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*Stochastic Characterization
of Cast Metal Microstructure*

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*Stochastic Characterization
of Cast Metal Microstructure*

Michael Steinzig

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STOCHASTIC CHARACTERIZATION OF CAST METAL

MICROSTRUCTURE

By

MICHAEL STEINZIG

ABSTRACT

The major goal of this work is to provide a means to characterize the final structure of a metal that has solidified from a melt. The thermally controlled solidification of a binary alloy, nucleated at isolated sites, is described by the evolution of a probability distribution function (PDF). The relevant equation required for propagating the PDF is developed with variables for grain size and distance to nearest neighbor. The phenomena of nucleation, growth, and impingement of the grains are discussed, and used as the basis for developing rate equations that evolve the PDF. The complementary equations describing global heat and solute transfer are discussed, and coupled with the microstructure evolution equations for grain growth and PDF evolution. The full set of equations is solved numerically and results are compared with experimental data for the plutonium 1 weight percent gallium system.

The three principal results of this work are:

1. The formulation of transient evolution equations for the PDF description of nucleation, growth, and impingement of a distribution of grain sizes and locations.
2. Solution of the equations to give a correlation for final average grain size as a function of material parameters, nucleation site density, and cooling rate.
3. Solution of the equations for final distribution of grain size as a result of the initial random spatial distribution of nucleation sites.

1. INTRODUCTION

The solidification of a binary alloy is a stochastic process. In particular, when the liquid to solid phase transition commences at isolated nucleation sites, there are at least three contributions to the random variations in subsequent grain growth and thus to the microstructure when solidification is complete. These sources to variability include

- The detailed circumstance of individual nucleation,
- the possible transition from stable to unstable growth and its consequences for growth rate,
- the specific configuration for impingement with adjacent grains.

To examine the effect of these and other factors we use a Liouville formulation [1] to follow the evolution of a probability distribution function (PDF) that describes the likelihood that a particular realization will occur in an ensemble of macroscopically identical solidification circumstances.

Many investigators have described the solidification of a binary alloy in global terms, [2], in which the analysis occurs on a scale somewhat larger than the scale of an individual grain at its early stages of growth. This global method allows numerical solution of casting problems in a time short enough to be useful at the industrial level, but at the cost of missing some of the microstructural details of the process. On the other hand, direct numerical solution (DNS) techniques have

been described by Charbon et al. [3] and by Juric and Tryggvasson [4]. The results from such analyses furnish much detailed information on grain structure that is not available from a global calculation, but these calculations can generally not be performed over realistic size scales due to limitations of the numerical solution process, particularly the computer hardware.

The PDF approach combines some of the advantages of both DNS and global models. In the analysis we solve coupled partial differential equations for the global transport of heat and solute. We use the global variables in a Liouville equation to evolve a PDF from prescribed initial conditions through grain nucleation, growth, impingement with neighbors and ultimately to full solidification. The evolution of the PDF thus includes the effects of occurrences on a microstructural scale, while some of the variables are evolved on a global scale. An additional advantage of the PDF approach is in the potential the technique enables for incorporation of other stochastic properties (for example, nonisotropic single-crystal elastic modulus and nonisotropic coefficients of heat conduction and expansion) from which the probable mean and variance of properties for the bulk cast piece can be deduced.

Previous researchers have applied PDF techniques to solidification processes controlled by either heat or solute transport. Lifshitz and Slyozov [5] performed an analysis to examine the self-similar evolution of the distribution of grain sizes. Chen and Voorhees [6] and other investigators have extended the technique, with

particular attention to Ostwald ripening. Masumura [7] considered a Fokker-Plank diffusion of the PDF in size space in order to describe the final distribution of grain sizes.

We have extended these ideas in order to investigate two phenomena not previously analyzed with the PDF method: the effect of cooling rate and nucleation parameters on the nucleation and growth of nominally spherical grains, and the effect of distance to nearest neighbor on the final distribution in grain size. In Chapter 3, we derive the relevant Liouville equation, and give some examples of its use.

Spherical grain size is characterized by the variable R . In Chapter 4, an $\dot{R}$ equation is derived from physical considerations, and the methodology is laid out for evolving the PDF in R space. We use a constant number of nucleation sites, some active and some inactive, that vary in size and are characterized by the initial PDF. The mechanism for activating these nucleation sites is based on the calculation of critical radius from the Gibbs-Thomson relation [8], which relates solidification temperature to surface tension. Since surface tension of a solid particle is related to its size, the number of active nucleation sites is dependent on the initial distribution in size and on the rate at which heat is extracted from a region. We consider the thermal transport to dominate the process, with local-scale species transport in the liquid phase able to accommodate rapidly to the results of thermally controlled growth. Growth can be either stable or unstable.

as dictated by the Mullins and Sekerka [9] stability criterion. In this phase of the study, there is no consideration of how grains are located in space, and the only effect grains have on one another is in ending the growth when all space is filled with solid. In Chapter 5, the equations are solved for a particular alloy, and the average final grain radius is compared with experimental data. From this comparison, a general formula for grain size is derived and used to make comparisons with experimental data from additional alloys.

In Chapter 6, the variable S , which describes the distance that a grain has to its nearest neighbor, is used to characterize the initial distribution of nucleation sites in space. An analysis is developed to evolve the PDF from this initial distribution to full solidification. In this case, all the nucleation sites are the same size, because we are interested in isolating the effect of impingement. Impingement models described by other authors usually limit the growth-rate expression by including a factor that varies with local volume fraction of the solidified material. We follow a variant of this approach and show that the PDF evolution results in a final distribution of grain size that is predominantly controlled by the probable initial distribution of nucleation-site distance to nearest neighbor. Thus, the final distribution of grain size is due to the initial distribution in location of the nucleation sites. The results of this approach are compared with experimental data.

The principal conclusions presented in this dissertation are Eq. 5.7, the (restricted) universal correlation for final grain size, and Eqs. 6.7 and 6.10, the relation between initial distribution in space and final distribution in size.

2. BACKGROUND IN SOLIDIFICATION

In most casting situations, the liquid melt is poured into a mold with some degree of superheat, that is, the temperature is higher than the equilibrium solidification temperature. Heat is then extracted through the walls, at a rate generally dependent on position. Some castings are intentionally cooled from a single wall to give a directionality to the casting. In general, the cooling rate is not constant, but varies as the temperature of the casting varies. In addition, the cooling rate at the wall is not the same as the cooling rate in the interior of the solidifying melt. For example, a common observation among castings is the very fine grain structure near a cooling wall, which transforms to a columnar microstructure, and then to an equiaxed microstructure in the center of the casting. Fig. 2.1 is a cylindrical section of a palladium button, and shows a very fine grained equiaxed microstructure on the right side of the casting, with the grains becoming larger toward the left.

Fig. 2.2 shows a Zirconium alloy, where solidification initiated at the top center of the figure, and the fine-grained structure rapidly transitions to a columnar microstructure. The final size and shape of the grains is a function of various parameters, including the number of grains nucleated which, in turn, is a strong function of the cooling rate.

Figure 2.1: Equiaxed microstructure, *courtesy of Deniece Korzekwa, Los Alamos National Laboratory*

Figure 2.2: Columnar microstructure, 50x, *courtesy of Carl Necker, Los Alamos National Laboratory*

2.1 Methods to Date

A variety of approaches to modeling solidification have been developed over the years, tailored to produce the particular information that is of interest, but restricted by the type of analytical and computational tools available.

2.1.1 Geometrical descriptions

Two important physical parameters of microstructure are grain size and distribution in grain size. The phenomenon of nucleation is largely responsible for the final number of grains, and several types of nucleation mechanisms have been suggested to explain the final grain size and distribution in size. There are several geometric models of nucleation and growth that have been proposed, two of the most common being the “cell” model proposed by Avrami [10] and the Johnson-Mehl model [11]. These geometric models do not consider the physics of the phase transition processes; they are only concerned with the subdivision of space around a distribution of nucleation sites. In the cell model, all nucleation sites begin to grow at the same time and with the same velocity in all directions. The results are the same as those of a Voronoi tessellation of the space around the sites. In the Johnson-Mehl model, the nuclei begin to grow at different times. In both cases, the nucleation sites can be randomly distributed in space, or placed according to some order, and growth proceeds in a given direction until impingement, and continues until all space is filled. These models were originally developed for any

type of phase transformation, and have often been applied to study solid-solid transformations. The rest of this discussion is in the context of a liquid to solid transformation.

The geometric properties of each model at solidification were studied in detail by Meijering [12], who showed mathematically the grain parameters (average number of faces, edges, vertices, etc) that would result from each type of nucleation law. He also studied the special case of the cell model in which the nucleation sites are not located randomly, but are located on a body-centered cubic lattice. This special case results in a symmetric geometry of grains, since all nucleation sites grow with the same velocity in all directions, and therefore impinge on neighbors at coincident times. If, however, the cell model is initiated with the nucleation sites randomly distributed in space, the final distribution in size is entirely a function of the initial distribution in space. In the Johnson-Mehl model, the final distribution in size is also affected by the rate at which nucleation sites become active. Neither of these models takes into account the variation of growth velocity with the local temperature and solute gradients.

In addition to the mathematical work of Meijering that led to geometrical descriptions of microstructure, computers have been used to generate and analyze microstructures resulting from various nucleation models. The first such simulations were reported by Mahin [13] for the cellular and Johnson-Mehl models. The simulation results are shown as a two-dimensional slice of a three-dimensional

occurrence, the technique of which can be found in Underwood's book on stereology [14]. The two-dimensional picture of grains can be analyzed to generate a histogram of frequency of grain size. Comparison with histograms generated from actual material specimens that have been sectioned and polished show that both models are fairly good at reproducing the trends in both number of final grains and distribution in grain size. The modification of the Johnson-Mehl model to include increasing and decreasing nucleation rates also compares fairly well with experimental results, as described by Seatre et al. [15]. Pictorially, there are slight differences between simulations generated from Johnson-Mehl and cellular models; in particular, the final cellular-model microstructure has grain boundaries that are straight lines, due to growth beginning simultaneously, while the final Johnson-Mehl microstructure may have both straight and curved intersections.

2.1.2 Global modeling

Global modeling is a technique for considering the average properties (such as temperature and solute concentration) over an area that is large compared to the microstructure. Although this type of modeling does not provide any information about the microstructure, it can be very useful in giving an overall picture of the casting solidification. For example, global modeling can describe the evolution of the location of a solid/liquid interface quite accurately by solving a simple heat equation. A detailed derivation of the equations governing this Stefan problem is given by Crank. [16]. For the special case of a pure material, an experiment was

designed by Wolff and Viskanta [17] to simulate the Stefan problem in two dimensions and measure the progress of a solid-liquid interface due to cooling at a wall. Tin was placed in a partially insulated box with two walls held at temperatures above the melting point. When all the tin had liquified, the temperature of one wall was lowered and held a few degrees below the solidification point. As heat was extracted through the cold wall, the tin solidified and the interface proceeded toward the warm wall, which was maintained a few degrees above the melting point. The final shape of the solid-liquid interface is curved because of buoyancy effects in the flow. The numerical scheme described by Steinzig [18] that couples energy and fluid flow can simulate this experiment quite well. In the numerical model, the material in a calculational cell becomes stationary when the temperature reaches the equilibrium solidification temperature. The amount of material that solidifies in the cell is then calculated based on the amount of energy that can diffuse out of the cell, and on the amount of latent heat that must be absorbed to allow solidification. For fluid flow, a Boussinesq approximation was made such that the density difference between cells contributes a source to the momentum equation. The results of this simple numerical scheme are in close agreement with the experimental results measured by Wolff and Viskanta.

