsov equation (tip solution), and for an array of directionally grown dendrites (tail solution combined with the only solution of the family of tip solutions which is consistent with the tail solution) they obtained a unique solution given below:

$$\rho = \frac{l_D \lambda_x \lambda_y}{2\sqrt{2kl_D[2l_T - l_D] + 2(1 - k)(\lambda_x \lambda_y)}}$$
(1.26)

where  $\lambda_x$  and  $\lambda_y$  are the spacings of the rectangular arrays as illustrated in figure 1.21 and  $l_D$  and  $l_T$  are the solute diffusion length and thermal length respectively. This equation is in a good agreement with the experimental results in the limit,  $l_D \ll l_T$ . While being similar in general form, this equation results in a smaller tip radius than that obtained by previously offered models (Kurz W., 1981; Makkonen, 2000) at the same growth conditions. Spencer et al. then offered a scenario explaining



Figure 1.21: Schematic of a rectangular dendritic array in directional solidification.(Spencer B.J., 1999)

the existence of a range stable spacings based on the findings of eq. 1.26. That is, the stable spacing (radius) obtained from the array solutions (a family of solutions) are confined between the two limits of marginal stability theory (upper limit) and overgrowth mechanism (lower limit), as depicted in figure 1.22. Dendrites are stable if the curvature is not lower than a critical value (marginal stability theory leading to tip splitting) and also if they are not too closely spaced (overgrowth mechanism leading to cell elimination). These upper and lower limits determine the stable range of sates of the array. It is noteworthy to mention that that upper limit might be set by the outgrowth of tertiary arms, in which case the upper stability limit lies below the tip splitting limit.



array solutions

marginal stability

overgrowth



stable

dendrite spacing

Figure 1.22: Stable array solutions bounded between the upper (marginal stability theory) and lower (overgrowth mechanism) limits (Spencer B.J., 1999)

### 1.4 Wavelength selection under unsteady heat flow

Although study of the steady state growth (typically regarded in the previously reviewed literature) is very helpful in elucidating different aspects of solidification, majority of real industrial applications are governed by unsteady state conditions. Thus, the analysis of dendritic microstructure under unsteady-state conditions is of great importance.

From theoretical point of view, Hunt and Lu (Hunt J.D., 1996) and Bouchard and Kirkaldy (Bouchard D., 1997) offered different equations for primary and secondary spacing under unsteady-state conditions. The one offered by H-L can be written as follows:

$$\lambda_1' = 0.07798 \, V'^{(\alpha - 0.75)} (V' - G')^{0.75} G'^{-0.6028} \tag{1.27}$$

where

$$\alpha = -1.131 - 0.1555 \log_{10}(G') - 0.007589 [\log_{10}(G')]^2$$
$$\lambda'_1 = \frac{\lambda_1 \Delta T}{\Gamma k_0}, \ G' = \frac{G_L \Gamma k_0}{\Delta T^2} \text{ and } V' = \frac{V_L \Gamma k_0}{D \Delta T}$$

and B-K's equations for unsteady-state spacing given by:

$$\lambda_1 = a_1 \left( \frac{16C_0^{\frac{1}{2}} G_0 \varepsilon \Gamma D}{(1 - k_0)m_L G_L V_L} \right)^{\frac{1}{2}}$$
(1.28)

$$\lambda_2 = 2\pi a_2 \left(\frac{4\Gamma}{C_0(1-k_0)^2 T_F} (\frac{D}{V_L})^2\right)^{\frac{1}{3}}$$
(1.29)

where D is the solute diffusivity in liquid,  $G_0\varepsilon$  is a phenomenological parameter  $\approx 600 * 6 \ Kcm^{-1}$ ,  $a_1$  and  $a_2$  are the calibrating factors and  $T_F$  is the melting temperature of the solvent. B-K suggested  $a_2 = 5$  for Al and Sn - Pb alloys and  $a_1 = 50$  for Sn alloys. These parameters were phenomenological and based mainly on the article by Okamoto and Kishitake (Okamoto T., 1975).

Experimental studies have also been carried out to investigate the unsteady state directional solidification (Rocha O.L., 2003b,a; Peres M.D., 2004; Su R.J., 1998; Ares A.E., 2009; Kovacs J., 2003; Cante M.V., 2008; Quaresma J.M.V., 2000; Cruz K.S., 2008) applying a chilling surface at the bottom of the mold. The majority of them have plotted primary spacing as a function of cooling rate rather than individual growth rate and temperature gradient due to the fact that in unsteady state region G and V depend on each other. The cooling rate immediately after the solidification

front passes the thermocouple positions is computed by plotting the cooling curves and determining the slopes of the curves  $(\dot{T}_L = G_L V_L)$ . It has been conjectured that in unsteady state conditions, there is a power law relationship in the form  $\lambda_1 = c_1 (\dot{T}_L)^{c_2}$ where  $c_1$  and  $c_2$  are constants. Bouchard and Kirkaldy (Bouchard D., 1997) showed that the equation  $\lambda_1 = c_1 (\dot{T}_L)^{-0.50}$  best replicates their experimental results. They also applied previously discussed analytical solidification expressions and solved the 1 - D heat flow equations for the solid, liquid and mushy zone, concluding that for unsteady heat flow the thermal gradient in the liquid changes almost linearly with the tip growth rate (Figure 1.23) ( $G_L = c V_L$ ) and consequently  $\dot{T}_L = c V_L^2$ .



Figure 1.23: Solidification rate vs. temperature gradient in liquid and mushy zone.(Bouchard D., 1997)

Regarding the effect of solute concentration on primary spacing in unsteady state directional solidification, there is no unanimous agreement in the literature. Spittle and Lloyd (Spittle J.A., 1979) reported that for unsteady state directional solidification, primary spacing decreases with increasing  $C_0$ . Rocha et al. (Rocha O.L., 2003b) also pointed out that under unsteady heat flow for Sn - Pb alloys, both  $\lambda_1$  and  $\lambda_2$  decrease as  $C_0$  increases and for Al-Cu alloys,  $\lambda_1$  is independent of solute concentration while  $\lambda_2$  decreases with increasing concentration. Okamoto and Kishitakes results (Okamoto T., 1975) contradicts these results in that they predicted an increase in primary spacing as solute concentration increases. However, the majority of the researchers reported that the effect of solute concentration in primary spacing selection is less important for unsteady state heat flow than for steady state conditions.

In steady state directional solidification, G and V can vary independently and any range of cooling rates can be obtained. However, in case of unsteady state heat flow G and V are interdependent. A constitutional supercooling parameter, defined as  $\beta = \left(\frac{C_0(k-1)m}{kG}\right) / \left(\frac{D}{V}\right) > 1$ , can be applied as a criterion to understand the transition regions between different structures. Because in steady state condition G and Vcan vary over a wide range of values, this parameter can range from very small to very large values. However, in unsteady state condition,  $\beta$  can only obtain large values due to small liquid temperature gradient values generated in unsteady heat flow. According to Kirkaldy et al. (Kirkaldy J.S., 1995) and McCartney and Hunt (McCartney D.G., 1981), at the cellular to dendritic transition  $\beta$  has the value of 20 and thus the possibility of covering the cellular regime in unsteady state conditions decreases. Figure 1.24 indicates the variation of  $\beta$  with time in Al-4.5wt%Cu system under unsteady heat flow calculated by B-K using numerical analysis.

It has been reported by Spittle and Lloyd (Spittle J.A., 1979) that for a given set of growth conditions (same G and V), under unsteady state condition smaller



Figure 1.24: variation of  $\beta$  with time in Al - 4.5wt%Cu system under unsteady heat flow.(Bouchard D., 1997)

values of primary spacing can be obtained compared to those under steady state conditions. Because, under unsteady state conditions, solidification starts from a chilling surface which introduces undercooling into the liquid close to the chill and thus more nucleation sites are produced at the beginning. Therefore, the initial spacing of the dendrites, which is affected by the number of initial nuclei adjacent to the chill, is smaller than the final steady state spacing. They also mentioned that under sufficiently high undercoolings the primary spacing may readjust itself to the value obtained for similar G and V under steady state conditions. It seems to be possible that as time elapses and steady state conditions are achieved, dendrites will adjust themselves by a choke off mechanism (to increase spacing) or tip splitting mechanism (to decrease spacing) to reach the steady state selected spacing. Figure 1.25 shows the unsteady state primary spacing as a function of cooling rate for an Al - 5wt%Cu alloy by Rocha et al. (Rocha O.L., 2003b). The comparison between experimental and theoretical primary spacing equations by H-L and B-K is also shown in the same figure. It should be mentioned that the analytical expression for cooling rate is applied by Rocha et al. into H-L and B-K equations to establish a relationship between  $\lambda_1$  and cooling rate.



Figure 1.25: Unsteady state primary spacing as a function of cooling rate in an Al - 5wt%Cu alloy. Eq. (19) is in Ref. (Rocha O.L., 2003b)

It should be noted that these results on unsteady-state dendritic growth are difficult to reconcile with the hypothesis of Langer and Warren and others that claim that dendrite spacing (particularly under highly transient conditions) falls in a range of values.

## 1.5 Effect of convection

Convection is a natural phenomenon that happens during solidification process because of density difference between solute and solvent (effect of gravity) and also the temperature difference between different parts of the melt. Natural convention flow caused by the mentioned reasons would affect the dendrite arm spacing dramatically. On the other hand, the melt flow caused by shrinkage of the solidified part may also have a significant effect on the final spacing. However, in case of upward solidification of the alloy systems wherein the solute density is larger than that of the solvent, natural convection does not play an important role in the final spacing and can be neglected.

Although in upward directional solidification natural convection is negligible, shrinkage flow through interdendritic spacing due to the density difference between the solid and liquid phases may cause experimental measurement to be inaccurate. This kind of flow in upward directional solidification of some alloys (including Al-Cu alloys) leads to the formation of inverse segregation so that the solute concentration at the bottom of the mold is higher than the equilibrium concentration. This shrinkage flow is more significant in systems wherein the density difference between solute and solvent atoms is large, especially when the solute boundary layer ahead of the interface is thick. However, Sharp and Hellawell (Sharp R.M., 1970) pointed out that for nonplanar interfaces the solute boundary layer is proportional to  $\frac{G}{V}$ . Thus, for unsteady state heat flow the thickness of this layer is small. Therefore, it is easier to avoid the shrinkage flow in unsteady heat flow compared to steady state conditions. By increasing the temperature gradient in the melt, the effect of shrinkage flow would be stronger because the large temperature gradient causes the pasty zone (mushy zone) to become narrow leading to the easier flow of the liquid through the interdendritic spacing (Liu C.Y., 1989). In a theoretical study carried out by H. wang et al. (Wang H., 2011) was determined that the effect of shrinkage flow on primary spacing in upward solidification is negligible. Moreover, it was pointed out that shrinkage flow influence on the solidification parameters, i.e. temperature gradient at the S/L interface and interface velocity, particularly in the first ten seconds of the solidification, can be neglected mainly because of the positive density gradient in direction of gravity. Figures 1.26 and 1.27 show the effect of shrinkage on G and V, and  $\lambda_1$ respectively (Wang H., 2011).