A more difficult problem is tracking the solid/liquid interface for an alloy. Unlike the well-defined solid/liquid interface of a pure material, an alloy usually solidifies with a 'mushy zone', a region of both solid and liquid. This mushy

zone can be made up of fingers of solid that extend into the liquid, or individual grains that float in the liquid ahead of the interface, or both. Even though a global model does not reveal much about the final microstructure, it is possible to derive a useful model by making several assumptions regarding the physics at the microstructure level. First, the diffusion in the liquid phase is large enough that the solute concentration is uniform; for liquid metals, this is often a good assumption. Second, the temperature is nearly the same in both phases, and, except for the heat-flux, can be considered uniform over areas that are somewhat larger than the scale of the evolving microstructure. Since there is a discontinuity of concentration at each grain interface, an additional assumption is used to calculate the solute in each phase. Either the lever rule (infinite solute diffusivity within the grain) or the Scheil rule (negligible solute diffusivity within the grain) can provide the connection between the two phases. A more realistic approach is some combination of these two, as described by the back diffusion model of Wang and Beckermann [19]. Coupling of fluid flow with heat transfer and solute conservation equations allows description of such mold-filling phenomena as cold shut, in which a portion of the melt solidifies and prevents sufficient liquid metal from reaching some areas of the casting, leaving voids.

Fluid flow also has the potential to influence nucleation by breaking or melting-off dendrite arms and circulating them into regions ahead of the interface. Sedimentation, flotation, and clustering are all phenomena driven by fluid flow, and

can play an important part in determining the final microstructure of a cast piece, as described by Feller and Beckermann [20]. By allowing different densities among phases, shrinkage or expansion that cause stress in the finished part or separation between the liquid and solid phase can be described, leading to the potential to describe porosity, cracking, and residual stress, as described by Chow et al. [21]. A good overview of the numerical techniques used to solve these types of problems is given by Voller [22].

2.1.3 Direct numerical simulation

Although the global approaches continue to be expanded and improved, their application is limited by a length scale that is too large to incorporate the detailed physics occurring on a microstructure scale. The small-scale physics of phase change is quite complex, and all the relevant phenomena are not currently known. The capability to explain these phenomena is being developed with direct numerical simulations (DNS), which resolve physical space into sub-micron size scales. This local modeling allows the simulation of many microstructure details, such as grain size and shape, texture, and coring, as well as many of the kinetic details of growth, such as the columnar to equiaxed transition and nucleation by dendrite arm breakage. For example, Juric and Tryggvason [4] have simulated an isolated grain in an undercooled melt, showing the initiation of growth at some critical undercooling, and the transition of spherical growth to dendritic (unstable) growth. The existence of a critical undercooling for solidification to occur has

been experimentally verified, and theoretically correlated by the Gibbs-Thomson relation. The transition to unstable growth was predicted by Mullins and Sekerka [9] to explain dendritic microstructures, such as those observed by Esaka and Kurz [23] in their experiments with succinonitrile. The DNS work to date agrees with many experimental observations, and has been useful in developing models for simulating the physics. Today's large scale computers make it possible to simulate several growing grains at the same time, thereby seeing the effect one has on another. However, even with expected increases in computational power, simulation of entire castings at the microstructure level will not be practical in the near future.

2.1.4 Combined global and local modeling

Microstructure formation is of prime importance for the control and prediction of the properties of cast products. There are numerous examples of microscale physics having a pronounced effect on the final macro-properties of a casting, such as those discussed by Beckermann and Wang [24]. As described by Stefanescu, [25] the need for practical modeling techniques has led to combined local and global approaches, in which the goal is to link microstructural evolution to macroscopic heat and flow calculations on a scale that is large enough to provide useful results. An approach to connect the two scales was first suggested by Oldfield in 1966, [26] with the specific goal of coupling the heat flow equation with the micro-physics. In a numerical calculation, the heat diffusion equation is solved on a macroscopic

scale, while the temperature at each calculational node is calculated using microscopic models of grain nucleation, growth, and impingement. Most of the current combined approaches are deterministic, being based on the evolution of a representative average grain, rather than probabilistic, in which a distribution function is employed for the description of an evolving distribution of grain properties. However, some probabilistic simulations such as those of Brown and Spittle [27] or cellular automata techniques such as those of Rappaz and Gandin [28] have been developed.

2.2 Use of a Probability Distribution Function

The research described here extends the use of stochastic techniques by deriving physics-based laws that are used to evolve a probability distribution function (PDF). This PDF carries information about the stochastics of the microstructure, including such properties as distribution in size. The technique is similar to that first proposed by Lifshitz and Slyozov [5] (LS) for the coarsening of smaller particles into larger ones until a single particle remains. This process (Ostwald Ripening) can be described with a conservation equation, where the time rate of change of the PDF (in this case the probability for grain radius R) is controlled by the growth rate function $\dot{R}$. In the LS treatment, an asymptotic solution was found, allowing extraction of a group of self-similar solutions relating the initial distribution to the final distribution. In our work, the evolution-equation solutions are not of a universal self-similar type. The LS method was extended by

Chen and Voorhees [6] to transient, or time dependent, Ostwald ripening. More recently, Masumura and Pande [7] have derived an analytical solution of a continuity equation (a Fokker-Planck type equation) for propagation of a PDF. Their solution requires the use of a growth rate equation, and the assumption that the grain size distribution is self similar. The result is a final distribution in grain size similar to that found experimentally. We use a similar strategy in setting up the problem, but evolve the PDF using physically realistic growth laws. Instead of a Fokker-Planck-type of equation, a Liouville equation is used to propagate the PDF.

3. PROBABILITY DISTRIBUTION FUNCTIONS

The major goal of this work is to provide a means to characterize the final structure of a metal that has solidified from a melt. Final structure might include everything from grain size and shape to crystal orientation, porosity, density, etc. For the characterization to be useful, the data must be arranged in a way that is amenable to extracting information, such as average values (grain size, orientation, etc), or local material properties such as elastic modulus or yield strength. In this research, the vehicle for collecting property information is a Probability Distribution Function (PDF), which describes the probable number of grains per unit volume per unit intervals of its variables having a certain set of characteristics. For example, the probable number of grains per unit volume that have a specific size R_1 in the interval dR would be designated as $P(R_1)dR$. Moments of the PDF can be taken to get global information about such quantities as average size, shape, orientation, etc. Information about other useful characteristics such as porosity, density, crystal orientation, and residual stress fields could also be generated as the PDF is being evolved in time. Material properties such as elastic modulus can then be extracted as moments from the final PDF, and used to determine response to externally applied stresses. This chapter discusses some of the properties of a PDF, and the specific variables we use to explore solidification.

In a molten liquid, solidification begins at any of N nucleation sites per unit volume. It is assumed in this work that N is a constant number of particles per

unit volume, some of which are active (solidifying) and some of which are inactive. depending on the local temperature and the initial size of the particle. With this assumption, the quantity

$$P(\vec{x}, R, S,)dR ds \quad (3.1)$$

is the probable number of particles per unit volume at position $\vec{x}$, with size R and distance to nearest neighbor S , within the interval $dR ds$.

To derive an evolution equation for the PDF, consider first a size distribution of nucleation sites, all spherical and all stationary in position, which might be small impurities in the melt (oxide, dust or other foreign material) on which solidification can begin. The number of nucleation sites per unit volume is constant, but not all of the sites are necessarily active. In general, sites that are growing we call grains. Let $P(R, t)$ be the probability per unit volume per unit size interval that a grain with a given size is found at a specified position and time. An equation to evolve the PDF in R space can be derived by considering the number of grains per unit volume, $N_{1,2}$, between the sizes R_1 and R_2 . Here, R_1 and R_2 are functions of time, growing at rates of $\dot{R}_1$ and $\dot{R}_2$, from arbitrarily chosen initial conditions. Integrating the probability gives the total number of grains per unit volume in the interval from R_1 to R_2 .

$$\int_{R_1}^{R_2} P(R, t)dR = N_{1,2}$$

Differentiating with respect to time and using Leibnitz's rule, we obtain

$$\frac{d}{dt} \int_{R_1}^{R_2} P(R, t) dR = \int_{R_1}^{R_2} \frac{\partial P}{\partial t} dR + \left[P(R_1) \frac{dR_1}{dt} - P(R_2) \frac{dR_2}{dt} \right].$$

The term in brackets can be written as an integral.

$$P(R_1) \frac{dR_1}{dt} - P(R_2) \frac{dR_2}{dt} = \int_{R_1}^{R_2} \frac{\partial}{\partial R} \left(P \frac{dR}{dt} \right) dR.$$

so the equation becomes

$$\frac{d}{dt} \int_{R_1}^{R_2} P(R, t) dR = \int_{R_1}^{R_2} \left[\frac{\partial P}{\partial t} + \frac{\partial}{\partial R} \left(P \frac{dR}{dt} \right) \right] dR. \quad (3.2)$$

The Liouville principle states that, provided all grains in the volume grow according to the same physical laws, no grains between the sizes R_1 and R_2 can ever cross these size boundaries, and the number of grains in the interval will remain constant, ie $\frac{dN_{1,2}}{dt} = 0$. Because the number of grains is constant, the left side of Eq. 3.2 is zero:

$$0 = \int_{R_1}^{R_2} \left[\frac{\partial P}{\partial t} + \frac{\partial}{\partial R} \left(P \frac{dR}{dt} \right) \right] dR.$$

This result is independent of the choice of R_1 and R_2 , so the integrand itself must be zero.

$$\frac{\partial P}{\partial t} + \frac{\partial P \dot{R}}{\partial R} = 0 \quad (3.3)$$

in which $\dot{R} = \frac{dR}{dt}$. This is a simple form of the Liouville equation, describing how the PDF changes in time because grains are growing in size. If the grains were also moving in space, the resulting Liouville equation would be

$$\frac{\partial P}{\partial t} + \frac{\partial P \dot{R}}{\partial R} + \frac{\partial P \dot{x}}{\partial x} = 0$$

Our analysis does not include fluid motion effects, so $\dot{x}$ is zero and the last term can be discarded. The Liouville equation can be extended to any number of variables in this way, provided the rate equation for the growth of the variable is known. In Chapter 4, we discuss the derivation of the $\dot{R}$ equation.

As a simple example of the evolution of a PDF in time, consider the situation in which R (grain radius for a spherical grain) is the only variable. A PDF that describes the initial distribution in size space might look like:

$$P_o(R) \equiv P(R, 0) = Ae^{-\left(\frac{R-R_{cen}}{R_w}\right)^2}. \quad (3.4)$$

Eq. 3.4 is a Gaussian distribution, centered around R_{cen} , with a width described by R_w , and the constant A is the maximum probability, which occurs at $R = R_{cen}$. This distribution is valid only for $R \geq 0$; for $R < 0$, $P(R) = 0$. As solidification progresses, grains grow in R space until all volume is filled with solid, or in terms of a mathematical moment, when the volume per unit volume (f_s) is 1.0.

$$f_s \equiv \int_0^\infty \frac{4}{3}\pi R^3 P(R, t) dR = 1.0 \quad (3.5)$$

The evolution in size space can be followed by solving the Liouville equation.

Using the Lagrange method, we have the equalities

$$\frac{dt}{1} = \frac{dR}{\dot{R}} = -\frac{dP}{P \frac{\partial \dot{R}}{\partial R}}.$$

If the growth is proportional to grain size, as with $\dot{R} = \alpha R$, in which α is a constant, then the solution to the equations is

$$P(R, t) = e^{-\alpha t} P_o(e^{-\alpha t} R) \quad (3.6)$$

which at $t = 0$ reduces to $P_o(R)$ as it should. This solution is plotted for three values of time in Fig. 3.1, which shows the evolution of the PDF in R space. Notice that the final height of the probability curve decreases, but the width increases, and the total area under the curve remains constant.

Figure 3.1: PDF at $t=0$, 1, and 2 s, for $A=1$, $\alpha = 1$, $R_c = 0.001$ cm, and $R_w = 0.0001$ cm.

The time required to achieve solidification can be found by combining Eqs. 3.4, 3.5, and 3.6 and solving for t .

$$\int_0^\infty \frac{4}{3} \pi R^3 e^{-\alpha t} P_o(e^{-\alpha t} R) = \int_0^\infty \frac{4}{3} \pi R^3 e^{-\alpha t} A e^{-\left(\frac{e^{-\alpha t} R - R_c}{R_w}\right)^2} = 1.0$$

The total number of nucleation sites, N , given by the area under the curve of $P(R)$, should be constant, and as a check on the solution, we compare the initial

area with that at a later time t_1 . Mathematically, this is stated as

$$\int_0^\infty P_o(R)dR \stackrel{?}{=} \int_0^\infty P(R, t_1)dR$$

Rearranging terms in the expression for $P(r, t)$ and substituting $\xi = Re^{-\alpha t}$ gives

$$\int_0^\infty P(R, t_1)dR = \int_0^\infty P_o(e^{-\alpha t_1} R)d(e^{-\alpha t_1} R) = \int_0^\infty P_o(\xi)d\xi,$$

and since $\int_0^\infty P_o(R)dR = \int_0^\infty P(\xi)d\xi$, the total number of grains is a constant. In reality, the form of the grain growth rate equation is more complicated than αR , and an analytical solution is not generally possible.

We have already mentioned the use of two moments in extracting useful information from the PDF, the total number of nucleation sites and grains, which is calculated as

$$\int_0^\infty P(x, R, t)dR = N,$$

and f_s , the volume per unit volume. Both these moments are useful in modeling the solidification process, but other moments are useful in analyzing the final PDF. For example, the average grain size is a material property of interest. Given a PDF of the variable R , average grain size is given as

$$\bar{R} = \frac{1}{N} \int_0^\infty RP(R)dR,$$

and in a similar fashion, other average quantities can be extracted from the PDF.

Another important quantity is the time derivative of a moment. For example, the time derivative $\frac{\partial f_s}{\partial t}$, used in evolving the PDF, is calculated by differentiating

with respect to time the integral expression for f_s (Eq. 3.5) to give

$$\frac{\partial f_s}{\partial t} = \frac{\partial}{\partial t} \int_0^\infty \frac{4}{3} \pi R^3 P(R, t) dR.$$

In general, this type of quantity can be rearranged by applying Leibnitz's rule in reverse. The time derivative is moved inside the integral by also evaluating the time derivative of the independent variable at the end points of the integration limits.

$$\frac{\partial}{\partial t} \int_0^\infty \frac{4}{3} \pi R^3 P(R, t) dR = \frac{4}{3} \pi \left(\int_0^\infty R^3 \frac{\partial P(R, t)}{\partial t} dR + \left[R^3 P(R, t) \dot{R} \right]_\infty - \left[R^3 P(R, t) \dot{R} \right]_0 \right)$$

Since there is zero probability of grains at infinite size, and the growth rate for grains with zero size is zero, the last two terms are zero. Using the Liouville equation (3.3) to substitute in for the term $\frac{\partial P}{\partial t}$, we obtain

$$\frac{\partial f_s}{\partial t} = - \int_0^\infty \frac{4}{3} \pi R^3 \frac{\partial P(R, t) \dot{R}}{\partial R} dR.$$

With integration by parts, the equation becomes

$$\frac{\partial f_s}{\partial t} = - \left[\int_0^\infty \frac{\partial}{\partial R} \left(\frac{4}{3} \pi R^3 P(R, t) \dot{R} \right) dR - \int_0^\infty P(R, t) \dot{R} \frac{\partial}{\partial R} \left(\frac{4}{3} \pi R^3 \right) dR \right].$$

Evaluating the first term, we get zero at the lower limit of integration, and since the probability of grains of infinite size is nil, the upper limit is also zero. Simplifying the second integral leaves the relationship we seek,

$$\frac{\partial f_s}{\partial t} = \int_0^\infty 4 \pi R^2 \dot{R} P(R, t) dR. \quad (3.7)$$

The same mathematics can be used on the time derivative of other moments.

4. MATHEMATICAL DESCRIPTION OF GRAIN GROWTH

In this chapter, we derive the global and local equations necessary to evolve the PDF in the single variable R , which leads to an expression for final grain size.

4.1 Equations

In order to propagate a PDF with the Liouville equation, several supporting equations are necessary. Each variable in the Liouville equation must have a corresponding rate equation, as described in Chapter 3. For this discussion, a PDF in the single variable R is propagated, for which the rate equation $\dot{R}$ is derived. The grains are assumed to grow spherically, and effect one another only when $f_s = 1$ and solidification is complete.

In addition to the Liouville and corresponding $\dot{R}$ equations, a set of relations describing the conservation of energy and solute are developed, along with a method for coupling these variables between the local and global scales. (For simplicity, fluid flow will not be taken into account, but is easily incorporated by setting $\dot{x}$ equal to the fluid velocity and coupling to the Navier-Stokes equations for fluid flow.) A visual description of the physical process of the liquid phase transforming to the solid phase by the growth of an individual spherical grain is given in Fig. 4.1. The solid phase is designated by a subscript $-$, and the liquid phase by subscript $+$; quantities that are evaluated at the interface are designated by superscript i . The bulk temperature is T_b .

Figure 4.1: Terminology for an individual solid-phase grain growing in a liquid melt

4.1.1 Global equations

The two global variables that are relevant to this discussion of alloy solidification are those of energy and solute. Solute refers to the alloying material, for which the variable is C , defined as the mass of solute divided by the total mass of a sample. The alloy discussed in this research is the plutonium one-weight-percent gallium system, in which the solute is gallium. The phase diagram for low gallium concentration is shown in Fig. 4.2. In particular, we are concerned with the transition from liquid to epsilon phase, for which we approximate the liquidus and solidus boundaries with constant slopes m_l and m_s , and define $\kappa = \frac{m_l}{m_s}$.

The variable used to characterize energy per unit volume is T , the temperature, through the relation $E = \rho c_p T$. For a representative volume that contains several growing grains, the temperature in each phase varies with position, as

$$T_-(\vec{x}) = T_b + \varepsilon_-(\vec{x}) \quad \text{and} \quad T_+(\vec{x}) = T_b + \varepsilon_+(\vec{x}).$$

Figure 4.2: Pu/Ga phase diagram, for low concentrations of Ga.

T_b is an average value of temperature over the volume that includes both phases, and by comparison with T_b the variation of temperature with position is quite small. Therefore, we make the assumption for the global derivation that the energy per unit volume in a given volume element can be described by choosing some appropriate T_b , using the relation $E = \rho c_p T_b$, and neglecting the local variations of temperature. These variations are, however, important for the local-equation derivation described in Section 4.1.2. An equation that expresses conservation of energy in a global volume element equates the change in energy with the amounts

fluxed in and out by diffusion and the amount released by latent heat, as

$$\frac{\partial}{\partial t} \left\{ T_b \left[f_s (\rho c_p)_+ + (1 - f_s) (\rho c_p)_- \right] \right\} = \frac{\partial}{\partial x_j} \left[k_- f_s \frac{\partial T_b}{\partial x_j} + k_+ (1 - f_s) \frac{\partial T_b}{\partial x_j} \right] + L \frac{\partial f_s}{\partial t}, \quad (4.1)$$

in which the summation convention is used for subscript j , and the area per unit area for diffusional flux is set equal to f_s for grains and $1 - f_s$ for liquid. For our discussion, the material properties are assumed constant and equal between phases, which allows simplification to the form

$$\rho c_p \frac{\partial T_b}{\partial t} = -\dot{E} + L \frac{\partial f_s}{\partial t}, \quad (4.2)$$

where the global diffusion term has been replaced by a specified energy extraction term, i.e.

$$-\dot{E} = k \frac{\partial}{\partial x_i} \left(\frac{\partial T_b}{\partial x_i} \right), \quad (4.3)$$

in which the negative sign indicates that energy is being extracted. Eq. 4.2 is integrated to give our working equation for energy,

$$\rho c_p (T_b - T_{b0}) = - \int \dot{E} dt + L (f_s - f_{s0}). \quad (4.4)$$

The global energy conservation is well approximated by integrating over the single variable T_b , which characterizes both the liquid and solid phases of the grains. In contrast, the solute concentration is significantly different inside and outside the grains. Thus for the derivation of global solute, we integrate over only the liquid (exterior) volume. Again, we define a global concentration variable C_b ,

which is an average value of concentration in the + phase; and thus the mass per unit volume of solute in the + phase is ρC_b . A statement of solute-mass conservation can be written for the entire domain outside of the grains,

$$\frac{\partial}{\partial t}[\rho C_b(1 - f_s)] = \frac{\partial}{\partial x_j} \left[\rho D_+(1 - f_s) \frac{\partial C_b}{\partial x_j} \right] - \frac{\partial M}{\partial t}. \quad (4.5)$$

The term $\frac{\partial M}{\partial t}$ is the amount of solute mass per unit volume that crosses the grain interfaces per unit time. In the case of the plutonium gallium system, gallium is being drawn out of the liquid and into the solid, and so the term is negative. Because the solid-phase diffusion coefficient D_- is orders of magnitude smaller than D_+ for the plutonium gallium system, the solid phase diffusion term has been ignored in the global equation.

We now draw a correspondence between the global and local circumstances. In Section 4.1.2 we consider the solute behavior around a single spherized grain, and derive solute transport jump conditions at the grain boundary. We compare Eq. 4.5 with the local solute jump conditions (Eq. 4.25), and note that the two left sides are identical, both denoting the rate of change of solute mass per unit volume in the liquid phase. On the right side of the equations, we note that the global diffusion term equates to the local flux at the edges of grains, i.e.

$$\frac{\partial}{\partial x_j} \left[\rho D_+(1 - f_s) \frac{\partial C_b}{\partial x_j} \right] = \left[\frac{3\rho D}{R_e} \frac{\partial C}{\partial r} \right]_e,$$

in which the final radius of a grain is expected to be R_e . Next we equate the solute crossing the interfaces in Eq. 4.5 with the two remaining terms (interface

advection and diffusion) in Eq. 4.25 and get

$$\frac{\partial M}{\partial t} = \frac{3\rho R^2 \dot{R} C_+}{R_e^3} + \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_+^i.$$

This relation is substituted back into Eq. 4.5, and we obtain a global-local equation.

$$\frac{\partial}{\partial t} [\rho C_b (1 - f_s)] = \frac{\partial}{\partial x_j} \left[\rho D_+ (1 - f_s) \frac{\partial C_b}{\partial x_j} \right] - \frac{3\rho R^2 \dot{R} C_+}{R_e^3} - \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_+^i \quad (4.6)$$

The terms on the right side describe, respectively, the global diffusion, the interface advection, and the interface diffusion. The variable r describes the distance from the center of the grain. In this equation, the interface terms are written for the liquid phase. Alternatively, they can be written in terms of the solid phase. This can be achieved by multiplying Eq. 4.26 (the solute jump conditions) by $\frac{3}{R_e^3}$ and rearranging terms to get

$$\frac{3\rho R^2 \dot{R} C_-}{R_e^3} + \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_-^i = \frac{3\rho R^2 \dot{R} C_+}{R_e^3} + \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_+^i.$$

This relation is used to replace the last two terms on the right in Eq. 4.6, to give

$$\frac{\partial}{\partial t} [\rho C_b (1 - f_s)] = \frac{\partial}{\partial x_j} \left[\rho D_+ (1 - f_s) \frac{\partial C_b}{\partial x_j} \right] - \frac{3\rho R^2 \dot{R} C_-}{R_e^3} - \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_-^i$$

Using the relation $C_- = \kappa C_+$ and considering ρ and D constant, we obtain

$$\frac{\partial}{\partial t} C_b (1 - f_s) = D_+ \frac{\partial}{\partial x_j} \left[(1 - f_s) \frac{\partial C_b}{\partial x_j} \right] - \left[\frac{3DR^2}{R_e^3} \frac{\partial C}{\partial r} \right]_-^i - \frac{3R^2 \dot{R} \kappa C_+}{R_e^3}. \quad (4.7)$$

The terminology is simplified by defining a global diffusion term

$$\dot{G} = \rho D_+ \frac{\partial}{\partial x_j} \left((1 - f_s) \frac{\partial C_b}{\partial x_j} \right). \quad (4.8)$$

The combined global-local solute equation is then

$$\frac{\partial}{\partial t} [C_b (1 - f_s)] = \frac{\dot{G}}{\rho} - \left[\frac{3DR^2}{R_e^3} \frac{\partial C}{\partial r} \right]_+ - \frac{3R^2 \dot{R} \kappa C_+}{R_e^3}. \quad (4.9)$$