Figure 1.26: Effect of shrinkage on temperature gradient (G) and interface velocity (V) in upward solidification. (Wang H., 2011)

#### **1.6** Orientation selection in dendritic patterning

In previous sections, dendrites growing along crystallographically favoured low-surface energy directions were explored. However, this is not the case in most practical solidification patterns. If the direction of heat extraction or temperature gradient differs from that of the main crystalline axes, the competition between the two effects establishes the final growth direction and morphology of dendrite branches. This is different from the interplay of the inherent crystal anisotropies studied by Haxhimali



Figure 1.27: Effect of shrinkage on dendrite arm spacing  $(\lambda_1)$  in upward solidification. (a) function of interface cooling rate  $(G.V)(^{\circ}C/Sec)$  and (b) function of position y (mm)(Wang H., 2011). Note that ref. (21) refers to (Peres M.D., 2004) in this thesis.

et al. (Haxhimali T., 2006). Experimental and numerical investigations of nonaxially growing dendrites in cubic materials, where the imposed thermal gradient was misaligned with respect to the main axes of the crystalline structure, offered insight into the effect that competing preferred growth directions have on the orientation that dendrites eventually select (Grugel R.N., 1989; Trivedi R., 1991; Borisov A.G., 1991; Oswald P., 1993; Okada T., 1996; Akamatsu S., 1995, 1997, 1998; He G., 1998; Utter B., 2001, 2002, 2005; Provatas N., 2003; Deschamps J., 2008). The studies revealed that in the absence of anisotropy or along the directions with a very small anisotropy or when two types of anisotropy at different directions compete with each other at comparable levels, another type of microstructure known as "seaweed" forms where no distinct growth direction can be defined. The interplay between the directions of thermal gradient and the minimum stiffness influences the growth direction and morphology of the primary branches in directional solidification of alloys (Utter B., 2001; Provatas N., 2003; Akamatsu S., 1997) such that for a given surface energy anisotropy operating at a specific angle with respect to the heat flow, increasing the thermal gradient favours the growth in the heat flow direction, once the pulling speed is kept constant. However, as the interface velocity decreases, the direction of growth becomes more sensitive to the strength of the thermal gradient (Provatas N., 2003; Akamatsu S., 1997). A 2D phase field study by Provatas et al. (Provatas N., 2003) on an organic alloy shows how the strength of thermal gradient affects the morphology. They imposed a continuously increasing unidirectional thermal gradients at 45° misoriented with respect to the surface energy and observed a transition from dendrite to seaweed microstructure as shown in figure 1.28. They also offered the following equation to find the temperature gradient at which the transition occurs. However, since only one growth velocity was explored, the accuracy of the equation with growth velocity was not validated.

$$G^* \approx P_f \sqrt{(V_p \cos\theta)/(Dd_0[1+15\varepsilon_4\cos4\theta])}$$
 (1.30)

At a constant temperature gradient, as the interface velocity is increased from the cellular threshold (Mullins and Sekerka velocity (Mullins W.W., 1964)) to the cell-todendrite limit, dendrite arrays favour growth in the direction of a crystal axis, rather than that of the thermal gradient (Trivedi R., 1991; Borisov A.G., 1991; Oswald P., 1993; Okada T., 1996; Akamatsu S., 1995, 1997, 1998; He G., 1998; Deschamps J., 2008). Deschamps et al. (Deschamps J., 2008) conducted a series of directional



Figure 1.28: Directional solidification of an organic alloy with surface stiffness minimized at 45° with respect to the thermal gradient leading to a dendritic microstructure at lower thermal gradient strengths (left) and a seaweed microstructure as the temperature gradient is continuously increased (right).(Provatas N., 2003)

solidification experiments and varied the tilt direction and growth velocity within the same order as the cell-to-dendrite transition limit. Their results presented in figure 1.29 show that at a fixed temperature gradient and disorientation angle, as the growth velocity is increased, dendrites tend to grow in the crystal anisotropy direction. Also, close to cellular threshold limit, increasing the tilt angle results in the formation of a seaweed microstructure, while at higher velocities (dendritic regime), the microstructure remains dendritic, and the secondary arms become more important.

The many types of possible microstructures together with the influence of the competing operating anisotropies on mechanical properties of the alloy make morphological transition an important topic in materials science. There is evidence that even in the dendrite regime the primary dendrite arm/cellular spacing is strongly



Figure 1.29: Directional solidification experiments of an organic alloy where the direction of surface energy (a) differs from that of the thermal gradient (G). As the velocity is increased towards the right, a dendritic microstructure in the direction of minimum surface stiffness is favoured. The effect of the tilt angle on the microstructure is more significant at lower growth rates.(Deschamps J., 2008)

affected by the relative direction of the imposed thermal gradient and preferred crystalline orientation, even for the same growth velocity, temperature gradient strength and composition (Grugel R.N., 1989; He G., 1998; Borisov A.G., 1991; Trivedi R., 1991). There is also evidence that the distribution of interdendritic phases could be greatly influenced by the misorientation angle as secondary dendrite arms start to overtake the primary ones (Grugel R.N., 1989). Both these effects are very crucial in establishment of the final mechanical properties of an as-cast alloy and thus need to be studied in depth.

# Chapter 2

# Methods

#### 2.1 Experimental procedure

My experimental work has mainly been done on an Al-0.34wt%Cu alloy provided by Novelis in Kingston and an Mg-0.5Al alloy provided by Dr. Pekguleryuz's magnesium laboratory in McGill University. The binary phase diagrams of Al-Cu and Al-Mg alloys are given in Figure 2.1.

The set-up originally applied for my solidification experiments was basically a tapered ceramic crucible with a thin copper plate attached to the bottom being water-cooled from below. Compared to metallic crucibles, ceramic crucibles loose heat much more slowly. Thus, a ceramic crucible maintains its initial temperature for a longer time. However, since the melt gets colder during solidification and the wall remains hot, it may lead to a temperature gradient in the direction normal to the growth direction from the wall to the center. That is the reason why the crucible was made tapered. The tapered shape of the crucible increases the distance between the wall and the center as the solidification front moves upward. But, in the



Figure 2.1: Al-Cu and Al-Mg binary phase diagrams (ASM-Handbook, 1992).

case that the chilling surface diameter is large enough to compensate for this radial temperature gradient (e.g. a metallic crucible) this taper is not required. A thin copper plate had also been selected to ensure that the heat flow inside the copper plate only occurs in the vertical direction and only 1 - D heat transfer occurs. The reason for upward solidification is to minimize convection through the melt. In case of downward solidification, hot melt is below the cold melt. Due to the fact that the hot melt tends to move up and replace the cold melt, a significant convection flow may occur, which influences the spacing.

The main drawback of this design is that since there is a difference in the thermal expansion of the ceramic paste and copper plate, while preheating the crucible some cracks form at the ceramic paste. These cracks, formed during the Waterjet cooling, make an easy path for water to go through the melt and destroy the microstructure, i.e. dendrite arms. Another problem with this set up regards the fact that the dendrite arm spacing, particularly in unsteady state solidification, is history dependent and by changing the copper plate for each experiment, different initial conditions are obtained, which increases the number of variables and may conflict with the other parameters affecting the dendrite arm spacing.

In light of the above problems, and after consulting with the author of some recent cited papers (Rocha O.L., 2003b,a; Peres M.D., 2004; Cante M.V., 2008; Quaresma J.M.V., 2000; Cruz K.S., 2008), I decided to exploit a metallic crucible. Specifically, it consists of a cylindrical stainless steel crucible that is water jet or gas (air and helium) cooled from below to promote upward solidification. The crucible is shielded by a cylindrical alumina insulation with a thickness of about 10 mm to prevent radial heat extraction. The top of the crucible is also covered by insulation

and only a slot is embedded in the insulation cap through which thermocouples pass. The inner, outer and bottom parts of the crucible were covered with a thin layer of sprayed boron nitride in order to reduce the heat extraction through the walls as well as providing a more uniform chilling surface at the bottom. The pressure of the spray was chosen high to prevent the formation of bubbles at the water-chilling wall interface due to the local vaporization. For directional casting of Mg-Al alloys, the entire procedure was carried out in a protective environment of  $CO_2SF_6 - 0.5\%$  gas to prevent explosion. An illustration of the experimental set-up is given in figure 2.2. The real set-up is shown in Figure 2.3. Depending on the coolant type, pressure of the cooling medium, and the front position relative to the chill wall, a wide range of growth velocities and temperature gradients are obtained.

To reveal the microstructure, the specimens are cut in longitudinal and transverse sections and polished down to  $0.05 \ \mu m$ . The Al-Cu samples are etched in a solution of 10% NaOH - Water for about 2 minutes and the Mg-Al samples are etched in a solution of 20-ml Water, 20-ml acetic acid, 60-ml ethylene glycol and 1-ml  $HNO_3$ (Pettersen K., 1990) for about 5 minutes. The microstructure was then imaged under a light microscope.

The temperature is measured at different heights from the bottom with K-type nickel-chromium based sheathed thermocouples that are tightened along a plate and are inserted into the melt through the top of the crucible as shown in figure 2.2. The diameter of the chilling surface is set to 50 mm (i.e. the bottom plate) and the thickness of the chilling surface to 3.5 mm. The large chilling diameter helps to reduce the influence of the thermocouples' diameter, about 1 mm, on the solidification process (Garcia, 2009). A set of thermocouples were aligned in the axial (vertical)


Figure 2.2: Schematic drawing of the crucible being utilized in the experiments.



Figure 2.3: The set-up being utilized to collect the temperature data of unidirectional solidification of alloys.

direction starting at 1 mm away from the chilling surface and separated from each other by 1 mm. In order to ascertain the one dimensionality of the heat flow in the vertical direction, an additional thermocouple was positioned 12 mm radially from the aligned thermocouples.

The output from the thermocouples is acquired through a NI SCXI-1600 data logger and the calibration of which was set at the melting point of pure aluminum and pure zinc. Before pouring the melt into the crucible, the crucible along with the surrounding insulation and the alloy were heated in the same furnace to a temperature of 1.1 times the liquidus temperature of the alloy, to compensate for the heat loss during the experiment (Rocha O.L., 2003a).

The height of the melt is around 60 mm of which only the first 20 mm is utilized to study the dendritic microstructure (corresponding to strip casting dimensions) and the rest acts as the heat reservoir.

The cooling curves obtained from the thermocouples define a region of radially uniform temperature that varies essentially in the growth direction (vertical). This region is referred to as our region of interest. Outside this region, there is a small temperature gradient towards the wall such that the unidirectional heat flow breaks down. Far from the bottom chilling plate, outside the region of interest, the solidification microstructure mostly consists of equiaxed dendrites. Within our region of interest the solidification microstructure is columnar in nature (i.e. oriented cells or dendrites). We disregard any data outside our region of interest. As will be shown below, the grains examined within the region of interest are large enough in the direction transverse to the heat flow to disregard boundary effects. Only data from grains with transverse size larger than 1 mm are reported here. In each sample solidified, three different directionally solidified grains emanating from the chill surface were analyzed for reproducibility and to provide the statistical error bars we report in our results.

The K-type nickel-chromium based sheathed thermocouples exploited in the experiments are of higher performance compared to other types. The thermocouple junction can be either exposed or unexposed. The applied thermocouples are unexposed to allow multiple usage. There are two different types of unexposed junctions, grounded and ungrounded as shown in Figure 2.4. Grounded probes offer faster response times than ungrounded probe, but the susceptibility of grounded probes to ground loops and electrical loops is higher. The response times of grounded and ungrounded probes are very close to each other (around 0.25 sec) for thermocouple sizes below 0.062" which is the range that is used in my experiments. Therefore, P.hD. Thesis - Morteza Amoorezaei McMaster - Materials Science and Engineering

an ungrounded junction was selected to measure the temperatures of different positions. The tolerance value of 2.2 °C or 0.75% (whatever is greater) for all K-type thermocouples has been quoted by the supplier (OMEGA).



Figure 2.4: Three different thermocouple junctions (www.omega.ca).

It has been suggested that to collect temperature data, the frequency of data acquisition be at least ten times faster than the response time of the thermocouples to assure that all the critical points have been collected. For instance, if the response time of the thermocouple is around four data per second, the frequency of data collection need to be at least 40 Hz, i.e. forty data per second would be collected.

To calibrate the thermocouples, at least three reference points need to be considered. The reference point can be the melting point of a pure material or the eutectic point of a eutectic alloy which melts at a unique temperature rather than a range of temperatures. In my experiments, I used pure aluminum, pure zinc and also the eutectic alloy Al - 33wt%Cu which melt at 660.43 °C, 419.58 °C and 548 °C respectively. I also tried to calibrate my thermocouples using boiling water, but the temperature data obtained exhibited fluctuations around the boiling point of water P.hD. Thesis - Morteza Amoorezaei McMaster - Materials Science and Engineering

 $(100 \circ C)$  of about 5 degrees, which was most likely because of air pressure and bobbles effects.



Figure 2.5: The thermocouple calibration procedure applying an induction furnace.

To obtain the first point, around 250 gr of pure aluminum was melted into a graphite crucible by applying an induction furnace. Upon melting the entire aluminum sample, the induction furnace was switched off and the thermocouple was inserted into the melt. At the melting point, the slope of the cooling curve changes and this point can be determined by drawing the dT/dt vs. t (derivative of temperature with respect to time vs. time). To make sure that equilibrium cooling is obtained, the surrounding of the graphite crucible was covered by insulation. The same procedure was done for pure zinc and Al-33wt%Cu. Figure 2.5 illustrates the thermocouple calibration procedure utilizing an induction furnace.

As the result of the above experiment, three values were obtained for the melting

point of pure aluminum, pure zinc and the eutectic point of Al - 33wt%Cu. Utilizing these points, one can construct a polynomial from between the points of the form,  $y = ax^2 + bx + c$  (different functions may also be used), where y represents the theoretical temperature and x the experimentally measured temperature. Thus, data obtained for that thermocouple can be inserted to the equation (the x-value) yielding a y-value that can be treated as the real value of the measured temperature. Figure 2.6 indicates the method of thermocouple calibration by constructing a polynomial equation from between the three data points.



Figure 2.6: Method of thermocouples calibration by constructing a polynomial equation from between the three data points.

The typical temperature profiles collected from the first six thermocouples are shown in Figure 2.7.

To determine the cooling rate during solidification, we use the cooling curves



Figure 2.7: Typical temperature profiles collected from the centrally aligned thermocouples before calibration obtained in an air cooling experiment. Thermocouples are located 1 mm apart from each other starting at 1 mm above the chilling wall.

obtained by thermocouples at different y-positions (see figure 2.2) along the center of the crucible (i.e. on a straight line at the center). First, the solid/liquid interface velocity and the temperature gradient at solid/liquid interface are determined. For this purpose, the time and temperature at which the change in the slope of the cooling curves happens is measured. To obtain this time and temperature, the derivative of temperature with respect to time (dT/dt) is calculated. The position at which a sharp change in dT/dt vs. time occurs indicates the time at which the solidification front passes the corresponding thermocouple (figure 2.8).

From the cooling curve in figure 2.8, the liquidus temperature can also be read by considering the abrupt change of the derivative curve. Repeating the same procedure for the other thermocouples on the central straight line, the time that the interface has passed the other thermocouples can be determined. Since the thermocouples are



Figure 2.8: A typical cooling curve (red curve) and its derivative (black curve) being applied to determine the cooling rate.

located at equally pre-set locations, the mean velocity of interface between thermocouples is calculated by dividing the thermocouples distance by the time intervals. The one-sided temperature gradient at the solid/liquid interface may also be calculated by the ratio of temperature difference to the distance between thermocouples at the time at which the interface passes a thermocouple. The product GV represents the cooling rate. A typical calculated interface velocity and temperature gradient from direct thermocouple measurements of Al-Cu is given in figure 2.9.

A typical longitudinal and transverse dendritic structures obtained from directional solidification of Al-0.34wt%Cu alloy are shown in figure 2.10. The top image portrays nearly parallel dendrites growing opposite to the heat flow direction. To measure the interdendritic spacing, only the grains larger than 1 mm in diameter are selected (this is justified below).



Figure 2.9: Effective front velocity and temperature gradient obtained from direct thermocouple measurements of Al-Cu, and the corresponding fitting curves.



Figure 2.10: Longitudinal (top) and transverse (bottom) cross sections of dendritic microstructure obtained in directional solidification of Al - 0.34wt%Cu alloy.

## 2.2 Power spectral analysis

To measure dendrite arm spacing in extended dendrite arrays, we apply power spectral analysis . The original idea of power spectral analysis is extracting the frequencies of a given signal and highlighting the significance of each frequency. For example, considering the sine wave in figure 2.11-a if the power spectrum versus wavelength is plotted, (b), the obtained peak denotes that a main average wavelength exists, which dominates the signal. In case of the other signal, (c), two peaks appear indicating the existence of two important wavelengths in the given signal.



Figure 2.11: Power spectrum vs. wavelength for two typical signals extracting their component frequencies.

The power spectrum utilizes the principles of Fourier transformation to extract the component frequencies. The Fourier transformation of a function f(x) can be expressed as:

$$f(x) = \frac{a_0}{2} + \sum_n (a_n \cos(\frac{2\pi nx}{L}) + b_n \sin(\frac{2\pi nx}{L}))$$
(2.1)

$$a_n = \frac{2}{L} \int_0^L f(x) \cos(\frac{2\pi nx}{L}) dx \tag{2.2}$$

$$b_n = \frac{2}{L} \int_0^L f(x) \sin(\frac{2\pi nx}{L}) dx \qquad (2.3)$$

Since the solute concentration along the dendrites is not a continuous function and exists as digitized pixels that are at a certain distance from each other, we have to apply discrete Fourier transformation instead, given by

$$\hat{F}_k = \sum_{x_i} C(x_i) e^{-ikx_i} \tag{2.4}$$

where  $F_k$  is the discrete Fourier transform, C(x) is the discrete function and k is the wave frequency. Power spectrum is defined as the magnitude square of  $F_k$ .

Figure 2.12 shows the longitudinal morphology of the dendrite microstructure cut out from a grain in one of our samples. The microstructure appears cellular in nature, while there is some evidence of side branching on the right of the figure, indicating the emergence of dendritic fingers. The microstructural length scale in the direction transverse to that of the heat flow (right to left in the figure) was analyzed statistically at different distances from the chilling surface using power spectral analysis. A typical power spectrum is shown in the bottom frame of figure 2.12. The x-axis of the power spectrum denotes the frequency of the corresponding wave vector. The main peak is associated to the primary dendrite spacing and is consistent with what is obtained by the ASTM line intersection method. The smaller frequency peaks correspond to fluctuations of primary variations away from the average, as well as smaller features such as tip splitting and pixelation. The long wavelength variations correspond to feature variations larger than the mean, including finite size effects. We disregard wavelengths corresponding to such finite size effects in our analysis.



Figure 2.12: (Top) cutaway of the longitudinal solidification microstructure, growing from left to right. (Bottom) Unidimensional power spectrum of a transverse cut extracted from the longitudinal microstructure at a position 13mm from the chilling surface.

Also, shown in figure 2.13 is the 1 - D power spectral analysis applied on a typical dendritic array obtained from phase field simulation. The position of the peak corresponds to the dominant wavelength. A very sharp peak indicates that there is only one dominant wavelength in the system whereas a broad peak represents a distribution of available wavelengths.

Another method applicable to two-dimensional images developed in 2D by Kuchnio et. al (Kuchnio P., 2008) is demonstrated in figure 2.14. The method generalizes that used by Greenwood et. al (Greenwood, 2004) by using a two-dimensional Fourier



Figure 2.13: Top two frames show the interface shape of a portion of a typical dendritic array. Grid lines map out the structure of the adaptive mesh. The bottom frame shows the corresponding power spectrum of the interface.

transform. The picture at the left illustrates a typical image of the corresponding transverse microstructure, cut away from a grain at distance 16 mm from the chilling surface, whereas the right side graph shows the length scale as a function of angle for the same picture. The origin has been selected to locate the center. The main drawback of this method is that it precludes the very important information about the distribution of available wavelengths present in the image and only maps out the average value in each direction.



Figure 2.14: (Left) Transverse dendritic microstructure at roughly 16 mm from the chilling wall. (Right) polar plot indicating average length scale versus orientation which treats the centre of the image as the origin of the measurement.

In order to obtain the wavelength distribution at different angles, a new 2D power spectrum analysis was developed (Amoorezaei M., 2010) which provides more information about the microstructure than the method developed by Kuchnio et al. Figure 2.15 shows the 2D power spectrum averaged over three grains at the same position as the one in the top frame (16 mm above the chill wall). The power spectrum was then circularly averaged about the origin, leading to an effective 1D power spectrum, represented in the bottom right frame. Since the transverse microstructure is essentially isotropic, the position of the radial peaks does not shift after averaging. We applied this method to analyze our experimental data as closely as possible to the way we analyze our 2D simulations. Here, the measure of dendrite spacing is defined as  $\lambda \equiv \sum_k kf(k)$  where f(k) is a probability density of finding features between the wavevector  $k \to k + dk$ , and is related to the power spectrum by  $f(k) = P(k) / \sum_k P(k)$ . In the analysis, the first nine wavevectors of the power spectrum were discarded as these were noted to correspond to features on the scale of the system size.

#### 2.3 Phase field model

Phase field theory has emerged in recent years as promising candidate of a fundamental and self-consistent theory for modeling solidification microstructures. The first simulations to test spacing versus pulling speed in alloys date back to the work of Warren and Boettinger (Boettinger W.J., 1999), who found a monotonic band of spacings versus pulling speed. The small system size used, however, precluded a quantitative comparison with experiments. Nowadays the phase field methodology has become more quantitative by "marrying" simulations of phase field models in the so-called *thin interface limit* (Karma, 2001; Echebarria B., 2004) with novel simulation techniques like adaptive mesh refinement (Provatas N., 1998; Athreya B.P., 2007; Ofori-Opoku N., 2010). A first step using phase field models to quantitatively model spacing in directional solidification was taken by Greenwood et. al (Greenwood M., 2004) in 2D and Dantzig and co-workers in 3D (Provatas N., 2005). These works

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Figure 2.15: (Top) Typical cross section of transverse dendrite microstructure. (Bottom left) Averaged 2D power spectrum averaged over three grains cut at the same transverse position as the grain in the top frame. The red curve corresponds to the mean wavelength obtained from the bottom right plot. (Bottom right) Circularly averaged power spectrum corresponding to the 2D power spectrum in the bottom left frame.

modeled steady state directional solidification in SCN alloys and found very good agreement (in the 2D limit) with the 2D steady state spacing experiments. These studies suggested that, at least under steady state (i.e. Bridgman growth) conditions and one type of initial condition (morphologically noisy initial interface), there could be a single crossover scaling function interpolating between the two power-law spacing regimes seen experimentally and modeled semi-empirically by geometrical models.

Despite the success of phase field modeling in predicting steady state spacing, as well as other steady state properties such as cell tip structure (Gurevich S., 2010b), the methodology has not been used systematically to explore spacing under transient solidification conditions. Indeed the ability to model cell, dendrite and seaweed structure, kinetic and surface tension anisotropy, different mobility, different thermal conditions and different initial condition makes phase field modeling an ideal theoretical test ground to explore transient spacing development and how it may relate to the steady structures.

This work used phase field simulations to model solidification of the Al-Cu and Mg-Al alloy systems in the dilute limit of the phase diagram, which comprises straight solidus and liquidus lines of slopes of m/k and m, respectively. The equilibrium interface concentration jump at any temperature is thus given by partition relation  $c_s = kc_l$ , where  $c_s$  ( $c_l$ ) is the molar concentration of impurities at the solid (liquid) side of the interface, and k is the partition coefficient.

Simulations formally neglected the latent heat by imposing the temperature field by the form  $T(z,t) = T_0 + G(t)(z - z_0 - \int_0^t V_p(t')dt')$ , where  $T(z_0,0) = T_0$ , a reference temperature, while G(t) and  $V_p(t)$  are the local thermal gradient and pulling speed, respectively. Since convection in the liquid does not significantly affect the final spacing in upward directional solidification (Wang H., 2011), it is neglected. Under these assumptions, mass conservation across the interface takes the form:

$$c_l(1-k)v_n = -D(\partial_n c|_l - \partial_n c|_s) \tag{2.5}$$

where D is the solute diffusion coefficient in the liquid and  $\partial_n|_l$  ( $\partial_n c|_s$ ) is the partial derivative in the direction normal to the interface, taken on the liquid(solid) side. The temperature at the interface, which is assumed to be in local equilibrium, is given by the Gibbs-Thomson relation:

$$T = T_m - |m|c_l - \Gamma\kappa - v_n/\mu_k \tag{2.6}$$

where  $T_m$  is the melting temperature of the pure material,  $\Gamma = \gamma T_m/L$  is the Gibbs-Thomson coefficient,  $\gamma$  is the interfacial free energy, L the latent heat of fusion per volume,  $\kappa$  is the interface curvature,  $v_n$  is the normal interface velocity and  $\mu_k$  is the atomic mobility at the interface.