We consider two limiting cases, in both of which diffusion in the liquid phase is so large that $C_+^i = C_b$, independent of position. In the Scheil assumption, the diffusion in the solid phase is zero, and the second term on the right is zero. We multiply the remaining terms by $P(R)dR$ and integrate over all R space to obtain the global equation for the entire ensemble of grains.

$$\int_0^\infty \frac{\partial}{\partial t} [C_b (1 - f_s)] P(R) dR = \int_0^\infty \frac{\dot{G}}{\rho} P(R) dR - \int_0^\infty \frac{3R^2 \dot{R} \kappa C_b}{R_e^3} P(R) dR \quad (4.10)$$

The equation can be simplified by recognizing that C_b , f_s , and $\dot{G}$ are not functions of R , and can therefore be taken outside the integrals. The relation $\int_0^\infty P(R) dR = N$ is used to simplify the term on the left and the first term on the right to get

$$\frac{\partial}{\partial t} C_b (1 - f_s) = \frac{\dot{G}}{\rho} - \frac{\int_0^\infty \frac{3R^2 \dot{R} \kappa C_b}{R_e^3} P(R) dR}{N}.$$

Now using the previously stated relation $\frac{1}{N} = \frac{4}{3}\pi R_e^3$, the equation becomes

$$\frac{\partial}{\partial t} C_b (1 - f_s) = \frac{\dot{G}}{\rho} - \kappa C_b \int_0^\infty 4\pi R^2 \dot{R} P(R) dR.$$

The remaining integral was identified in Eq. 3.7, as

$$\int_0^\infty 4\pi R^2 \dot{R} P(R) dR = \frac{\partial f_s}{\partial t},$$

and so the equation becomes

$$\frac{\partial}{\partial t} C_b (1 - f_s) + \kappa C_b \frac{\partial f_s}{\partial t} = \frac{\dot{G}}{\rho}. \quad (4.11)$$

Eq. 4.11 can be integrated to give

$$C_b = (1 - f_s)^{(\kappa-1)} \left[A + \int \frac{\dot{G}}{\rho(1 - f_s)^\kappa} dt \right]. \quad (4.12)$$

In the special case $\dot{G} = 0$, the integration yields the Scheil rule for concentration as a function of fraction solidified, in which C_{bo} and f_{so} describe initial conditions.

$$C_b = C_{bo} \left(\frac{1 - f_s}{1 - f_{so}} \right)^{\kappa-1} \quad (4.13)$$

The other special case is the lever rule, which assumes the diffusion is infinite in the solid phase. In this case, because D_- is infinite, $\left[\frac{\partial C}{\partial r} \right]_-^i$ must be zero, and the second term on the right in Eq. 4.9 is indeterminate. To resolve this indeterminance, we use a different form of the local equation, equating the time rate of change of solute mass both inside and outside of the grain to $\dot{G}$, the global diffusion rate, times the volume.

$$\frac{d}{dt} \int_0^{R_e} 4\pi r^2 \rho C dr = \frac{4}{3} \pi R_e^3 \dot{G} \quad (4.14)$$

The integral can be broken into two parts, one inside and one outside the grain, resulting in the following expression

$$\frac{d}{dt} [(\kappa f_s + (1 - f_s)) C_b] = \frac{\dot{G}}{\rho},$$

which can be integrated to give

$$[1 + (\kappa - 1)f_s] C_+ = \int \frac{\dot{G}}{\rho} dt + [1 + (\kappa - 1)f_{so}] C_b. \quad (4.15)$$

In the special case of $\dot{G} = 0$, the integration yields the well known lever rule

$$C_b = C_{bo} \left(\frac{1 + f_{so}(\kappa - 1)}{1 + f_s(\kappa - 1)} \right). \quad (4.16)$$

4.1.2 Local equations

For the local equations, we consider an individual grain and the space from $r=0$ to $r=R_e$, and ask what happens to a single grain of radius R , as if every grain had that radius. In the local case, we cannot simply equate T to T_b , but we do neglect the variation of T with r inside the grain. The energy is controlled by the rate at which heat can diffuse through the region, according to the equation

$$\frac{\partial}{\partial t} \rho c_p T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k \frac{\partial T}{\partial r} \right) + L \dot{R} \delta(r - R), \quad (4.17)$$

in which it is recognized that latent heat is released only at $r = R$. Multiplying the equation by $4\pi r^2 dr$ and integrating we obtain

$$4\pi \int_0^{R_e} r^2 \frac{\partial}{\partial t} \rho c_p T dr = 4\pi \int_0^{R_e} \frac{\partial}{\partial r} \left(r^2 k \frac{\partial T}{\partial r} \right) dr + 4\pi \int_0^{R_e} r^2 L \dot{R} \delta(r - R) dr.$$

Leibnitz's rule can be used to move the time derivative outside the integral in the term on the left. Evaluating the two terms on the right leads to

$$\frac{d}{dt} \int_0^{R_e} 4\pi r^2 \rho c_p T dr = 4\pi R_e^2 k \left[\frac{\partial T}{\partial r} \right]_e + 4\pi L R^2 \dot{R}. \quad (4.18)$$

The integral part of the term on the left is the energy from 0 to R_e , and our global variable T_b is defined in such a way that

$$\frac{4}{3} \pi R_e^3 \rho c_p T_b = \int_0^{R_e} 4\pi r^2 \rho c_p T dr,$$

so that we can make a correlation between the right side of Eq. 4.2 and the right side of Eq. 4.18 , or

$$\frac{4}{3} \pi R_e^3 \left(-\dot{E} + L \frac{\partial f_s}{\partial t} \right) = 4\pi R_e^2 k \left[\frac{\partial T}{\partial r} \right]_e + 4\pi L R^2 \dot{R}. \quad (4.19)$$

Recalling the relation

$$\frac{\partial f_s}{\partial t} = \frac{3R^2}{R_e^3} \dot{R},$$

and using it in Eq. 4.19, we see that the latent heat terms cancel. The remaining two terms give

$$-\frac{4}{3}\pi R_e^3 \dot{E} = 4\pi R_e^2 k \left[\frac{\partial T}{\partial r} \right]_e, \quad (4.20)$$

which we can solve for $\dot{E}$, in terms of the gradient of temperature at the final edge of the grain.

$$\dot{E} = -\frac{3k}{R_e} \left[\frac{\partial T}{\partial r} \right]_e \quad (4.21)$$

To derive the interface jump conditions, we start from Eq. 4.18 and separate the term on the left into three different integrals. Then, using Leibnitz's rule on each, and considering material properties constant, we have

$$\begin{aligned} & 4\pi\rho c_p \left(\int_0^{R_-} r^2 \frac{\partial T}{\partial t} dr + [r^2 T \dot{R}]_{R_-} + \frac{\partial}{\partial t} \int_{R_-}^{R_+} r^2 T dr + \int_{R_+}^{R_e} r^2 \frac{\partial T}{\partial t} dr - [r^2 T \dot{R}]_{R_-} \right) \\ &= 4\pi R_e^2 k \left[\frac{\partial T}{\partial r} \right]_e + 4\pi L R^2 \dot{R}, \end{aligned}$$

in which R_- and R_+ are the interface radii inside and outside the nominal grain radius, R . The integral over the interface goes to zero as $R_- \Rightarrow R_+$, because the integrand is bounded. To evaluate the other two integrals, we use Eq. 4.17 over the range of each integral, and note that the delta function term is zero over each of these ranges. Thus for the two integrals in question, we can use the relation derived by setting the delta function to zero in Eq. 4.17, or

$$r^2 \rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial r} \left(r^2 k \frac{\partial T}{\partial r} \right).$$

Substituting this relation in the terms on the right side of the equation and performing the integrations we obtain the following jump condition.

$$\left[R^2 k \frac{\partial T}{\partial r} \right]_{R_-}^i - \left[R^2 k \frac{\partial T}{\partial r} \right]_{R_+}^i + \left[R^2 \dot{R} \rho c_p T \right]_{R_-}^i - \left[R^2 \dot{R} \rho c_p T \right]_{R_+}^i = L R^2 \dot{R} \quad (4.22)$$

Because we assume T is independent of r within the grain, and that there is no temperature jump across the grain boundary, this jump condition simplifies to the form

$$- \left(k \frac{\partial T}{\partial r} \right)_{R_+}^i = L \dot{R} \quad (4.23)$$

Next we derive local equations for the conservation of solute, starting with an equation that is very similar to the thermal equation.

$$\frac{\partial \rho C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho D \frac{\partial C}{\partial r} \right) \quad (4.24)$$

This equation is multiplied by the volume element $4\pi r^2 dr$ and integrated from R_+ to R_e .

$$\int_{R_+}^{R_e} 4\pi r^2 \frac{\partial \rho C}{\partial t} dr = \int_{R_+}^{R_e} 4\pi \frac{\partial}{\partial r} \left(r^2 \rho D \frac{\partial C}{\partial r} \right) dr$$

Performing the right-side integration, and using Leibnitz's rule on the left side gives

$$\frac{\partial}{\partial t} \int_{R_+}^{R_e} 4\pi r^2 \rho C dr + 4\pi R^2 \dot{R} \rho C_+ = 4\pi \left[r^2 \rho D \frac{\partial C}{\partial r} \right]_{R_+}^{R_e}.$$

The first term can be identified as the rate of change of total solute mass in the $+$ phase, which can also be written in a global sense using the variable C_b , and in terms of the fraction solidified, i.e.

$$\frac{\partial}{\partial t} \int_{R_+}^{R_e} 4\pi r^2 \rho C dr \Rightarrow \frac{\partial}{\partial t} \left[\frac{4}{3} \pi \rho C_b (R_e^3 - R^3) \right] \Rightarrow \frac{4}{3} \pi R_e^3 \frac{\partial}{\partial t} [\rho C_b (1 - f_s)]$$

Substituting this in the equation, dividing through by $\frac{4}{3}\pi R_e^3$, we get

$$\frac{\partial}{\partial t}[\rho C_b(1 - f_s)] = \left[\frac{3\rho D}{R_e} \frac{\partial C}{\partial r} \right]_e - \frac{3\rho R^2 \dot{R} C_+}{R_e^3} - \left[\frac{3\rho R^2 D}{R_e^3} \frac{\partial C}{\partial r} \right]_+^i. \quad (4.25)$$

As in the thermal case, this local equation has the same term on the left as the global equation does, and hence we associate the right sides of the two equations, to get

$$-\frac{3R^2 \dot{R} C_+}{R_e^3} - \left[\frac{3DR^2}{R_e^3} \frac{\partial C}{\partial r} \right]_+ + \left[\frac{3D}{R_e} \frac{\partial C}{\partial r} \right]_e^i = \frac{\dot{G}}{\rho} - \left[\frac{3DR^2}{R_e^3} \frac{\partial C}{\partial r} \right]_+^i - \frac{3R^2 \dot{R} C_+}{R_e^3}.$$

Canceling terms, we arrive at the boundary condition for the solute.

$$\dot{G} = \frac{3\rho D}{R_e} \left[\frac{\partial C}{\partial r} \right]_e$$

Then the jump conditions are derived by stating that the total mass of solute can be expressed as an integral from $0 \Rightarrow R_e$ and the time rate of change of this integral must be equal to the amount of mass that leaves through the edge, as derived in the boundary condition above.

$$\int_0^{R_e} 4\pi r^2 \frac{\partial \rho C}{\partial t} dr = 4\pi R_e^2 \rho D \left[\frac{\partial C}{\partial r} \right]_e$$

The reduction of this equation to jump conditions is very similar to the procedure described above for the derivation of the thermal jump conditions. Leibnitz rule is used to move the partial derivative term outside the integral; then the integral is split into three terms covering the $-$ phase, the interface, and the $+$ phase. The integral over the interface again goes to zero, and Leibnitz's rule is used in reverse

on the remaining two integrals. Equation 4.24, for local solute, is then used to substitute a diffusion term for the time rate of change of energy terms, and the following jump condition results.

$$\left[\rho D R^2 \frac{\partial C}{\partial r} \right]_-^i - \left[\rho D R^2 \frac{\partial C}{\partial r} \right]_+^i + \rho R^2 \dot{R} (C_- - C_+) = 0 \quad (4.26)$$

4.1.3 Growth rate of an isolated grain

The solute and thermal jump conditions can each be reduced to an expression for the growth rate $\dot{R}$ in terms of the gradient of temperature or solute. In the research discussed here, it is assumed that the thermal conditions govern the growth of a grain, i.e. that the diffusion of solute does not impede the solidification in any way because D_+ is very large. In this case, we solve for the temperature profile and develop a set of equations governed by the thermal $\dot{R}$ equation.