For cubic systems such as Al-Cu, the underlying crystalline structure that defines the anisotropy of surface tension (or interface mobility) is modelled by through a commonly used fourfold symmetry anisotropy function  $a(\hat{n}) = 1 - 3\epsilon + 4\epsilon(\hat{n}_x^4 + \hat{n}_y^4 + \hat{n}_z^4)$ , where  $\epsilon$  is the anisotropy strength and  $\hat{n}$  is the unit normal at the the interface. In two dimensions this function can be re-written as  $a(\theta) = 1 + \epsilon \cos(4\theta)$ , where  $\theta$  is the angle between the normal direction to the interface and an underlying crystalline axis (e.g < 100 > in a cubic crystal). For hexagonal systems such as Mg-Al, the anisotropy function  $a(\hat{n}) \equiv a(\theta) = 1 + \epsilon_0 + \epsilon_6 \cos[6(\theta - \theta_0]]$  is defined to represent the sixfold crystal symmetry of the hcp structure in the basal plane, where  $\theta$  is the angle between the normal to the interface and an underlying crystalline axis in the  $< 11\overline{2}0 >$  direction (in the basal plane) and  $\theta_0$  is the angle between the direction of heat extraction and the crystalline axis. This anisotropy function is the projection in the basal plane of the spherical harmonics expression representing the space group of the hcp crystal lattice:  $\gamma(\theta, \phi) = \gamma_0(1 + \epsilon_{20}y_{20}(\theta, \phi) + \epsilon_{40}y_{40}(\theta, \phi) + \epsilon_{60}y_{60}(\theta, \phi) + \epsilon_{66}y_{66}(\theta, \phi) + \cdots)$  where  $\epsilon_{20}, \epsilon_{40}, \epsilon_{60}$  and  $\epsilon_{66}$  are constant coefficients weighting the contribution of each of the spherical harmonic functions:

$$y_{20}(\theta, \phi) = \sqrt{5/16\pi} [3\cos^2(\theta) - 1]$$
  

$$y_{40}(\theta, \phi) = 3/(16\sqrt{\pi}) [35\cos^4(\theta) - 30\cos^2(\theta) + 3]$$
  

$$y_{60}(\theta, \phi) = \sqrt{13}/(32\sqrt{\pi}) [231\cos^6(\theta) - 315\cos^4(\theta) + 105\cos^2(\theta) - 5]$$
  

$$y_{66}(\theta, \phi) = \sqrt{6006/64\sqrt{\pi}} [\sin^6(\theta)\cos(\phi)]$$
(2.7)

while  $\theta$  and  $\phi$  are the inclination (or elevation) and azimuth spherical coordinate angles, respectively. The 2D surface energy anisotropy function projected in the basal plane is obtained by substituting  $\theta = \frac{\pi}{2}$ ,  $\epsilon_{20} = -0.026$  and  $\epsilon_{66} = 0.003$  (Sun D.Y., 2006). The contributions of  $\epsilon_{40}$  and  $\epsilon_{60}$  can be neglected (Sun D.Y., 2006). We then obtain  $\gamma(\phi) = 1.008 + 0.002 \cos(6\phi)$ . The stiffness anisotropy function  $a(\phi)$  is defined by

$$a(\phi) = \left(\gamma(\phi) + \frac{\partial^2 \gamma(\phi)}{\partial \phi^2}\right) / \gamma_0 = 1 + \epsilon_0 - \epsilon_6 \cos(6\phi);$$
  

$$\epsilon_0 = 0.008, \epsilon_6 = 0.07$$
(2.8)

Taking as reference the concentration on the liquid side of the solid/liquid interface,  $c_l^0 = c_0/k$  (where  $c_0$  is the average alloy concentration), the following standard one-sided sharp interface directional solidification kinetics are modelled:

$$\partial_t c = D\nabla^2 c - \vec{\nabla} \cdot \vec{j}_c \tag{2.9}$$

$$c_l(1-k)v_n = -D(\partial_n c|_l - \zeta \partial_n c|_s) + \hat{n} \cdot \vec{j_c}$$
(2.10)

$$c_l/c_l^0 = 1 - (1-k)\kappa d_0 a(\theta) -(1-k)\left(z - \int_0^t V_p(t')dt'\right)/l_T - (1-k)\beta' v_n$$
(2.11)

where  $d_0 = \Gamma/\Delta T_0$  is the solutal capillary length,  $\Gamma$  is the Gibbs Thomson coefficient,  $\Delta T_0 = |m|(1-k)c_l^0$  the freezing range,  $l_T = \Delta T_0/G$  the thermal length,  $\zeta$  the diffusivity of solute in the solid over that in the liquid,  $\kappa$  the interface curvature, and  $\beta' = \beta/\Delta T_0 = 1/(\mu_k \Delta T_0)$  the kinetic coefficient. The anisotropy function  $a(\theta)$  makes the interface stiffness dependent on the orientation through the anisotropy strength and misorientation angle from the crystal axis, imposing minimum stiffness at the main crystal axes directions.

In order to promote sidebranching realistically, thermal noise-induced concentration fluctuations are included in the liquid by following Ehebarria et al. (Echebarria B., 2010) and introducing the current  $\vec{j}_c$ , whose components are random variables obeying a Gaussian distribution with variance

$$< j_c^m(\vec{r},t) j_c^n(\vec{r}',t') >= 2DF_c \delta_{mn} \delta(\vec{r}-\vec{r}') \delta(t-t').$$
 (2.12)

where the magnitude  $F_c$  is determined through the fluctuation-dissipation relation

$$<(\delta c)^2>=\frac{c}{(N_A/v_0)\Delta V}=\frac{F_c}{\Delta V},\qquad(2.13)$$

and  $\langle (\delta c)^2 \rangle$  is the equilibrium average of the square of the departure of the concentration from its equilibrium value in a microscopically large but macroscopically small volume  $\Delta V$ . The first equality in Eq. (2.13) follows from the standard relation  $\langle (\delta n)^2 \rangle = n$ , where *n* is the number of solute atoms in the small volume  $\Delta V$ , while using the definition c = n/N and that the number of solvent atoms in the same volume is  $N = \Delta V N_A/v_0$ , where  $N_A$  is Avogadro's number and  $v_0$  is molar volume of solvent atoms. The second equality (right-hand-side) of Eq. (2.13) is obtained by computing  $\langle (\delta c)^2 \rangle$  directly from the sharp-interface equations (2.9-2.11). By the procedure outlined in ref. (Karma, 1993) this incorporation of noise can be shown to yield the appropriate equilibrium interface fluctuation spectrum in the sharp-interface limit.

The phase-field model employed to emulate eqs. 2.9 - 2.11 is designed for quantitative simulations through the use of a thin interface analysis developed by Karma and co-workers (Karma, 2001; Echebarria B., 2004). This analysis makes it possible to emulate a specified capillary length and kinetic coefficient to second order accuracy in the ratio of the interface width to capillary length. The details of this model have been presented and discussed at length in refs. (Karma, 2001; Echebarria B., 2004) and thus only a brief description is included below. A general review of the phase-field method can be found in (Boettinger W.J., 2002; Provatas N., 2005, 2010).

A scalar phase field parameter  $\phi$  is employed, which takes on a constant value in each phase and varies sharply but smoothly across a diffuse interface. The phase field is used to interpolate the free energy density and mobility between the bulk phases. Its equation of motion guarantees the system evolves towards a minimum of the free energy of the system. We define a phase-field variable which takes the value  $\phi = 1(\phi = -1)$  in the solid (liquid). The concentration  $c(\vec{x}, t)$  is characterized through a generalization of the field  $\tilde{U} = (c - c_l^0)/(c_l^0(1 - k))$ , which represents the local supersaturation with respect to the point  $(c_l^0, T_0)$ , measured in units of the equilibrium concentration gap at temperature  $T_0$ . This generalized supersaturation field is given by

$$U = \frac{1}{1-k} \left( \frac{c/c_l^0}{(1-\phi)/2 + k(1+\phi)/2} - 1 \right)$$
(2.14)

In term of the fields  $c, \phi$  and U, the phase-field model referred to above is given by

$$\tau(\hat{n}) \left( 1 - (1-k)\frac{(z-z_{\text{int}})}{l_T} \right) \frac{\partial \phi}{\partial t} = w_0^2 \vec{\nabla} \left[ a(\hat{n})^2 \vec{\nabla} \phi \right] + \phi - \phi^3 - \lambda (1-\phi^2)^2 \left( U + \frac{z-z_{\text{int}}}{l_T} \right)$$
(2.15)  
$$\left( \frac{1+k}{2} - \frac{1-k}{2} \phi \right) \frac{\partial U}{\partial t} = \vec{\nabla} \left[ q(\phi) D \vec{\nabla} U \right] - \alpha w_0 \left( 1 + (1-k)U \right) \hat{n} \frac{\partial \phi}{\partial t} \right] + \left( \frac{1+(1-k)U}{2} \right) \frac{\partial \phi}{\partial t} - \vec{\nabla} \cdot \vec{J}_u$$
(2.16)

where  $z_{\text{int}} \equiv \int_0^t V_p dt'$  is the interface position,  $\hat{n} \equiv -(\vec{\nabla}\phi)/(|\vec{\nabla}\phi|)$  defines the unit vector normal to the interface,  $\tau(\hat{n}) = \tau_0 \cdot a^2(\hat{n})$  is the phase-field orientation dependent relaxation time.  $a(\hat{n}) = 1 - 3\epsilon + 4\epsilon[(\partial_x \phi)^4 + (\partial_z \phi)^4]$  and  $a(\hat{n}) \equiv a(\theta) = 1 + \epsilon_0 - \epsilon_6 \cos[6(\theta - \theta_0]]$  impose fourfold and sixfold anisotropies in two dimensions, respectively.  $\theta$  is the angle between the normal to the interface and an underlying crystalline axis, taken to coincide with the direction of the thermal gradient in Al-Cu simulations. For Mg-Al simulations, the misorientation angle between the thermal gradient direction and crystalline axis was set at  $\theta_0 = \pi/6$ , the maximum misorietation for hexagonal dendrites growing on the basal plane in the (<  $11\bar{2}0$  >) direction. The function  $q(\phi) = (1 - \phi)/2$  dictates how the diffusivity varies across the interface. The interface thickness is given by  $w_0$  while  $\lambda$  is treated as numerical convergence parameter of the model.

The fluctuating current  $\vec{J}_u$  obeys the correlation

$$< J_u^m(\vec{r},t) J_u^n(\vec{r}',t') > = 2Dq(\phi) F_u \delta_{mn} \delta(\vec{r}-\vec{r}') \delta(t-t'),$$
 (2.17)

and depends explicitly on the phase-field  $\phi$  via the solute diffusivity  $Dq(\phi)$ . The magnitude  $F_u = F_u^0[1 + (1 - k)U]$  is defined by the relation

$$<(\delta U)^2>=\frac{<(\delta c)^2>}{(\Delta c_0)^2}\equiv\frac{F_u}{\Delta V}.$$
(2.18)

and the constant noise magnitude

$$F_u^0 = \frac{kv_0}{(1-k)^2 N_A c_0} \tag{2.19}$$

is the value of  $F_u$  for a reference planar interface at temperature  $T_0$  (U = 0), while

 $\Delta c_0 = c_l^0 (1-k) = c_0 (1/k-1)$  is the concentration jump across the reference solidliquid interface at temperature  $T_0$ .

m  (K/wt%)	$c_0 (wt\%)$	k	$D \ (\mu m^2/s)$	$\Gamma (K \cdot \mu m)$	$\epsilon$
3.00	0.34	0.15	3400	0.10	0.02

Table 2.1: Material parameters defining the AlCu system. m is the liquidus slope,  $c_0$  the alloy composition, k the partition coefficient, D the diffusivity of impurities in the liquid,  $\Gamma$  the Gibbs-Thomson constant and  $\epsilon$  the anisotropy strength.

m  (K/wt%)	$c_0 (wt\%)$	k	$D \ (\mu m^2/s)$	$\zeta$	$\Gamma (K \cdot \mu m)$	$\epsilon_0$	$\epsilon_6$
5.5	0.5	0.4	1800	$10^{-4}$	0.62	0.008	0.07

Table 2.2: Material parameters defining the MgAl system.  $\zeta$  is the diffusivity of solute in the solid over that in the liquid,  $\epsilon_0$  the constant in the projected 2D anisotropy function and  $\epsilon_6$  the anisotropy strength.

The parameters  $\lambda$ ,  $w_o$  and  $\tau_o$  can be shown to be inter-related through the thin interface relations developed in refs. (Karma, 2001; Echebarria B., 2004) to map the above phase field model onto eqs. 2.9-2.11 . Specifically, once a particular lambda is chosen, the thin interface relations establish a unique choice of  $w_0$  and  $\tau_0$  such as to yield the same  $d_o$  and  $\beta$  in simulations. The aim is to choose a rather diffuse value of  $w_0$  in order to expedite numerical efficiency. In this work, we assume the interface kinetics coefficient  $\beta \approx 0$ , to lowest order. This ability to quantitatively model the same materials parameters  $\beta$  and  $d_0$  is largely due to the term containing the constant  $\alpha$  in eq. 2.16. The term is called the so-called "antitrapping current", whose function is to self-consistently counter the spurious effects of an interface thickness that is artificially enlarged for practical purposes. The phase-field equations were simulated utilizing the adaptive mesh refinement (AMR) scheme developed by Provatas et al. (Provatas N., 1998; Athreya B.P., 2007; Ofori-Opoku N., 2010).

The material parameters employed in the phase field simulations corresponding to the Al-Cu and Mg-Al alloys studied here are presented in tables 2.1 and 2.2.

# Chapter 3

# Spacing characterization in directional solidification of Al-Cu alloys

This chapter examines spacing selection in Al-Cu alloys. Three different solidification growth conditions are examined in this work. In the first case, direct thermocouple data from a unidirectional solidification experiment (Amoorezaei M., 2010) was used to extract the local thermal gradient across the solid-liquid interface and the effective front velocity. These were then fitted to provide the functions representing G(t) (local thermal gradient) and  $V_p(t)$  (local solidification speed). The corresponding plots are shown in figure 2.9. Since the interface is initially positioned at  $T_L$  (the liquids temperature), the initial interface velocity is systematically lower than the actual front velocity, the discrepancy decreasing as the system evolves. In the second case, the thermal gradient is kept constant while the pulling speed is discretely incremented over a pre-determined range at varying rates. In the third case, both pulling velocity and temperature gradient are kept constant during the simulation. The first two cases lead to the transient growth conditions while the steady state growth conditions result from the third type of growth conditions.

In order to systematically study the evolution of interface structure, and, in particular, the selection of the columnar microstructure spacing, power spectral analysis is applied on simulated interface profiles using a Fast Fourier transform, as described in detail before. Figure 3.1 shows an example of a typical sequence of directionally solidified dendrite arms growth under steady state conditions, i.e. a constant thermal gradient ( $G = 5 \ K/mm$ ) and puling speed ( $V_p = 10 \ \mu m/sec$ ). The mean wavelength associated with the dendrite spacing for the simulations was calculated from the power spectrum using the same formula as the experiments. It is noted that the emergence of a split in the main peak of the spectrum at the earlier stage reveals a long wavelength modulation of the dendrite tips that eventually leads to cell elimination and the emergence of a new mean spacing.



Figure 3.1: (Left) An example of simulated evolution of a directionally solidified dendrite array grown under constant velocity and thermal gradient. The interface is initially morphologically noisy. Distances are in  $\mu m$ . (Right) Power spectrum of the last recorded interface structure (black line) as well as that of a close earlier time (red line).

Figure 3.2 shows a typical spatiotemporal evolution of dendritic microstructures from the transient dynamic simulations. The morphological evolution has features in common with the experimental morphology in figure 2.12. Specifically, at early times, when the velocity is fastest, the morphology is cellular and then starts to exhibit some kinetically-induced tip-splitting instabilities, giving rise to seaweed structures along the body of some primary stalks. Note that the kinetically induced tip splitting of primary tips is short-lived and occurs on length scales smaller than those controlling primary branch formation. They are thus expected to have only a minor effect on the evolution of the primary branch spacing, which is the main focus of this study. At slightly later times, dendritic primary arms with side branches emerge. Even though the width of the simulation domain was  $2.5 \ mm$ , it features only small subsections of the interface to be able to appreciate the details of the interface morphology.

#### **3.1** Finite Size Effects of Grains

In order to avoid boundary effects on the dendrite arm spacing, I study the arm spacing in as large a single grain as possible. The simulations, on the other hand, are more time consuming for larger systems. To estimate a convenient grain (or system) size to use experimentally and theoretically in the spacing selection analysis, the dependence of dendrite spacing on the system size is studied using phase field simulations with constant control parameters. Figure 3.3 shows the final steady state spacing as a function of transverse system size (i.e. grain size) for four different puling speeds. In all cases, it is started with a morphologically noisy interface.

These results indicate boundary effects become negligible at systems (grain sizes) larger than about  $10^3 \ \mu m$ , even for the smallest rate of solidification, which leads to the



Figure 3.2: Dendritic microstructure evolved during the PF simulation utilizing adaptive mesh refinement at the positions(a) 600 (b) 1200 (c) 3600 and (d) 11400 microns from the initial position of the interface, corresponding to  $T_L$ . Each image is a zoom-in of the interface and is 65 microns in dimension. The colour represents concentration.



Figure 3.3: Steady-state spacing versus transverse sample width for different pulling speeds. The effect of the boundary becomes less prominent as the sample width increases. G=5~K/mm.

largest spacing. The solidification rates studied experimentally and theoretically in the transient solidification analysis below are higher than those studied here, making finite size effects even more negligible in systems of  $10^3 \ \mu m$  or larger.

## 3.2 Transient growth

#### 3.2.1 Dendrite spacing evolution: experiments

Figure 3.4 shows experimental (black curve) and simulated (red curve) plots of the transverse dendrite spacing as a function of the front velocity, which varies during solidification. In the experiments, temperature gradient is coupled with the velocity and are not independent. The solidification rate is extracted from the cooling curves

by considering that a thermocouple registers a sharp change in the temperature slope (with respect to time) when the solidification front passes through it. The experimental spacing shown is that obtained from transverse sections. Analysis of the longitudinal sections shows the same qualitative behaviour, although the values are different, as expected. It is recalled that the experimental spacing data is obtained from different grains of the same experiment.



Figure 3.4: Spacing as a function of velocity obtained experimentally (black curve) and numerically (red curve). The blue curve corresponds to the relationship obtained by Hunt et al. (Hunt J.D., 1996) for unsteady state solidification applying the same growth conditions. Note that G(t) is dynamically changing at each point.

The experimental results in figure 3.4 are consistent with those reported by Losert et al (Losert W., 1996), as well as with older experiments of Huang et. al (Huang W., 1993) on succinonitrile. Namely, the spacing exhibits ranges of interface velocity where the spacing changes very slowly, between which it changes rapidly. It is noteworthy that the experimental data does not compare well quantitatively and, especially, qualitatively with the unsteady state model of Hunt et al. (Hunt J.D., 1996) as indicated in figure 3.4. Plausible reasons for this will be addressed in section 3.4.

Losert et al associate a rapid change or jump in spacing at a particular velocity with a period doubling instability, as predicted by Warren and Langer (Warren J.A., 1990, 1993), citing boundary effects to account for the discrepancy of the jump being less than a factor of two. For a small number of dendrite branches in a system such as the one studied by Losert et al, the change in the spacing is sharp, i.e. the entire system can shift to a new wavelength almost simultaneously. The existence of such a jump can be associated with overcoming an energy barrier for a wavelength of a given spacing to become unstable and change (these barriers will be discussed further in section 3.4. Conversely, for a large system comprising a distribution of wavelengths, the change in the mean spacing should exhibit a *smoother* evolution as not all wavelengths will satisfy the Warren and Langer instability criterion at the same time (i.e. at the same interface speed). In this work, large systems comprising tens to hundreds of dendrites are studied and a distribution of wavelengths present in the system are captured.

To support the above argument, figure 3.5 shows the 2D power spectrum averaged over three grains, and the corresponding circularly averaged power spectrum for three different velocities in figure 3.4, namely, one in the lower plateau, one in the transition region, and one in the higher plateau. The left plots in figure 3.5 indicate that the system does not contain a single wavelength, but rather a distribution of wavelengths centered about the mean. In the transition region, as the velocity decreases, some wavelengths will become unstable to period doubling (i.e. overcome the aforementioned energy barrier associated with that range of wavelengths), while the rest remain stable. Consequently, the mean spacing, defined as the average of the wavelengths, by virtue of sampling a distribution of wavelengths, will change gradually rather than abruptly. This mechanism is also at work during the plateau region. In that case, the entire distribution of wavelengths is likely to be stable to period doubling or spacing change, leading to a constant mean spacing.

#### 3.2.2 Dendrite spacing evolution: simulations

In order to approximate the growth conditions similar to those in the experiments, the directional solidification simulations included a variable thermal gradient and pulling speed, the values of which were set by fitting the corresponding curves obtained from experiments. Of-course, the pulling speed is not the same as the front velocity, especially under transient effects, since the interface moves within the coexistence region as growth conditions vary. This discrepancy is largest at the early stages of the simulation due to the initial conditions.

The two dimensional transient simulation data shown in figure 3.4 (red curve) show remarkably similar behaviour to the experiments with regards to the step-like fashion that mean spacing changes with interface velocity. Also, the behaviour of the entire distribution of wavelengths in the simulated data is analyzed and it is found that it changes with interface speed analogously to the experimental data in figure 3.5. It is noted that quantitative discrepancies between experiments and numerical results are to be expected due to the different growth conditions of the simulations



Figure 3.5: (Top) Transverse cross section of dendritic microstructure at 2500 microns (top left), 5800 microns (top middle) and 10000 microns (top right) above the chilling wall. The images below (Left frames) represent the 2D power spectrum averaged over three grains and (right) corresponding effective 1D power spectrum of the transverse images at (a) 2500 microns (lower plateau) (b) 5800 microns (transition region) and (c) 10000 microns (higher plateau) above the chilling wall. The red line in the left frames represent the mean spacing.

compared to the experiments and that the simulations are two dimensional. It is also noted that the initial interface conditions in simulations were different from those in experiments.

It is also noteworthy that the mean peak of the power spectra of the simulation data captures the main branch spacing and not the seaweed-like sub-structure evidenced in some of the branches of figure 3.2 (as previously discussed). The latter structures are present at early times and likely arise due to interface kinetics induced by the high solidification rate. Evidence of these structures also appear in the experimental data. Such tip splitting instabilities may, in fact, play a role in establishing the initial interface conditions close to the chill wall in the experiments. To illustrate their emergence experimentally, a sample at very low rate is cooled for a short period of time an then increased the cooling rate abruptly. The resulting microstructure is shown in figure 3.6. At low cooling rates, where the microstructure is larger, the microstructure comprises cellular branches. As cooling rate is increased, it is clear that some of the new initial, finer spaced branches that emerge, come about through tip splitting.

#### Ramping the rate of pulling speed

Experimental studies of the history dependence of primary spacing have focused on ramping the pulling speed slowly enough that the system is assumed to reach a steadystate in between each ramping step of the velocity (Lin X., 1999; Losert W., 1996). As an intermediate between this behaviour and that studied experimentally (section 3.2.1), a scenario whereby the pulling speed is ramped in discrete steps between



Figure 3.6: Cast Al-Cu alloy showcasing the sharp change in morphology and spacing that occurs during a transition from low cooling rate (large-scale structure) to rapid cooling rate (finer structure).



Figure 3.7: Spacing evolution versus pulling speed  $v_p$ , as  $v_p$  is ramped from 10  $\mu m$  to 20  $\mu m$  in N time intervals, as well as continuously at each numerical time step. G = 5 K/mm. The starred data are the mean steady state spacing for the corresponding pulling speed. Depending on the particular growth conditions, the full width of the simulation domain, 4 mm, accommodates (in the case of larger spacing) more than 40 dendrite arms.
$10\mu m/s$ - $20\mu m/s$  at different rates is numerically studied. This is achieved by varying the number (N = 2, 5, 10) and duration of time intervals over which the pulling speed is kept constant before changing its value. The mean primary spacing is registered at the end of each interval. The results from these simulations are shown in figure 3.7.

The starred data are obtained by starting from a morphologically noisy interface pulled at a constant speed of 10  $\mu m/sec$  until a statistically stable-state is reached, and then using the last configuration as an initial condition for a simulation with a constant pulling speed of 20  $\mu m/sec$ , until a new stable-state is reached. The curves in figure 3.7 represent simulations starting with the same initial condition, take an equal total amount of time  $t_{tot}$  to obtain, while the pulling speed is increased from 10  $\mu m/sec$  to 20  $\mu m/sec$  in N discrete steps such that the  $n^{th}$  interval has a constant pulling speed of  $v_p = 10(1 + n/N) \ \mu m/sec$  and lasts  $t_{tot}/N$  seconds. In an additional case the pulling speed is varied "continuously", namely it is ramped at each iteration in the same way described above, taking N as the total amount of intervals required for the simulation to last  $t_{tot}$ .

It is noteworthy that figures 3.4 and 3.7 exhibit the same qualitative behaviour for the time evolution of the mean spacing, even though the control parameters in these two figures cover very different ranges of pulling speed and thermal gradient, and begin with very different initial conditions. As mentioned above, the general behaviour is consistent with the theory of Langer and Warren and the experiments of Losert et. al, and point to that fact that dendritic arrays are stable over extended ranges of solidification rate, at least under transient conditions.

The transient data of figure 3.7 show that competitive growth between neighbouring cells is negligible during periods where the mean spacing remains roughly

constant, while it dominates the evolution of the array during the transition between those states. To explain this, note that the creation of new dendrites, or elimination of existing ones, due to competitive growth, is not instantaneous but requires some characteristic time. Even in an ideal periodic array, transitions between stable states will occur over some time. A distribution of spacings will thus shift its mean value gradually, which will result in an extended transition period. As the pulling speed increases, the distribution of primary spacings remains roughly unchanged, until a critical velocity is exceeded. At this point wavelengths in the distribution larger than some maximum value become most unstable to competitive growth and tip splitting and cell re-adjustment occurs. The weight of the spacing distribution thus shifts toward a smaller mean spacing (i.e. higher frequency). This is illustrated in figure 3.8. During discrete increments in the pulling speed, it is expected that entire ranges of spacings will be affected at each step.



Figure 3.8: Shift of the main peak of the power spectra of a dendritic array as  $v_p$  is increased from a lower (black) to higher (red) value of  $v_p$ . It is evident that larger wavelengths in the early time shift to shorter wavelengths at later time, when  $v_p$  is increased. These power spectra correspond to the transition period during the seventh interval in the simulation with N = 10 ramping steps illustrated in figur 3.7.