We begin with the thermal jump conditions, Eq. 4.23, which can be written

$$\dot{R} = - \left[\frac{k}{L} \frac{\partial T}{\partial r} \right]_{R_+}. \quad (4.27)$$

In order to solve for $\dot{R}$, it is necessary to calculate the gradient in the + phase. Two approaches have been used to obtain the temperature outside of the grain. Schaefer and Glicksman [29] use a transient self-similar technique that accounts for thermal transport between R and R_e . We assume, however, that on a local scale the process is in quasi-equilibrium, and therefore Eq. 4.17 reduces to the Laplace equation. The justification is based on a comparison of thermal transport time to the characteristic time for significant change in grain radius. With boundary

conditions $T = T_b$ at $r = R_e$, and $T = T_c$ at $r = R$, the temperature profile is thus

$$T = T_b + \frac{T_c - T_b}{\frac{1}{R} - \frac{1}{R_e}} \left(\frac{1}{r} - \frac{1}{R_e} \right),$$

in which T_c is the critical temperature, or the surface temperature of the grain.

Taking the derivative, we obtain the growth rate equation

$$\dot{R} = \frac{k_+}{LR} \left(\frac{T_c - T_b}{1 - \frac{R}{R_e}} \right).$$

Because we do not consider impingement effects, we simply let $R_e \rightarrow \infty$. We use the Gibbs-Thomson relation (with constant slope m_l for the liquidus line) to write an equation for the critical temperature

$$T_c = T_s + m_l C_+ - \frac{K_2}{R}, \quad (4.28)$$

in which T_s is the melting temperature of pure plutonium, and $K_2 \equiv \frac{2\sigma T_s}{L}$. The latent heat is L , and σ is the solid/liquid interface energy of plutonium. Thus

$$\dot{R} = \frac{K_1}{R} \left(\Delta T - \frac{K_2}{R} \right), \quad (4.29)$$

in which $\Delta T \equiv T_s - T_b + m_l C_+$, and $K_1 \equiv \frac{k_+}{L}$. With this form, the growth rate can be calculated using the values of C_+ and T_b . Since we have shown that D_+ is very large in comparison to the thermal diffusion rate, C_b is the same as C_+ , and can be calculated from either the Scheil or lever rule.

4.1.4 Transition to unstable growth

Observations of the growth of a solid from a liquid phase show that many different types of microstructure develop. Pure substances usually grow with a

smooth solid-liquid interface, while alloys tend to have a very irregular interface, characterized by branching arms called dendrites. For an isolated grain in a melt, the growth of a solid from a liquid can become unstable under the right circumstances. This instability can be seen in the transformation of a planar to a dendritic interface, [23] or the transformation of a spherical grain into dendrites. The phenomena of unstable growth can be studied in more detail by considering a spherical nucleation site activated at some undercooling as determined from the Gibbs-Thomson relation. For the idealization of a pure material, the critical radius is defined as

$$R_c \equiv \frac{K_2}{\Delta T}.$$

In this case the growth rate Eq. 4.29 can be re-expressed as

$$\dot{R} = \frac{K_1 K_2}{R} \left(\frac{1}{R_c} - \frac{1}{R} \right), \quad (4.30)$$

which is plotted in Fig. 4.3. The growth rate rises rapidly, reaches a maximum, and then decreases asymptotically to zero. The size at which maximum growth rate occurs is

$$R_{mg} = \frac{2K_2}{\Delta T} = 2R_c.$$

Note that the value of R_{mg} is dependent on R_c , and thus changes with time, because the critical radius is dependent on the undercooling. Substituting the value for R_{mg} into the growth rate Eq. 4.30, we obtain an expression for the

Figure 4.3: Plot of grain growth-rate formula, for $R_c = 0.0001$ cm.

maximum growth rate

$$\dot{R} = \frac{K_1 K_2}{4R_c^2} = \frac{K_1}{4K_2} \Delta T^2. \quad (4.31)$$

According to the work of Mullins and Sekerka [9], the onset of unstable growth for a purely spherical grain occurs when the grain reaches a size of $7R_c$. In reference to the plot of $\dot{R}$ in Fig. 4.3, a grain grows through the maximum growth rate at $2R_c$, and grows more slowly as a sphere until $R = 7R_c$, at which point the growth becomes unstable. We expect that the transformation from stable to unstable occurs over some finite transition time, at which stage the tips of the growing dendrite are of size $2R_c$, and therefore at the maximum growth rate given by Eq. 4.31. It is interesting to note that $\dot{R}$ proportional to ΔT^2 is a commonly used expression for the growth rate of grains, and has been experimentally validated in

many cases. Many researchers use the ΔT^2 form to model the entire period of grain growth, because in many cases the transition from spherical grain to dendritic growth occurs so soon after nucleation that the initial growth circumstances have little if any effect on the global solidification process. In our work, however, we show that the early stages of grain growth are critical to determining the number of grains that nucleate (and thus the final grain size), and so we use Eq. 4.30 while $R < 7R_c$, and use the ΔT^2 form to follow the tip-led growth when $R > 7R_c$.

This stability discussion is based on the idealization of a pure material, which would not usually solidify as a dendrite, because growth initiates on the wall of the mold, and hence no thermal undercooling in front of the solid-liquid interface can occur. In real circumstances, however, almost any material has some impurities, which preferentially solidify at a different temperature from that of the pure material. For example, the plutonium phase diagram (Fig. 4.2) is greatly affected by a small amount of gallium added to the system. The temperature at which solidification can begin goes up with an increase in gallium, as approximated by $T_c = T_s + m_l C_+$. Because the solid forms with a higher concentration of solute than is in the liquid, gallium diffuses through the liquid toward the solid in the growing grains. This depletes the amount of gallium in the liquid, consequently lowering T_c . This phenomena undercools the liquid in front of the interface, and allows the potential for dendritic solidification to occur in a material with only a slight amount of impurity.

4.2 Summary of Equations

To summarize, we have global equations for the variables T_b and C_b , local equations for $\dot{R}$, and PDF equations for the evolution of $P(R)$ and f_s .

$$\rho c_p \frac{\partial}{\partial t} T_b = -\dot{E} + L \frac{\partial f_s}{\partial t}$$

$$C_+ = C_{+0} \left(\frac{1 - f_s}{1 - f_{s0}} \right)^{\kappa-1} \quad \text{or} \quad C_+ = C_{+0} \left(\frac{1 + f_{s0}(\kappa - 1)}{1 + f_s(\kappa - 1)} \right)$$

$$\dot{R} = \frac{K_1}{R} \left(\Delta T - \frac{K_2}{R} \right), \quad \text{when} \quad R/R_c < 7$$

$$\dot{R} = \frac{\beta K_1}{4K_2} \Delta T^2, \quad \text{when} \quad R/R_c > 7$$

$$\Delta T \equiv T_s - T_b + m_l C_+$$

$$\frac{\partial P}{\partial t} + \frac{\partial P \dot{R}}{\partial R} = 0$$

$$\frac{\partial f_s}{\partial t} = -\frac{4}{3}\pi \int_0^\infty R^3 \frac{\partial P \dot{R}}{\partial R} dR = \int_0^\infty 4\pi R^2 \dot{R} P(R) dR$$

5. RESULTS FOR FINAL GRAIN SIZE

In this chapter, the equations derived for our model are applied to specific problems about characterizing the final properties of a cast binary alloy. Analytical and numerical methods for solving the equation sets are presented, and solutions are given for the plutonium-gallium alloy.

The particular items of interest to us are final average grain size (Chapter 5) and distribution in final grain size (Chapter 6). The characterizations of grain size and distribution in size are obtained by detailed evolution of a PDF. The results are compared to experimental data from the plutonium one-weight-percent gallium system. Grain shape and texture, on the other hand, can be inferred from initial conditions and the results of the detailed characterization of size, distribution in size, and other controlling features.

5.1 The System

We have chosen the plutonium gallium system for simulation because of its interesting complexity. No fewer than six allotropes exist between room temperature and the melting point (640°C). Five of the allotropes are designated conventionally as alpha through epsilon. The sixth, delta-prime, is appropriately named, since the crystal structure is very similar to that of the delta phase. Many of the properties of plutonium (thermal expansion and conductivity, for example) do not vary with temperature in ordinary ways. For example, Fig. 5.1 shows that the metal actually expands upon cooling from the epsilon to delta phase [30].

Table 5.1 gives the physical properties of plutonium used in this study, as taken from the *Plutonium Handbook* [30].

Figure 5.1: Expansion behavior of pure plutonium

Table 5.1: Plutonium Properties

Property	Symbol	Value	Units
Density	ρ	17.0	g/cm^3
Thermal Conductivity	k	2.09×10^6	$\text{ergs}/(\text{cm s } ^\circ\text{C})$
Specific Heat	c_p	4.01×10^6	$\text{ergs}/(\text{g}^\circ\text{C})$
Latent Heat	L	2.83×10^{10}	ergs/cm^3
Interface energy	σ	535.0	g/s^2
Solidification Temperature	T_s	640.0	$^\circ\text{C}$
Liquidus slope	m_l	3000.0	$^\circ\text{C}/\text{wt. \%}$
Solidus slope	m_s	2000.0	$^\circ\text{C}/\text{wt. \%}$

Because of the interest in plutonium one-weight-percent gallium alloys, there is a considerable amount of experimental data available. The phase diagram for small concentrations of gallium is shown in Fig. 4.2 in Chapter 4. The diagram

shows equilibrium conditions as a function of temperature and concentration at atmospheric pressure. Variations with pressure and the effects of nonequilibrium kinetics are not shown, and are irrelevant to the consideration of this study.

The results presented here focus on the liquid to epsilon phase transition, and on the final properties of epsilon grains. Experimental results for this phase are, of course, difficult to obtain because of the high temperature involved. Inferences regarding the epsilon grain structure can be drawn from an examination of the room-temperature delta-phase grain structure, so that some discussion of the epsilon to delta phase transition is also relevant.

5.1.1 Nucleation

The initiation of phase change is only partially understood. It is known that even in a pure material the liquid to solid phase transformation does not begin at the equilibrium solidification temperature T_s , but requires at least some undercooling. The explanation for this undercooling is related to the requirement that the liquid must have something to solidify on, a bit of something solid, or in our terminology, a nucleation site. The relationship between the size of a nucleation site and the actual solidification temperature is given by the Gibbs-Thomson relation

$$T_c = T_s + m_l C_+ - \frac{K_2}{R}, \quad (5.1)$$

in which T_c is the critical temperature at which solidification can begin on a nucleation site of size R . In the most extreme cases, liquids can be purified to such an extent that no nucleation sites exist, and, in order for solidification to begin, such liquids must be cooled far below $T_s + m_l C_+$, to the homogeneous nucleation temperature. In contrast, heterogeneous nucleation occurs on impurities in the melt. A good example of nucleation caused by impurities is in the process of seeding, in which particles are added to a melt to initiate nucleation. If all grains that are nucleated grow to the same size, the final grain size can be estimated by

$$R_f = \left(\frac{3}{4\pi N_a} \right)^{\frac{1}{3}}, \quad (5.2)$$

in which N_a is the number of nucleation sites that are active. However, even without the effects of impingement, we expect some distribution of grain sizes, since nucleation sites begin growing at different times, depending on initial size.