As the pulling speed is increased further, shorter wavelengths are affected until

another critical pulling speed is reached when all wavelengths have been affected, after which the system stabilizes into a new stable state characterized by a smaller mean spacing. Figure 3.9 shows the power spectra corresponding to two steps of the last interval in the simulation with N = 10 ramping steps in figure 3.7, exemplifying the statistical stability of the spacing distribution during the incubation periods.



Figure 3.9: Power spectra of the dendritic array during two stages of the incubation period corresponding to the last interval in the simulation with N = 10 ramping steps illustrated in figure 3.7.

The mechanism discussed above depends on the applicability of the theory of Warren and Langer to an array with a distribution of primary spacings. In that case, the critical values of pulling speed are expected to depend in some as yet unknown way on the rate of change of pulling speed. This proposed mechanism is consistent with the analytical expressions for the critical values of pulling speed that have been proposed by Ma (Ma, 2002). Unfortunately, in the spirit of most geometrical theories, these critical values of ref. (Ma, 2002) depend on heuristic fitting parameters, while assuming the creation of new dendrites is only due to tertiary branching. As a result, these value of critical velocities agree only qualitatively with the simulations.

With regards to thermal gradient, given its stabilizing effect, it is expected that a

larger thermal gradient would reduce not only the average spacing but also the spread (in absolute values) of the spacings present in the array. Thus, it would be expected that a reduction in the duration of the transition periods, and accordingly different critical values of the pulling speed limiting the transition, not because of a change in how the pulling speed affects different wavelengths but because less wavelengths are present in the array. In the same way, it is expected that the initial state of the system (growth conditions, initial concentration distribution, morphology of the interface) will affect the values of the critical pulling speeds that limit the transition periods by influencing the initial spectrum of wavelengths composing the array.

Figure 3.7 suggests that the higher the rate of change of  $v_p$  (larger N), the shorterlived is the unstable growth regime. This may be due to the fact that the shorter the time between step changes in  $v_p$  ( $t_{tot}/N$ ), the longer a particular wavelengths remains stable against splitting or merging. As a result, a particular  $v_p$  is eventually attained where a large number of wavelengths simultaneously become unstable, leading to an abrupt change in mean spacing. Conversely, the longer the interval between steps (lower N), the more time each wavelength in the system has to become unstable in accordance to the current  $v_p$ . When that is the case, the evolution becomes more monotonic, and closer to the predictions for steady-state growth (starred data in figure 3.7).

#### 3.3 Steady state growth

#### 3.3.1 Initial conditions and history dependence

The accumulated evidence on the history dependence of the morphology of an extended array under stable growth conditions presents an opportunity to extend our numerical study of transient growth conditions. Figure 3.10 plots the mean primary spacing  $\lambda_1$  once a stable state is reached for a constant  $v_p$ , for different initial interface morphologies. One set of  $\lambda_1$  Vs.  $v_p$  consist of starting from a morphologically noisy flat interface, which is the same as the case previously examined by Greenwood et al. (Greenwood M., 2004). In the other data sets, the initial conditions consist of an initially sinusoidal interface of wavelength half, equal, and double the value of the spacing  $\lambda_1(v_p)$ , i.e. the mean spacing of the stable-state reached under random initial conditions. The results show certain dispersion in the final spacing, but are nonetheless confined within a narrow band.

The dispersion in figure 3.7 is larger than the band size in figure 3.10 at the same velocity (see, for example 20  $\mu m/sec$ ). This is because the spacings in figure 3.7 did not have enough time to converge toward the stable band predicted in figure 3.10 . The convergence of the mean spacing, for a fixed  $v_p$  is illustrated in figure 3.11. If this is a general feature of convergence, it would imply that a large enough spread in the initial conditions will lead to a mean spacing that asymptotically falls within a progressively narrowing band of values. When the evolution of the system is interrupted before reaching convergence, as when ramping the pulling speed or under transient conditions, the width of the band within which the spacing falls will depend on the proximity of the (evolving) band to its converged values. The broader the



Figure 3.10: Primary spacing for different morphologically distinct initial interfaces, where  $\lambda_1$  approximates the mean spacing registered when starting form a morphologically noisy interface. The other data sets correspond to the spacing reached from initial interfaces with a sinusoidal perturbation corresponding to the harmonic of  $\lambda_1$  indicated.

distribution of initial states, the longer the system is expected to require to approach stability.

Further insight into the history dependence and transient evolution of primary spacing can be found in the sets of simulations summarized in figure 3.12. Each set corresponds to a series of simulations with (different) constant pulling speed, where the state reached at the end of a simulation serves as the initial condition for the next one. The first simulation in each set starts with a flat interface roughened by adding morphological random noise. In the set connected by black arrows, the first simulation has a constant pulling speed of  $v_p = 10 \ \mu m/sec$ . Once the system reached stability, the resulting state served as the initial condition for three simulations with different constant pulling speeds of  $v_p = 20$ , 30 and 50  $\mu m/sec$ . When stability is reached in each of these cases, each of the resulting stable configurations ( $v_p = 20$ , 30



Figure 3.11: Evolution of the spacing when  $v_p = 10 \ \mu m/sec$ , starting from three different initial cell spacings  $\lambda_{init}$  corresponding to each curve.  $G = 5 \ K/mm$ .

and 50  $\mu m/sec$ ) serves as an initial condition for simulations where the pulling speed is set (back) to a constant value of  $v_p = 10 \ \mu m/sec$ . The Second and third sets in figure 3.12, connected by red and green arrows, follow an analogous procedure. The second set starts with  $v_p = 20 \ \mu m/sec$ , the result of which serves as the initial condition for simulations with constant pulling speeds of  $v_p = 30 \ \mu m/sec$  and  $v_p =$  $50 \ \mu m/sec$ , respectively. Each of these results then serves as the initial condition for two simulations where the pulling speed is set (back) to a constant value of  $v_p =$  $20 \ \mu m/sec$ . The third set starts at  $v_p = 30 \ \mu m/sec$ , the result of which serves as the initial condition for simulations with a pulling speed of  $v_p = 50 \ \mu m/sec$ , the result of which, in turn, serves as the initial condition for simulations where the pulling speed of  $v_p = 50 \ \mu m/sec$ , the result of which, in turn, serves as the initial condition for simulations where the pulling speed is set back to  $v_p = 30 \ \mu m/sec$ .

Figure 3.12 exhibits the same qualitative behaviour as figure 3.10, both presenting an apparent tight band of accessible mean spacings. It is noteworthy that the limits of the apparent bands in figures 3.10 and 3.12 are very similar since the stable states have been reached in both cases. It is also noted that the power-law decay of the mean dendrite spacing in figure 3.10 corresponds to the power-law branch of the spacing function developed by Greenwood et al. (Greenwood M., 2004).



Figure 3.12: Mean spacing registered once the system stabilizes under different constant pulling speeds, for sets of simulations where the stable state reached at the end of a simulation serves as initial condition for the next one. The first simulation in each set starts with a flat interface roughened by adding morphological random noise. G = 5 K/mm.

### **3.4** Mechanisms for Spacing Plateaus

The existence of plateaus connected by rapid changes in spacing points to a dynamics in which an energy barrier has to be overcome for the spacing to adapt. Specifically, for the dendrite branch tip to split, it effectively needs to pass through a flattening stage in which the tip radius becomes effectively infinite. This lowers the efficiency of solute rejection into the liquid since the dendrite tip curvature becomes zero. Therefore, tip splitting is prevented until a larger local interface velocity is reached. Increasing the velocity reduces the diffusion length and shortens the distance over which solute is rejected. This effect acts to reduce arm spacing. Hence, there will be a competition between the two effects, the first effect keeping the spacing stable until the driving force provided by second phenomenon is large enough to force dendrites or cells to split and reduce their spacing. Figure 3.13 schematically represents the stages of tip splitting.



Figure 3.13: Schematic representation of different stages during the tip splitting mechanism. In the flattening stage (b), the undercooling due to the Gibbs Thomson effect is essentially zero.

This effect of an energy barrier leads to a so-called "incubation time" used by Ma to describe the existence of plateaus in transient directional solidification spacing data of Huang (Huang W., 1993) using a geometrical model of transient solidification in succinonitrile (Ma, 2002).

An increase in branch spacing via cell elimination occurs when a dendrite is blocked by either the secondary arms (in low speed solidification) of an adjacent dendrite or by the main stalk (in high speed solidification) of an adjacent dendrite. As shown in figure 3.14, in both cases, the seizing arm grows at an angle with a velocity component perpendicular to the growth direction of the primary arms (which is the direction of lowest energy, obtained as the product of anisotropy direction and heat flow direction). Unlike equiaxed growth, in directional solidification the growth rate of secondary branches is negligible compared to that of the main trunks. Thus, the seizing mechanism described above is not able to act until diffusion-mediated interactions through the melt become significant. As growth velocity decreases, solute diffuses a longer distance and if the diffusion length of a dendrite is large enough, it interacts with adjacent diffusion fields. It is at this point that a jump in system energy can occur.



Figure 3.14: Cell elimination caused by the neighbouring (a) primary arms or (b) secondary arms (Losert, 2009) at high and low velocity solidification respectively.

In the case of cell elimination, there is an energy increase due to the growth in any of the undesired directions and an energy decrease for changes that increase the distance between dendrites (i.e. characterized by non-interacting diffusion fields). These two phenomena dynamically compete, with the spacing change eventually determined by the dominant effect, where the former effect acts as a barrier against the change in the spacing and the latter provides the driving force for cell elimination. It is also plausible that over a small range of cooling conditions (i.e. solidification rate, temperature gradient) these effects may balance each other, causing the spacing not to change very much, at least over some long-lived transient time (i.e. the plateau regions in the data). Furthermore, the farther from steady state spacing the initial condition of the system, the higher the energy and the larger the driving force required for the system to perform branch elimination. Thus, it is possible that different spacings can also exist at the same cooling conditions depending on the history of the system. Conversely, as the rate of change of the solidification front decreases, it is expected that the spacing versus velocity should start to fall within a tight band of spacings for a given velocity.

## Chapter 4

# Orientation selection in directional solidification

#### 4.1 Morphological Transitions

Previous studies on dendritic morphology during directional solidification of binary alloys have focused mainly on cubic materials, which has a distinctive fourfold crystal symmetry. These studies elucidated important aspects of the evolution of the individual and collective morphology of extended dendrite arrays forming microstructure, under both constant and transient growth conditions (Warren J.A., 1993; Losert W., 1996; Greenwood M., 2004; Amoorezaei M., 2010; Gurevich S., 2010b).

Experimental studies in fundamental solidification phenomena are often conducted in organic analogous of metals such as SCN or pivalic acid systems to allow in-situ recording through optical means. They are also commonly conducted at pulling speeds not much higher than that of the cell-to dendrite transition, due to inherent experimental difficulties. Numerical studies of orientation selection at higher growing speeds are at present scarce, and findings at velocities close to the cell-to-dendrite transition have been generalized to higher growth speeds. Far less is known about the selection and evolution of dendritic morphologies in hexagonal systems, particularly under directional growth where the preferred directions of growth determined by the main crystalline axes and that of the applied thermal gradient compete to select the growth direction of the dendrites. Molecular Dynamics simulations conducted by Sun et al. (Sun D.Y., 2006) reveal that Magnesium is weakly anisotropic and therefore the dendrites are susceptible to alter their orientation if heat extraction through a sample is imposed in a direction that differs from that of one of the main crystal axes. This makes Magnesium alloys an ideal system to explore the morphologies arising from these competing growth directions. Sun et al. (Sun D.Y., 2006) also show that for Magnesium-base alloys dendrites grow preferentially in the  $< 11\overline{20} >$  direction on the basal plane.

Extensive phase field simulation of directional solidification in Mg-Al alloys were conducted using the phase field model defined and described previously. Dendritic morphologies in Mg-Al alloys obtained through extensive phase-field simulations are organized via the morphological phase diagram shown in figure 4.1 (Amoorezaei M., 2012). Several regimes can be identified in the figure. The transitions between these regimes are gradual hence no sharp limit can be defined between them. Nevertheless, in order to guide our discussion we have included empirically determined dashed lines separating the main regimes of observed morphologies. At velocities just above the planar-cellular instability (Mullins-Sekerka)(Mullins W.W., 1964), cells grow in the direction of the thermal gradient. As the growth speed increases towards the cellto-dendrite transition, cells begin to deviate towards the preferred crystallographic direction until the primary stalks grow along a main crystalline axis, in agreement with the findings of Trivedi el al. (Trivedi R., 1991). At velocities below the vertical dashed line, the growth orientation is more sensitive to the strength of the thermal gradient. In the dendritic region, lower temperature gradients favour growth along the direction of the main crystalline axes, whereas higher thermal gradient strengths above the horizontal dashed line favour a so-called *seaweed* microstructure where dendrites tips continuously split and change orientation, consistent with previous experiments (Utter B., 2001) and simulations (Provatas N., 2003). Note that at pulling speeds lower than the vertical dashed line, the thermal gradient required to favour seaweed structures increases with pulling speed, making the horizontal dashed line curved. The dotted line represents the cell-to-dendrite transition velocity wherein  $l_D = 2k l_T$ (Trivedi R., 1994a).