There are several common models of nucleation: in the cellular model, all the nucleation sites initially present start to grow at the same time. The Johnson-Mehl model assumes that nucleation is a (possibly nonlinear) function of time, and can continue in the liquid regions until solidification is complete. In this chapter, we use a model that is based on a fixed number of nucleation sites in the melt, distributed in size. The nucleation sites are spherical, and characterized by their radius R in a probability distribution function. The distribution of nucleation sites is characterized by a maximum size R_m and by an initial magnitude P_0 , as shown in Fig 5.2.

Figure 5.2: Initial distribution of nucleation sites

Our theory can accommodate any distribution of initial grain sizes, but we choose this form because of its clarity for illustration of the process. As an example of the nucleation process, consider a liquid metal in a mold being cooled from a wall. As the liquid is cooled, an activation temperature $T_a = T_s + m_l C_+ - \frac{K_2}{R_m}$ is reached, at which the largest nucleation sites begin to grow. The temperature continues to drop, activating smaller and smaller nucleation sites from the distribution. The rate at which the temperature drops, however, is now modified because the growing grains are giving off latent heat. The initial distribution of nucleation sites is depleted until a time when the latent heat release equals the rate of heat extraction from the area by diffusion towards the wall. We define this turnaround point by R_{cmin} , the size of the smallest nucleation site activated. No

additional nucleation sites are activated, and the temperature actually can rise, because as the grains get larger they grow at a faster rate (as long as $R < 2R_c$), and thereby release more latent heat per unit time. This effect is called recalcence of temperature. In our model, the number of grains activated from the nucleation distribution is not specified, allowing the local interplay between heat extracted and latent heat released in a region to determine the number of grains nucleated. This is similar to the method used by Thevoz et al. [31].

For pure plutonium, the equilibrium solidification temperature is 640°C, and for the one-weight-percent gallium alloy, the solidification temperature is given by

$$T = T_s + m_l C_+ - \frac{K_2}{R_m},$$

in which $K_2 = 2.4 \times 10^{-5}$ °C cm for plutonium. With a maximum nucleation site size of $R_m = 0.0001$ cm (1 μm), the undercooling at which growth begins is about 0.25 °C. From the phase diagram, we estimate a slope of the liquidus line of about 30 °C per weight percent of gallium, and thus with one percent gallium the largest nucleation sites will become active at about 669.75 °C. The minimum critical radius achieved is R_{cmin} , which can be used to calculate the number of nucleation sites activated from our initial distribution using Eq. 5.3.

$$N_a = P_o(R)(R_m - R_{cmin}) \equiv P_o(R)\Delta R_c \quad (5.3)$$

If each nucleation site rapidly achieves unstable growth, then all grains thereafter grow at the same rate (according to the ΔT^2 rate formula), and at solidi-

fication the final grains would be separated in size by an amount ΔR_c . For the special case in which all nucleation sites are the same size, and therefore are all activated at the same time, the PDF would propagate as a delta function and, in the absence of impingement effects, there would be a sharp distribution in grain size at solidification.

5.1.2 Growth

We assume that the nucleation sites are initially spherical, or rapidly spherize when growth commences. The grains grow as spheres for $R/R_c < 7$, according to the growth rate equation

$$\dot{R} = \frac{K_1}{R}(\Delta T - \frac{K_2}{R}),$$

in which $\Delta T = T_s + m_l C_+ - T_b$. If $R/R_c > 7$, we model the resulting dendritic growth with the following growth rate equation,

$$\dot{R} = \frac{\beta K_1}{4K_2} \Delta T^2$$

in which β is a factor that is some fraction of the distance to the dendrite tips; if $\beta = 1.0$, the grain is a sphere growing at the speed of a dendrite tip. For lack of data, we have chosen $\beta = 0.8$. We have observed that the choice of β has little effect on the final average grain size, especially in the case of hard impingement, defined in Section 5.1.3. In nature, the transition between stable and unstable growth occurs by some smooth transition; however in our simulations the switch occurs immediately when the grain exceeds seven times the current critical radius.

There are a variety of circumstances that can occur because of the dual growth rate formulation. The two simple cases are (a) all grains that are activated grow to solidification at the stable growth rate, and (b) all grains that are activated begin with stable growth, grow to a size such that $R/R_c > 7$, and grow to solidification with the unstable growth rate. However, it is possible that some grains grow with a stable growth rate, while others are unstable, producing a much larger distribution in grain size than when all grains are governed by either stable or unstable growth. It is also possible that some nucleated grains are later overtaken by R_c , and stop growing. In a real situation, these grains would begin to remelt. Our model simply freezes these grains at the size they are when overtaken by R_c . This circumstance is discussed in Section 5.4.

5.1.3 Impingement

In the simulations of this chapter, the spherical grains that are activated (and not overtaken by R_c) continue to grow unimpeded until all space is filled by solid phase, which we call hard impingement. This is not a realistic occurrence, because the mathematical constraint of sphericity would mean that the grains must overlap to fill all of space. However, in this chapter we are interested mainly in the final average grain size, which is simply a function of the number of grains activated, and thus the hard impingement model is satisfactory.

5.1.4 Global transport

Nucleation, growth, and impingement are all local phenomena. In addition, the global variables temperature and concentration must be modeled. First, we consider the concentration of gallium in both the solid and liquid phases. Because of the shape of the phase diagram, gallium is absorbed from the liquid and incorporated into the solid grains, with a discontinuity in concentration at the interface. In some materials, phase change is limited by how quickly the solute can diffuse in the liquid phase. Available data for the plutonium one-weight-percent gallium system indicates that the gallium diffusion coefficient in liquid plutonium is much larger than the thermal diffusivity, i.e.,

$$D_+ \gg \frac{k_+}{\rho c_p}.$$

The process is therefore dominated by the rate at which the heat can be extracted from the vicinity of the interface, and not by the rate that the gallium can diffuse through the liquid to get to the solid, except in the case of very high cooling rates. There is also the question of how quickly gallium can diffuse within the solid epsilon phase. The final average size of a grain is estimated by

$$\bar{R}_f = \frac{1}{\left(\frac{4}{3}\pi N_a\right)^{\frac{1}{3}}}, \quad (5.4)$$

in which N_a is the number of grains activated per unit volume. The time to diffuse across a grain of this size is approximately

$$t = \frac{\bar{R}_f^2}{D_-}.$$

The time to solidify is approximately

$$t = -\frac{L}{\dot{E}}.$$

If these two times were equal, the diffusion coefficient in the solid epsilon phase would be

$$D_- = -\frac{\bar{R}_f^2 \dot{E}}{L}.$$

Using the latent heat of plutonium, a typical cooling rate of 10^7 ergs/cm³/s, (approximately 0.25°/s) and a typical final average grain size of 100 μ m, we get a calculated diffusion coefficient on the order of 10^{-12} cm²/s for the two times to be approximately the same. Available data for the diffusion of gallium in epsilon phase plutonium gives values on the order of 10^{-7} cm²/s, which means that the epsilon grains should homogenize very rapidly, i.e. they achieve a flat concentration profile. Thus, the diffusion of gallium in plutonium in both the solid and liquid phases is sufficiently high that the lever rule formulation derived in Chapter 4 is valid.

$$C_+ = C_{+0} \left(\frac{1}{1 + f_s(\kappa - 1)} \right)$$

The modeling of global temperature is accomplished by means of the energy equation in Chapter 4. For most of our discussion, we consider that the diffusion term in the energy equation is specified as $\dot{E}$, an energy extraction rate. Thus the energy equation can be integrated to give

$$\rho c_p (T_b - T_{b0}) = - \int \dot{E} dt + L f_s$$

in which f_s is calculated by an integral over the PDF, and the initial value of f_s (the volume per unit volume of nucleation sites) has been considered negligible.

5.2 Summary of the Process

In summary, the process for spherical grain growth in a zero-dimensional space with hard impingement is:

1. T_b drops to the critical temperature, $T_c = T_s + m_l C_+ - \frac{K_2}{R_m}$. No solidification has occurred.
2. T_b drops slightly more, and the largest nucleation sites begin to grow according to the stable growth rate formula, releasing latent heat, increasing f_s and evolving $P(R)$ in R space. The solute concentration drops in the liquid and increases in the solid.
3. T_b and R_c reach minima when the energy extraction rate equals the energy release rate, and recalescence commences, with T_b and R_c increasing. No additional nucleation sites are activated.
4. $P(R)$ evolves, and the latent heat released per unit time is nearly equal to the amount being extracted. Nucleation sites that are activated often grow to radii that exceed $7R_c$. Depending on the circumstances, the grains may then continue with unstable growth, or return to stable growth.
5. Grains grow until $f_s = 1.0$, at which time solidification is complete.

5.3 Solution Procedure

The system of equations used to represent this process is summarized below.

$$T_b = T_{bo} - \int \dot{T} dt + \frac{L f_s}{\rho c_p}, \quad \text{in which} \quad \dot{T} = \frac{\dot{E}}{\rho c_p}$$

$$C_+ = C_{+o} \left(\frac{1}{1 + f_s(\kappa - 1)} \right)$$

$$f_s = \int \frac{4}{3} \pi R^3 P(R) dR$$

$$\dot{R} = \frac{K_1}{R} \left(\Delta T - \frac{K_2}{R} \right), \quad \text{when} \quad R/R_c < 7$$

$$\dot{R} = \frac{\beta K_1}{4 K_2} \Delta T^2, \quad \text{when} \quad R/R_c > 7$$

$$\Delta T \equiv T_s - T_b + m_l C_+$$

$$\frac{\partial P}{\partial t} + \frac{\partial P \dot{R}}{\partial R} = 0$$

A finite-difference approximation to this set of equations is solved numerically.

For numerical solution purposes, the Liouville equation is cast as the following Lagrangian finite difference statement.

$$P(R_j) (R_{j+\frac{1}{2}} - R_{j-\frac{1}{2}}) = C$$

The j subscript labels a finite-difference cell, and C is a constant equal to the initial value of the left side of the equation. The probability P is a cell centered

quantity, and the values of R are located at both cell centers and edges. In the solution, the edges of each cell move through R space according to the appropriate rate equation, and hence the number of grains represented by each cell remains constant. Of course, as the cells become larger, the value of $P(R_j)$ decreases. The computer code used for solving this set of equations is given in the appendix.

5.4 Nucleation Results in R Space with Hard Impingement

The results presented in this section show the nucleation process and how it is affected by such parameters as the cooling rate. We show first a pair of cooling curves describing bulk temperature (T_b) as a function of time. Cooling curves are shown in Fig. 5.3 for pure plutonium and the plutonium-one-weight percent gallium alloy. The parameters for this calculation are $R_m = 0.0001$ cm, $P_o = 1 \times 10^9$ cm⁻⁴, and $\dot{T} = 0.062$ °C/s.

For the pure material, the value of C_+ is zero in the Gibbs-Thomson equation, and hence the alloy starts to solidify at a bulk temperature 30°C higher than that of the pure material. For comparison in Fig. 5.3, the pure material curve has been shifted up by 30°C. Although granular solidification of a pure material is not very realistic, this comparison is a good way to show that the effects of the alloy on grain activation are not large. The number of grains activated in either case is nearly the same, because the activation occurs over a brief time span when the surface tension term far outweighs the concentration term in the Gibbs-Thomson relation. The curves differ appreciably only after recalescence, and then the pure material

Figure 5.3: Cooling curve for pure Pu (solid line) and 1% Ga alloy (dashed line)

continues to increase in temperature while the alloy is constrained to follow the slope of the liquidus/solidus lines, and therefore decreases in temperature.

The number of grains nucleated is a function of R_{cmin} , the value of which depends strongly on the cooling rate. Cooling curves for various cooling rates (Fig. 5.4) show that the smallest of the minimum bulk temperature occurs for the largest cooling rate. Only a small portion of the entire cooling curve is shown to emphasize the difference in minimum bulk temperature achieved for the three cooling rates.

The smaller the minimum bulk temperature, the more nucleation sites are activated from the initial distribution, and thus the number of grains activated increases with cooling rate. The relation between number of grains activated and

Figure 5.4: Temperature curves for cooling rates of 0.25, 0.062, and 0.028 °C/s (left to right)

final average size is estimated by Eq. 5.4 for a monodispersed distribution of grain sizes that grow all stable or all unstable. In any case, the final average grain size decreases with increasing number of activated grains. The actual relationship between cooling rate and final grain size is discussed in detail in Section 5.5.