At higher growth speeds the morphology becomes less sensitive to the thermal gradient and the resulting morphology, termed *seaweed*, is a result of comparable influences from the competition of the heat extraction direction and the preferred crystalline axes. To date, it has not been shown that a directionally solidified tilted dendrite branches in an alloy system growing at one of the crystallographic axes can transition to a seaweed as the pulling speed is increased, rather than remaining stable until the absolute stability limit. Evidence of the transition from dendrite to seaweed has been reported when the thermal gradient or the tilt angle is sufficiently increased (Provatas N., 2003; Utter B., 2001; Deschamps J., 2008; Borisov A.G., 1991; Akamatsu S., 1997; Okada T., 1996). Only dendrite-to-dendrite transitions from one to another available dendrite states, and the formation of doublon dendrites has been previously observed as the front speed is increased from the initial dendritic region



Figure 4.1: Phase diagram of simulated crystal morphologies in directional solidification of Mg-0.5 wt% Al alloy. The colour bar represents the solute concentration and the dashed lines estimate the boundary between the different regimes. The dotted line represents the cell-to-dendrite transition velocity. Note the change in scale in the temperature gradient axis (Y-axis) at G = 20K/mm. The width of each subsection corresponds to  $250\mu m$ .

(Akamatsu S., 1995; Utter B., 2005).

The dendrite-to-seaweed transition occurs as the curvature contribution of the tip undercooling (misoriented with respect to the cooling direction), which increases with velocity becomes comparable to the solutal undercooling, leading to alternating tip splitting and change of the tip growth direction, a characteristic inherent in degenerate or fractal seaweeds (Akamatsu S., 1995; Utter B., 2002). The transition from dendrite to seaweed is highly dependent on the anisotropy strength and material parameters, and shifts to much higher speeds for largely anisotropic systems. For example, as shown in figure 4.2, for a hexagonal system with the same Mg-Al parameters as above except  $\epsilon = 35\epsilon_6$  and  $\Gamma = 0.14 \ K.\mu m$  we find the dendrite-to-seaweed transition occurs at  $V = 3000 \ \mu m/sec$ , almost 15 times higher than that for the nominal Mg-Al system studied in figure 4.1. Note that the thermal gradient induced transition (the equivalent of horizontal dashed line in figure 4.1) also shifts to much higher temperature gradients, further implying the strong dependence of the transition on the anisotropy strength.

At the highest growth velocities probed in the data above, the direction of the temperature gradient dominates and columnar (forward-directed) seaweeds form independently of the strength of the temperature gradient. beyond the limit of degenerate seaweeds, the spacing between the two advancing seaweed tips is a decreasing function of velocity as depicted in figure 4.3. The maximum distance between the tips before either undergoes an instability,  $\lambda_t$  (see figure 4.3), follows a power law relationship with respect to the pulling speed with the slope of the line in logarithmic scale corresponding to -0.46. This value is in conformity with the measured instability wavelength of a single seaweed tip by Utter et al (Utter B., 2001) and also with the



Figure 4.2: Phase field-generated phase diagram of morphological transitions at a range of growth conditions in directional solidification for a strongly anisotropic hexagonal system.

instability wavelength of a flat interface (Mullins W.W., 1964),  $\lambda \alpha V^{-0.5}$ . The two advancing seaweed tips reduce the spacing between them as the pulling velocity is increased until the wavelength becomes comparable to the width of the stem. This gives rise to the formation of a "compact seaweed" microstructure, where the tips have less curvature and branching is less frequent. An example of such structure can be found at the rightmost part of figure 4.1. The transition from Fractal to compact structure has been previously reported by Brener et al (Brener E., 2000) for pure materials. It is noteworthy that at  $V = 750 \ \mu m/sec$  and  $G = 2 \ K/mm$  a combination of doublon dendrites with developed sidebranches and seaweed structures (dendriticlike structure with unstable tips) can be observed. The formation of sidebranches is attributed to the larger spacing available between the dendrites due to the lower operating temperature gradient.



Figure 4.3: Different seaweed morphologies at  $G = 20 \ K/mm$  and pulling speeds of a)100, b)250, c)500 and d)750  $\mu m/sec$ . The white line represents the interface between primary phase branches. The graph plots the tip spacing against the pulling speed and follows a power law relationship with an exponent of -0.46.

We assume that the surface energy anisotropy is the only factor that interplays with the heat flow direction to establish the growth orientation of the stalks. This is in contrast with the linear stability analysis by Sekerka (Coriell S.R., 1976) and the weakly-nonlinear stability analysis by Young (Young G.W., 1987), which imply that the interface attachment kinetics governs the growth orientation selection in the vicinity of the cellular threshold limit. However, the effect of surface tension anisotropy is largely underestimated in these theories due to the linear nature of their analyses. In the fully nonlinear regime, the surface energy anisotropy becomes more important and needs to be considered. More importantly, in metallic systems the kinetic coefficient is three orders of magnitude smaller than in organic analogous to metals, e.g. SCN and pivalic acid alloys (Xia Z.G., 2007; Akamatsu S., 1997; Bragard J., 2002) which are commonly exploited in dendritic growth experiments. Interface kinetics are thus not very relevant for such transition in metal alloys. Even for the highest growth velocity studied herein, the curvature contribution to the undercooling is almost two orders of magnitude larger than that of kinetic attachments. Moreover, Okada et al (Okada T., 1996) reported observing stem rotation towards the crystalline axis as the velocity is increased in Steel containing Ni and Cr impurities, while neglecting kinetic effects.

Remarkably, the morphologies shown in figure 4.1 can be obtained in the same crystal if different sections of the materials have locally different thermal conditions –a situation that is quite common in experiments. This will lead to each of these sections having a different growth speed and thermal gradient. Based on our findings, this will result in different sections of the material solidifying into different morphologies of depicted in figure 4.1. To demonstrate how achieve a spectrum of the morphologies shown in figure 4.1 in a single crystal material, we simulated a tilted dendrite at the right corner of a channel as shown in figure 4.4. As the tip moves up, a secondary arm grows freely towards the left boundary of the channel, perpendicularly to the direction of the thermal gradient. The tertiary arms emerging from it grow in the same direction as the initial dendrite branch (upward), but at a higher undercooling (than the parent stalk) as they are retarded since they emerge from the secondary branch. In order to catch up and reach the steady state tip undercooling these tertiaries grow at a very rapid rate. The resulting morphology shown in figure 4.4 exhibits spatial transitions from dendrite to seaweed, and to partially columnar going from right to left in the figure, which corresponds to increasing front speed.

The interplay of different sources of anisotropies and their influence on the emerged microstructure has been investigated in the work by Haxhimali et al (Haxhimali T.,



Figure 4.4: Phase field simulation of a single crystal with branches growing at different velocities, promoting a spectrum of morphologies. The growth velocity increases towards the left, leading to the formation of seaweed and columnar structures. The image is a subsection of the entire domain. The width corresponds to  $300\mu m$  and the temperature gradient is  $G = 10 \ K/mm$ . The colours represent solid (red) and liquid (blue) phases.



Figure 4.5: Dendritic microstructure of a directional solidification of Mg-0.5 wt%Al alloy. Two initial grains misoriented with respect to the upward thermal gradient are shown. The initially misoriented dendrites tilt towards the heat flow direction after a short transient time.

2006), where they varied the strength of two composition dependent anisotropy parameters and showed that the orientation of equiaxed dendrites varies continuously. Their results, however, do not provide the ability to control the emerging microstructure for a given alloy composition, since the anisotropy parameters are implicitly controlled by concentration. Our results are similar to Haxhimali's in that the interplay of two sources of anisotropies is shown to lead to a continuous orientation variation. However, since the cooling rate and direction in our directional solidification experiments and simulations are adjustable control parameters, the emerging microstructure can be controlled for a given alloy composition, as needed.

Our results on orientation selection are supported by our directional solidification experiments in Mg-Al alloys. Figure 4.5 shows a typical dendritic microstructure of a directionally solidified Mg-0.5 wt% Al alloy. The initial morphology encompasses two different grains, highlighted in the figure. The right grain starts misoriented with respect to the thermal gradient but after a short transient undergoes a transition towards the direction of the thermal gradient. The transient in the left grain is not as clear, but it also ends up orienting with the thermal gradient after a short transient of similar duration. In terms of the phase diagram in figure 4.1, the temperature gradient strength of this experiment falls on the lower range of values. The velocity of the experimental front, however, is beyond the highest value shown in the phase diagram, which is predicted to lead to a columnar-type growth in the upward (gradient) direction consistent with figure 4.5. In casting situations, as in our experiments, the interface velocity at the chill surface is significantly higher than the values probed in our simulations. In this regime, we also expect kinetic effects to become important.

The 2D simulations presented here predict the same qualitative morphological

orientation variations with growth speed as the 3D experiments. The quantitative difference being due to the discrepancy in dimensionality. This is analogous to recent results of Gurevich et al (Gurevich S., 2010a), where primary spacing results do not change qualitatively between 2D and 3D directional solidification simulations and experiments. It is thus concluded that 3D morphological structures will present qualitatively the same transitions as predicted by 2D simulated morphologies, with the critical transition values appropriately shifted. Specifically, given that the tip undercooling for a 3D steady state cell falls below that of the equivalent 2D shape (Gurevich S., 2010a), the transition velocity and the transition temperature gradient are expected to shift to lower values for a 3D shape.

Following Hunt's approach to dendrite tip undercooling as a function of growth velocity and temperature gradient, a criterion for the dendrite-to-seaweed transition (vertical dashed line) was sought. A common assumption, introduced by Hunt (Hunt, 1979), is that dendrites grow at minimum undercooling. In terms of the tip position, dendrites that advance faster than their neighbours will expel solute laterally and hinder the development of the slower growing dendrites, eventually becoming dominant in the structure. With these assumptions, we can gain insight into the distribution of morphologies in figure 4.1 by comparing the tip undercooling of dendrites which may develop in the direction of the thermal gradient with those which may develop in the direction of maximum surface tension anisotropy.

The tip undercooling,  $\Delta T = T_L - T_{tip}$ , where  $T_L$  is the liquidus temperature and  $T_{tip}$  is the temperature at the tip, can be determined from the the Gibbs-Thomson relation according to

$$\Delta T = \Delta T_c + \Delta T_R + \Delta T_v \tag{4.1}$$

where the different contributions are

$$\Delta T_c = |m|(c_{tip} - c_0)$$
$$\Delta T_R = \Gamma a(\theta) \kappa$$
$$\Delta T_v = \beta v$$

)

Disregarding kinetic effects ( $\Delta T_v \approx 0$ ) there are two contributions to the tip undercooling. The contribution of the tip concentration  $c_{tip}$ ,  $\Delta T_c$ , and the contribution due to the tip curvature,  $\Delta T_R$ . Figure 4.6 illustrates two dendrites, one growing in the direction of the thermal gradient (dendrite 1) and the other growing in the direction of crystalline anisotropy axis (dendrite 2). According to the assumption of growth at minimum undercooling, if the undercooling difference  $\Delta_1 - \Delta_2 =$  $(\Delta T_{c_1} + \delta_1) - (\Delta T_{c_2} + \delta_2)$  (where  $\delta_i$ , i = 1, 2, represents the transient contribution to the tip undercooling) is much larger than the undercooling difference due to the tip curvature effect,  $\Delta T_{R_1} - \Delta T_{R_2}$ , the morphology of the resulting structure will be dominated by dendrites growing at the direction of the thermal gradient. If the opposite is true, the structure will be dominated by dendrites growing at the direction of maximum anisotropy. Here,  $\Delta T_{Ri} = \gamma_0 (1 + \epsilon_0 - 35\epsilon_6 \cos(6\phi_i))\kappa_i$ ; i = 1, 2. Defining  $\phi$  as the angle between the direction of growth and the axis of crystalline anisotropy gives, for the case illustrated in figure 4.6,  $\phi_1 = \Phi$ , and  $\phi_2=0$ .

We found empirically from our simulations that for a given misorientation angle the ratio  $\Delta_1/\Delta_2$  is almost constant. As a result, increasing  $\Delta_1$  will increase the difference and favour growth towards the heat flow direction. Increasing the misorientation angle will also favour growth towards the heat flow direction.