Once a grain has been nucleated, it has the potential to grow spherically or dendritically, depending on the value of R/R_c . A plot of the ratio R/R_c indicates the growth mechanism (stable or unstable) of a particular grain. In Fig. 5.5, the ratio is plotted for the largest grain size in the distribution. The parameters for this calculation are $R_m = 0.0001$ cm, $P_o = 1 \times 10^9$ cm⁻⁴, and three different values of $\dot{T}$. For all three cooling rates, the grains exhibit transition from stable to

Figure 5.5: R/R_c for $\dot{T} = 0.028, 0.062, \text{ and } 0.25 \text{ }^\circ\text{C/s}$ (top to bottom)

unstable growth, but shortly thereafter R/R_c drops below 7, and the grains again grow in a stable phase. Each grain begins growth as a sphere, commences transition to a dendritic structure, then re-spherizes and grows thereafter as a sphere. If R/R_c asymptotes very close to 7, some of the grains in the distribution might be stable while others are unstable. In this case, a much wider final distribution in size occurs than when all the grains are growing as either stable or unstable.

The evolution of R/R_c as a function of time also varies with the initial density of nucleation sites, as shown in Fig. 5.6. The parameters for this calculation are $R_m = 0.0001 \text{ cm}$, $\dot{T} = 0.062 \text{ }^\circ\text{C/s}$, and three different values of P_o . For $P_o = 1 \times 10^8 \text{ cm}^{-4}$, (the top curve) the growth remains unstable after the transition from initially stable growth. For $P_o = 1 \times 10^{10} \text{ cm}^{-4}$, (the bottom curve), the

Figure 5.6: R/R_c for $P_o = 10^8, 10^9$, and 10^{10} cm^{-4} (top to bottom)

growth returns to stable after a brief period of instability in which R/R_c is greater than 7.

5.5 Final Grain Size for Hard Impingement

Because of the importance of grain size in determining the mechanical properties of a material, many studies have been done on the parameters that affect as-cast grain size. In addition to cooling rate, nucleation parameters such as $P_o(R)$ and R_m can have substantial effects.

In order to quantify the effect of each of these parameters, we non-dimensionalize the set of equations together with their initial and final conditions. For the case

of stable growth only, and constant $\dot{T}$, the equations are

$$\begin{aligned}\frac{\partial \tilde{P}}{\partial \tilde{t}} + \frac{\partial \tilde{P} \frac{d\tilde{R}}{d\tilde{t}}}{\partial \tilde{R}} &= 0 \\ \left(1 - \frac{1}{\tilde{R}_c}\right) &= -\sigma_1 \tilde{t} + \sigma_2 \int_{\tilde{R}_c}^{\infty} \frac{4}{3} \pi \tilde{R}^3 \tilde{P}(\tilde{R}) d\tilde{R} \\ \frac{d\tilde{R}}{d\tilde{t}} &= \frac{1}{\tilde{R}} \left(\frac{1}{\tilde{R}_c} - \frac{1}{\tilde{R}} \right) \\ \sigma_1 &= \frac{\dot{T} R_m^4}{K_1 K_2^2} \quad \sigma_2 = \frac{L R_m^5 P_o}{\rho c_p K_2}\end{aligned}$$

For unstable growth, the same nondimensionalization is applicable. The tilde indicates nondimensionalization of each variable:

$$\tilde{R} = R/R_m \quad \tilde{R}_c = R_c/R_m \quad \tilde{t} = \frac{K_1 K_2}{R_m^3} t \quad \tilde{P}(\tilde{R}) = R_m N P(R).$$

The initial and final conditions can also be written in dimensionless form without introducing any additional parameters. We conclude that the dimensionless final grain size is only a function of the two parameters σ_1 and σ_2 , and thus write

$$\tilde{R}_f = f(\sigma_1, \sigma_2). \quad (5.5)$$

The functionality is determined by numerical solution with the same code that produced the nucleation results. The simulation results for final grain size are plotted as a function of the cooling rate in Fig. 5.7. These results suggest the possibility of a power-law relationship. The best linear fit of our results is obtained by plotting final grain size as a function of the inverse cube root of the cooling rate. A graph of this result is given in Fig. 5.8, for three different values of the

Figure 5.7: Simulations for $R_m = 0.0001$ cm, $P_o = 10^9$ cm⁻⁴

Figure 5.8: Simulations for $R_m = 0.0001$ cm, $P_o = 10^8, 10^9, 10^9, 10^{10}$ cm⁻⁴ (top to bottom)

initial nucleation parameter P_o . The simulations with $P_o = 1 \times 10^8 \text{ cm}^{-4}$ produce grains that grow to solidification as fully stable spheres. With $P_o = 1 \times 10^{10} \text{ cm}^{-4}$, the simulations produce grains that grow to solidification in the unstable mode. In the simulations with $P_o = 1 \times 10^9 \text{ cm}^{-4}$, however, the average ratio of R/R_c is close to 7, and some of the grains grow according to the unstable growth-rate equation, whereas others grow according to the stable rate. The result is a wide distribution in final grain size, and the two middle curves of Fig. 5.8 show the largest and smallest grain sizes in the distribution. From this figure, we conclude that the functionality in Eq. 5.5 can be expressed in the form

$$\tilde{R}_f = \frac{1}{\sigma_1^{0.33}} f(\sigma_2).$$

The parameter σ_2 is a measure of the initial number of nucleation sites per unit volume, P_o . We plot grain size as a function of P_o to get an idea of the relationship, as shown in Fig. 5.9. Again, the appearance suggests a power-law relation, as confirmed in Fig. 5.10. The relation can thus be written as

$$\tilde{R}_f = \frac{F}{\sigma_1^{0.33} \sigma_2^{0.22}}, \quad (5.6)$$

in which the constant F is independent of material parameters and of the specific values of cooling rate and initial nucleation-site density. Using the material-property values of plutonium, the constant F can be determined from the numerical solution of the set of equations as

$$F = 5.08,$$

Figure 5.9: Simulations for $R_m = 0.0001 \text{ cm}$, $\dot{T} = 0.062 \text{ }^\circ\text{C/s}$

Figure 5.10: Simulations for $R_m = 0.0001 \text{ cm}$, $\dot{T} = 0.016, 0.062, \text{ and } 1.0 \text{ }^\circ\text{C/s}$ (top to bottom)

and thus our equation for final grain size (independent of the type of material) is

$$\bar{R}_f = \frac{5.08}{\sigma_1^{0.33} \sigma_2^{0.22}} \quad (5.7)$$

Eq. 5.7 is one of the principal conclusions of this investigation.

Substituting in for σ_1 and σ_2 (with property values for plutonium in dimensions of gm. cm. s, and °C) the grain size equation becomes

$$\bar{R}_f = \frac{5.06 \times 10^{-6}}{\dot{T}^{0.33} P_o^{0.22} R_m^{1.43}} \quad (5.8)$$

Equations 5.7 and 5.8 are limited to cases of equiaxed solidification of isolated grains. for which the solidifying alloy acts like a pure material in the sense that the solute is rapidly diffused in the liquid phase. The effect of random impingement discussed in Chapter 6 has not been included in this determination of final grain size, but a moderate spread of final grain sizes has a minor effect in determining the final average grain size. which is basically set by the number of grains activated. The analysis has been exhibited for the case of stable growth; the same conclusion is also drawn for the case of growth that becomes unstable. Equation 5.7 applies only to the liquid-solid phase transition. but it can be adjusted to describe the subsequent solid-solid phase transition (e.g. from epsilon phase to delta phase in plutonium). The adjustment includes as a factor the number of delta-phase grains that nucleate in each epsilon-phase grain, which varies with cooling rate during the solid-solid transition, and depends on whether the nucleation occurs on the boundaries and/or in the interior of the preexisting solid.

5.6 Final Grain Size Equation Comparison with Experimental Data

Although no data are available for nucleation parameters, Gardner [32] and Ferrera et al. [33] have studied the effect of cooling rate on average grain size in delta-phase plutonium. The average grain diameter is measured as the width of the elongated grains apparent in microstructural samples, such as those of Ferrera et al. in Fig. 5.11.

Figure 5.11: Microstructure of Pu 1 wt% Ga for cooling rates of 1, 10 (as cast), 10 (polished), and 100 °C/minute, from Ferrera et al.

Gardner's data leads him to conclude that delta-phase grain size is a linear function of the inverse square root of the cooling rate, as shown in Fig. 5.12, and for

comparison we have plotted Ferrera's data in the same figure. Note that the curves are roughly parallel but not quite coincident, perhaps indicating differences in the initial distribution of nucleation sites in the two different sets of experiments. If this interpretation is correct, it indicates relatively little sensitivity to the details of initial nucleation site distribution, suggesting that our choice for $P_o(R)$ contains enough of the essential features for meaningful analysis.

Figure 5.12: Experimental data for delta-phase plutonium; Ferrera et al. (top) and Gardner (bottom)

The Ferrera data do not fit the square root form, but show a better fit to the inverse of the cube root of the cooling rate. If we eliminate the quench point from Gardner's data, and plot the remaining points on a reciprocal cube root graph, we note that the data sets are both relatively linear, as shown in Fig. 5.13.

Figure 5.13: Experimental data for delta-phase plutonium; Ferrera et al. (top) and Gardner (bottom)

The main point of Fig. 5.13 is to show that the final grain size is well described for both sets of data (omitting Gardner's quench-cooling point) by a linear function of the inverse cube root of cooling rate.

It should be noted that all of the available data are for delta-phase grains, which have grown out of the epsilon phase, and so to make more direct comparisons with results from our correlation, we have had to make inferences about the nucleation that occurs in the *solid/solid* phase transition. We believe that a good estimate of the final size of an epsilon grain can be obtained from interpretation of micrographs such as the one given by Johnson and reproduced in Fig. 5.14, which shows the acicular grains of delta-phase plutonium resulting from quench cooling through the epsilon-delta transition. In this view of delta phase grains, regions

Figure 5.14: Delta-phase microstructure of Pu 1 wt% Ga (Johnson), showing epsilon grain signatures; The width of the figure is 250 μm

where the grains are aligned are apparent. It is our inference that these regions are the outline of epsilon-phase grains. A high cooling rate nucleates many delta grains in an existing epsilon grain. and because of a Kurdjumov-Sachs [34] type preference, all the delta grains grow in the same direction, as dictated by the crystal orientation of the particular epsilon grain. Thus the patchwork view of grains allows us to extract the approximate size of the epsilon grains. In Fig. 5.14, the average epsilon-phase grain radius is thus inferred to be about thirty microns. From Eq. 5.7, we calculate a necessary value of $P_o = 2.5 \times 10^{13} \text{cm}^{-4}$ to have a final grain size of thirty microns, for the parameters $R_m = 0.0001 \text{ cm}$ and $\dot{T} = 1.0 \text{ }^\circ\text{C/s}$. Extending the simulation curve of Fig. 5.10 with this calculated value provides a check on the correlation derived from the simulated data. The extended linear relationship is apparent, as shown in Fig. 5.15.

With Eq. 5.8, we can thus generate an entire curve in the range of the data collected by Gardner and Fererra, assuming that one delta-phase grain is nucleated for each epsilon-phase grain, which is different, of course, from the acicular delta-phase circumstance shown in the quench-cooling results of Johnson in Fig. 5.14. For neither set of data do we know the values of R_m or P_o . Our correlation shows that these two quantities occur through their presence in the factor

$$\frac{5.06 \times 10^{-6}}{P_o^{2.22} R_m^{1.43}}$$

which is the slope. We choose values of R_m and P_o such that Eq. 5.8 gives a slope in the range of the experimental data. For example, the slope of the Gardner and

Figure 5.15: Calculated extension of $\dot{T} = 1.0$ °C/s curve from Fig. 5.10

Ferrera data is $0.016 \text{ cm}/(^{\circ}\text{C}/\text{s})$. With $R_m = 0.0001 \text{ cm}$, a value of $P_o = 1.23 \times 10^{10}$ gives the same slope. The form of our equation is such that the curve generated from it goes through the origin. It is apparent from Fig. 5.16 that if either of the actual data curves were extrapolated to an infinite cooling rate, neither would go through the origin; in fact, the grain size at infinite cooling rate would be slightly negative, which is not physically realistic. Even at very large cooling rates, only a finite number of grains could be nucleated, so we expect the curves to flatten toward some minimum grain size at very high cooling rates. This effect is not accounted for in our simulations.