Figure 4.6: Illustration of the relative position and growth velocity of the dendrites oriented in thermal gradient and crystalline axis directions.

Evaluating the total undercooling,  $\Delta T$ , requires an expression for the concentration or temperature at the tip. The simplest estimation comes from the model developed by Bower, Brody, and Flemings (BBF) (Brody H.D., 1966; Bower T.F., 1966) where the impurity flux at the tip position  $v(c_{tip} - c_0)$  is assumed to balance the flux -GD/m induced by the variation of concentration ahead of the interface, assumed linear to lowest order. This flux balance, which only considers one-dimensional solute diffusion along the growth direction, yields  $\Delta T_c = T_L - T_{tip} = |m|(c_{tip} - c_0) = GD/v$ . In order to account for lateral variations in the concentration field, Hunt (Burden M.H., 1974) added an extra term to the flux induced by the variation of concentration along the interface, leading to  $\Delta T_c = GD/v - mvR(1-k)c_0/D$  where R is the radius of the tip, assumed spherical. This consideration further leads to  $\Delta T_R = 2\Gamma/R$ . Minimizing the total undercooling for the tip curvature  $R = R^*$ , Hunt obtained the following expression for the minimum undercooling  $\Delta T(R^*) = \Delta T_c(R^*) + \Delta T_R(R^*)$ ,

$$\Delta T = \frac{GD}{V} + 2\left(\frac{2|m|C_0(1-k)\Gamma V}{D}\right)^{1/2}$$
(4.2)

where the first term is dominant at high gradients and low speeds.

Figure 4.7 plots eq. 4.2 as a function of the interface velocity, for different temperature gradients. These curves can be used to understand the qualitative behaviour of the morphological transitions in figures (4.1) and (4.2). Figure 4.7 shows that at the high velocities regimes when the second term in eq. 4.2 dominates,  $\Delta T$  becomes insensitive to the strength of the temperature gradient. In contrast, at the lower velocities regime where the first term dominates,  $\Delta T$  increases with the strength of the temperature gradient. The crossover between dendritic and columnar morphologies occurs when  $\Delta T_c \sim \Delta T_R$ , the solution of which is largely independent of the thermal gradient at high velocities. We thus expect that the orientational selection will be independent of the temperature gradient strength at high velocities. On the other hand, at low interface velocities the selected orientation is controlled by the thermal gradient, favouring growth at the direction of maximum anisotropy at low *G* and a crossover to seaweed, and ultimately cellular growth, as the thermal gradient increases.

The dendrite-to-cell transition is represented in figure 4.1 by the  $l_D = 2kl_T$  line, where  $l_D$  is the diffusion length and  $l_T$  the thermal length. In its proximity  $\Delta T_c$ decreases with the growth velocity, while the significant increase of the dendrite tip curvature gives rise to  $\Delta T_R$  favouring the growth in crystalline axes directions.

The phase field results summarized in figure 4.1 are consistent with the above predictions. However, the consistency has not been investigated for other crystal structures and anisotropy values.



Figure 4.7: Tip undercooling as a function of growth velocity at various temperature gradients for Mg - 0.5 wt% Al alloy. Note that the contribution of the temperature gradient to the value of tip undercooling is significant only at velocities close to that of cell-to-dendrite transition.

#### 4.2 Orientation Selection in multiple grains

Orientation selection plays an important role in the competition between grains. In effect, grains formed from dendrites whose orientation is better aligned with the thermal gradient grow faster and gradually dominate the structure as can be seen in figure 4.8, where the evolution of different seeds oriented at  $-\pi/6$ , 0 and  $\pi/6$  from the direction of the thermal gradient is shown. The influence of the interaction between the grains is notable. Specifically, the coexistence of columnar and hexagonal structures within the same grain, as a neighbouring grain falls behind in its development. In order to simulate the growth of multiple grains we employed a modified phase-filed model, expanded to include as many order parameters as grains with distinct orientations are present. Grain boundary interactions, based on the Read-Shockley equation, are also present in the model. Details on this multi-phase-field model, developed by Ofori-Opoku et al. can be found in (Ofori-Opoku N., 2010).



Figure 4.8: Three misoriented grains of Mg - 0.5wt% Al grown with a pulling speed  $V_p = 0.35mm/s$  under a thermal gradient of strength G = 16K/mm. The system width is 4mm. The orientations of the grains are, from left to right, and in units of  $2\pi$ : -0.5, 0 and 0.5. These specify the angle between the  $< 11\overline{2}0 >$  direction in the basal plane of the underlying crystalline hcp structure and the thermal gradient (the vertical direction in the figure). The color scheme represents the concentration of impurities.

## Chapter 5

## Conclusions

The notion of a unique spacing selection mechanism is challenged by series of experiments in Al-Cu alloys and corresponding phase field simulations under transient and steady state conditions. Experiments under transient growth conditions suggest that mean spacing vs. front speed evolves in a series of plateaus connected by rapid changes. In the plateau regions, the spacing changes very slowly so that within the existing error bars, it is reasonable to consider it statistically constant. These results are in agreement with the findings of Losert et al (Losert W., 1996). However, they do not compare well quantitatively and, especially, qualitatively with the unsteady state model of Hunt et al. (Hunt J.D., 1996). The jump between the two plateause was shown to be gradual, in contrast with the period doubling instability analysis by Warren and Langer (Warren J.A., 1990, 1993), which suggests a sharp jump between the plateaus. This discrepancy is explained showing that the system does not contain a single wavelength, but rather a distribution of wavelengths. In the transition region, as the velocity decreases, some wavelengths will become unstable to period doubling (i.e. overcome the energy barrier associated with period doubling for that range of wavelengths), while the rest remain stable. Therefore, if the Warren and Langer period doubling instability theory is examined in the context of the stability of a distribution of wavelengths, it is expected that a gradual transition will result. A remarkably similar behaviour to our experiments, with regards to the step-like changes in mean dendrite spacing changes with interface velocity, is also found in new two dimensional transient phase field simulations of Al-Cu solidification. However, the agreement between simulations and experiments is not quantitative since the simulations are two-dimensional and, the simulated pulling speed is determined through a fit of the experimentally registered front velocity. Also, the initial interface conditions in simulations were different from those in experiments.

Our results show that under transient conditions, the power-law behaviour predicted by most previous heuristic models is incorrect. In fact, under transient conditions the mean spacing appears relatively stable over a broad range of pulling speeds, changing relatively rapidly at specific values, which depend on the rate of change of the pulling speed.

The phase field simulations of directional solidification conducted under steady growth conditions show that there is a dependence of the dendrite spacing on initial conditions and history of the system. Long-time spacing, however, fall in a narrow band that appears to follow a power-law behaviour. This power-law scaling is similar to that predicted by previous geometrical models, steady state experiments on organic alloys and 2D phase field simulations (Greenwood M., 2004).

New results from simulations and experiments on directional solidification of Mg-Al alloys were presented that demonstrate the emergence of a spectrum of dendritic and fractal-like solidification patterns in alloys when anisotropies in the processing environment compete with the inherently anisotropic interface properties of the material. It suggests that the variety of controllable morphologies arising from varying the solidification rate are much more complex than previously thought. It is shown that at a constant growth rate, increasing the temperature gradient favours the formation of seaweed microstructure in accord with the findings of Provatas et al. (Provatas N., 2003) and Utter et al. (Utter B., 2001). The effect of velocity, however, reveals a more complex behaviour. increasing the velocity at a constant thermal gradient favours the growth in the crystalline axes direction. Further increase of the velocity has an opposite effect on the growth direction, favouring the seaweed and doubloons in the direction of thermal gradient. The simulation results are supported by new experimental observations on the cast microstructure of Mg-0.5wt%Al alloys.

## Appendix A

## 2D power spectrum MATLAB code

For spacing analysis on the digitized images of transverse cross section of the cast samples, I developed the following 2D power spectrum code in MATLAB. The input comprises three images of different scales and resolutions at the same height from the chill wall. Before running the code, one needs to manually calculate the size of each pixel in microns for each image. The image with the largest pixel size is chosen as the reference and the resolution of the other two images is changed such that each pixel represents the same size in micron as that in the reference image. The rest of the image matrix up to the size of the reference image matrix is filled by zeros in order for all image matrices to have the same dimensions. At this point, three matrices with the same dimensions are available for further analysis and average spacing calculations. It is best to make the resolution (matrix dimension) a power of two, e.g. 1024\*1024 in the case we analyzed here.

%image1– each pixel 0.8998 microns %image2– each pixel 1.326 microns %image3—each pixel 0.741 microns

% pick image 2

%fix((1024\*0.8998)/1.326)=694—size of the new image one. fill the rest of the indices by zeros to make it 1024x1024

%fix((1024\*0.741)/1.326)=572—size of the new image three. fill the rest of the in-

dices by zero to make it  $1024 \times 1024$ 

%image 2 remains 1024x1024

%code starts here

deltax = 1.326;

im1=imread('im1.jpg');

im2=imread('im2.jpg');

im3=imread('im3.jpg');

I1=rgb2gray(im1);

I2=rgb2gray(im2);

```
I3=rgb2gray(im3);
```

figure

imi1=I1;

imi2=I2;

imi3=I3;

Gcomp1=imcomplement(imi1);

```
Gcomp2=imcomplement(imi2);
```

```
Gcomp3=imcomplement(imi3);
```

```
s1=max(size(Gcomp1));
s11=s1+1;
s2=max(size(Gcomp2));
s3=max(size(Gcomp3));
s33=s3+1;
L1=double(Gcomp1);
L2=double(Gcomp2);
L3=double(Gcomp3);
sum1=0;
for i=1:s1,
for j=1:s1,
sum1=sum1+L1(i,j);
end
end
average1=sum1./(s1.^2);
image1=L1-average1;
sum2=0;
for i=1:s2,
for j=1:s2,
sum2=sum2+L2(i,j);
end
end
average2=sum2./(s2.^2);
image2=L2-average2;
```

sum3=0; for i=1:s3, for j=1:s3, sum3=sum3+L3(i,j); end end average3=sum3./(s3.^2); image3=L3-average3; %deduct the average values

%deduct the average value from each component so that the values fluctuate around zero.

%in the next step, the resulting matrices are zero padded to get the final dimension of 1024x1024 for i=s11:s2, for j=s11:s2, image1(i,j)=0; end end for i=s33:s2 for j=s33:s2 image3(i,j)=0; end end F1=fft2(double(image1));F2=fft2(double(image2));

```
F3=fft2(double(image3));
power1 = (abs(F1))^2;
power1(1,1)=0;
power2 = (abs(F2)).^2;
power2(1,1)=0;
power3 = (abs(F3)).^2;
power3(1,1)=0;
v=max(size(power1))
N1=0
for i=1:v,
for j=1:v,
N1=N1+power1(i,j);
end
end
N2=0
for i=1:v,
for j=1:v,
N2=N2+power2(i,j);
end
end
N3=0
for i=1:v,
for j=1:v,
N3=N3+power3(i,j);
```

end

end

power1=power1./N1;

power2=power2./N2;

power3=power3./N3;

%this is to get a more clear image. other exponents may also be used power=(((power1+power2+power2))

N = 1024;

x = linspace(1, N, N);

nyquist = N/2/max(x);

freq = (1:N/2)/(N/2)\*nyquist\*2\*pi/deltax;

period = 2\*pi./freq;

[Px, Py]=meshgrid(freq, freq);

cut = 200;

```
surf(Px(1:cut,1:cut),Py(1:cut,1:cut),power(1:cut,1:cut))
```

colormap jet

```
axis equal axis([0 \ 0.3 \ 0 \ 0.3 \ 0 \ \max(\max(power))])
```

view([0,90])

figure(2)

```
count = zeros(1, (v/4));
```

```
bin=zeros(1,(v/4));
```

for i=1:v/4,

for j=1:v/4,

 $amp = (i-1).^2 + (j-1).^2;$ 

for k=1:v/4,
```
if (amp;=(k-1).^2) & (amp;k.^2)
bin(k) = bin(k) + (power(i,j).^2);
count(k) = count(k) + 1;
end
end
end
end
bin=bin./count;
plot(freq(10:v/4),bin(10:v/4),'r','LineWidth',2)
xlim([0 \ 0.7])
xlabel('frequency (2 \pi/\lambda)')
ylabel('average power spectrum')
title('angular average power spectrum')
sigmabin=0;
sigma=0;
for i=10:v/4,
sigmabin=sigmabin+bin(i)
end
for i=10:v/4,
sigmak = freq(i).*bin(i);
sigma=sigma+sigmak;
meanvalue=sigma./sigmabin;
end
meanvalue=2.*pi./meanvalue
```

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