We can also speculate on the reason for the difference in the two experimental virtual intercepts. The results of our calculations show that the slope of the

Figure 5.16: Experimental and calculated data for delta-phase plutonium; PDF results, (top), Ferrera et al. (middle), and Gardner (bottom)

calculated curve in Fig. 5.16 is dependent on initial nucleation parameters, which could be quite different for the two experimental data sets. On the other hand, the discrepancies could be due to measurement error in the original experiments. Despite the limits of validity of the analysis developed here, it is useful in estimating final grain size if the appropriate nucleation parameters are available.

5.7 Other Materials

Nastac and Stefanescu [35] measured the final grain radius in Inconel 718. In Fig. 5.17 we have plotted their data against the inverse cube root of the cooling rate, and added a straight line to compare with the data.

Figure 5.17: Experimental data for Inconel 718, from Nastac and Stefanescu

In addition, Green [36] made plots of grain size as a function of cooling rate for several magnesium alloys. In Fig. 5.18, we have replotted the data for alloy AZ63A as a function of the inverse cube root of the cooling rate, and added a straight line for comparison with the data points for which the cooling rate still has an effect on final grain radius. Both of these results show that our theoretical description of final grain size can apply to a variety of materials and circumstances.

Figure 5.18: Experimental data for alloy AZ63A, from Green

6. IMPINGEMENT MODEL

The equations discussed in Chapter 5 ignore the effects that impingement can have on individual grains, except as a method to stop growth. In this chapter, we investigate that effect impingement can have on the distribution in size of the final grains. We postulate that initial distribution in space of nucleation sites is largely responsible for the final distribution in size, and use the PDF transport equation and experimentally observed distributions to investigate this assertion.

6.1 Previous Impingement Models

Many other researchers have addressed the question of impingement. DNS techniques using a constant isotropic growth velocity were studied by Mahin et al. [13], with the result of a final distribution in grain size that compared favorably to experimental data. It is pointed out by Mahin that the nucleation model chosen in these simulations has an effect on the final microstructure. Johnson-Mehl and cellular models were explored by Mahin et al, and variations of these nucleation models were calculated by Saetre et al. [15]. Charbon and Lesar [37] modified growth rates using a growth-rate limiter, i.e. $\dot{R} = \dot{R}(1 - f_s)$, to account for the impingement of grains at late stages of the process, but this modification did not show the consequences for final size distribution. Masumura and Pande [7] developed a Fokker-Plank equation that allows for the diffusion in size space of a distribution of grain sizes during growth, generating a final distribution that compares fairly well to experimental results.

6.2 Derivation of an Impingement Model for PDF Transport

We model growth as if the grains were spheres, which has the nonphysical consequence of overlap when all space is filled. In this chapter we modify the hard-impingement model of Chapter 5 to consider the influence of the distance to each grain's first nearest neighbor.

6.2.1 Probable distance to neighbors

In this section, we derive an expression for the probability of finding the n^{th} nearest neighbor to a particle. We assume that nucleation sites are randomly distributed in space. For a given volume V , the Poisson distribution

$$Z_n(V) = \frac{N_t^n e^{-N_t}}{n!} \quad (6.1)$$

gives the probability of finding n particles in the volume V . In Eq. 6.1, $N_t = VN$, in which N is the average number of particles per unit volume. Thus for a particle located at position O and centered in a spherical volume described by radius a , we can write

$$Z_{n-1}(V) = \frac{\left(\frac{4}{3}\pi a^3 N\right)^{n-1} e^{-\frac{4}{3}\pi a^3 N}}{(n-1)!}, \quad (6.2)$$

for the probability of finding $(n-1)$ particles (in addition to the particle at O) in the spherical volume. The probability of finding a single particle in a shell of volume $4\pi a^2 da$ at a is found by using $n = 1$ in Eq. 6.1, and putting $N_t = 4\pi a^2 N da$, to get

$$Z_1(dV) = 4\pi a^2 da N e^{-4\pi a^2 da N} \Rightarrow 4\pi a^2 da N. \quad (6.3)$$

To reiterate our purpose, we want the probability of finding the n^{th} nearest neighbor (to a particle at O) in the spherical shell of volume described by width $a + da$. We call this probability $P_n(a)da$. As cited by Chandrasekhar [38], it is equal to the probability that $(n - 1)$ particles exist from $O \rightarrow a$, (Eq. 6.2), times the probability that one particle exists in the shell from $a \rightarrow a + da$, (Eq. 6.3). The product of these two equations is

$$P_n(a)da = 4\pi a^2 N \left[\frac{\left(\frac{4}{3}\pi a^3 N\right)^{n-1} e^{-\frac{4}{3}\pi a^3 N}}{(n-1)!} \right] da, \quad (6.4)$$

The variable a represents distance to the n^{th} nearest neighbor, and if we integrate $P_n(a)da$ over all a , the integral is 1 for any value of n . Our goal, however, is to find the value of n such that the probable total volume per unit volume, V_n , carried by a distribution of spheres of radii equal to the distance to the n^{th} nearest neighbor is 1.0, i.e. the spheres exactly fill all space. The volume per unit volume of a sphere of radius a is $\frac{4}{3}\pi a^3 N$, so that the total volume per unit volume is

$$V_n = \int_0^\infty \frac{4}{3}\pi a^3 N P_n(a) da. \quad (6.5)$$

We can solve Eq. 6.5 for the value of n that makes $V_n = 1.0$.

$$\int_0^\infty \frac{4}{3}\pi a^3 N (4\pi a^2 N da) \frac{\left(\frac{4}{3}\pi a^3 N\right)^{n-1} e^{-\frac{4}{3}\pi a^3 N}}{(n-1)!} = 1.$$

which reduces to

$$\frac{(4\pi N)^{n+1}}{3^n (n-1)!} \int_0^\infty a^{3n+2} e^{-\frac{4}{3}\pi a^3 N} da = 1.$$

This equation can be manipulated to the form

$$\frac{\Gamma(n+1)}{\Gamma(n)} - 1 = 0.$$

which is solved by $n = 1$. Thus, all space is filled with solid when each grain grows to a radius equal to the probable distance to its first nearest neighbor. With $n = 1$ in Eq. 6.4. we have

$$P_1(a)da = (4\pi a^2 N)e^{-\frac{4}{3}\pi a^3 N} da. \quad (6.6)$$

We use the variable S to specifically represent the distance to the first nearest neighbor. Eq. 6.7 gives the probability per unit interval in S space that a particle has nearest neighbor at a distance S ,

$$G_0(S) \equiv 4\pi S^2 N e^{-\frac{4}{3}\pi S^3 N}, \quad (6.7)$$

which is normalized to unity when integrated over all S space.

6.2.2 Solution in R and S space

The relevant Liouville equation is

$$\frac{\partial P}{\partial t} + \frac{\partial P \dot{R}}{\partial R} + \frac{\partial P \dot{S}}{\partial S} = 0. \quad (6.8)$$

For our derivation. we assume that the grains do not move in space, and thus $\dot{S} = 0$. The equation is solved subject to the initial condition

$$P(R, S) = F_o(R)G_o(S)$$

in which $F_o(R)$ is the initial distribution in size of nucleation sites, and $G_o(S)$ is the initial distribution of distance to nearest neighbor. We express the size

growth rate as $\dot{R} = \alpha(1 - \frac{R}{S})^m$, in which $\alpha = \frac{K_1}{4K_2}(\Delta T)^2$, and for this derivation ΔT is constant. This form of the growth rate equation describes the slowdown of growth as grains approach one-another, i.e. as $R \Rightarrow S$, $\dot{R} \Rightarrow 0$. The solution to the Liouville equation is

$$P(R, S, t) = F_o \left[S - S \left(\frac{\alpha t}{S} (1 - m) + \left(1 - \frac{R}{S} \right)^{1-m} \right)^{\frac{1}{1-m}} \right] \times G_o(S) \left[\frac{\frac{\alpha t(1-m)}{S(1-\frac{R}{S})^{1-m}} + 1}{1} \right]^{\frac{m}{1-m}}. \quad (6.9)$$

Integration of this equation over S space gives $P(R, t)$, the distribution of grain size as a function of time.

To illustrate the properties of this solution we consider the case in which the nucleation sites are (initially) all the same size, which is described by a delta function

$$F_o(R) = N\delta(R - R_1).$$

With this initial condition, Eq.6.9 can be integrated over S , which requires finding the value of S for which the argument of the delta function vanishes. For an arbitrary value of m the analysis is complicated. For the special case of $m = 1$, the solution for $P(R, S, t)$ reduces to

$$P(R, S, t) = \frac{-Ne^{\alpha t}}{1 - e^{\alpha t}} \delta \left(S - \frac{R_1 - Re^{\alpha t}}{1 - e^{\alpha t}} \right) G_o(S),$$

which can be integrated over all S space to give

$$P(R, t) = \frac{-Ne^{\alpha t}}{1 - e^{\alpha t}} G_o \left(\frac{R_1 - Re^{\alpha t}}{1 - e^{\alpha t}} \right).$$

Complete solidification occurs only as $t \Rightarrow \infty$, and we see that

$$P(R, \infty) = NG_o(R). \quad (6.10)$$

independent of R_1 . With $m = 1$, however, the solution is not reasonable; it requires infinite time for solidification. Indeed, the premise for growth rate with $m = 1$ is also not reasonable because it indicates nearest-neighbor growth-rate modification even from the beginning of growth.

For the more reasonable cases of $m < 1$, Eq. 6.10 is still valid, and the analysis shows that solidification takes place in a finite time. With the delta function distribution in initial size space substituted into Eq. 6.9, the probability $P(R, t)$ exists only when the argument is zero, and when $R = S$ in the argument, i.e.

$$\left[S - S \left(\frac{\alpha t}{S} (1 - m) \right)^{\frac{1}{1-m}} - R_1 \right] = 0$$

The time for solidification can be extracted by solving for t to get

$$t_s = \frac{S}{\alpha(1-m)} \left[\frac{S - R_1}{S} \right]^{1-m}. \quad (6.11)$$

This gives a finite solidification time for $m < 1$, even though the time is unbounded as $S \Rightarrow \infty$. This is not a concern, however, because the probability of a grain having its nearest neighbor an infinite distance away is negligible. In the distribution function

$$G_o(S) \equiv 4\pi S^2 N e^{-\frac{4}{3}\pi S^3 N}$$

the probability is negligible even for an exponent value of -10 or so. For the value

of -10 , an estimate for the maximum value of S is

$$S_{max} = \left(\frac{30}{4\pi}\right)^{\frac{1}{3}} N^{-\frac{1}{3}} \sim 1.3N^{-\frac{1}{3}},$$

which for S_{max} very large compared to R_1 in Eq. 6.11 gives

$$t_s = \frac{1.3N^{-\frac{1}{3}}}{\alpha(1-m)}$$

There is a small difference in the final average grain size $\bar{R}_f$ for a distribution of sizes that is monodispersed at all times compared to one that is spread from the effects of nearest neighbors. If the grains solidify as a purely monodispersed distribution in R , then the final average grain size is given by Eq. 5.2. In the case with the nucleation sites initially distributed in nearest-neighbor space, however, the final grain size is given by

$$\bar{R}_f = \frac{1}{N} \int_0^\infty N R G_o(R) dR = \left(\frac{3}{4\pi N}\right)^{\frac{1}{3}} \times \Gamma\left(\frac{4}{3}\right). \quad (6.12)$$

which departs from that for the monodispersed final grain size by the factor $\Gamma\left(\frac{4}{3}\right)$, which has the value 0.89.

6.3 Comparison of the Model Results with Experimental Data

In order to compare with experimental results, the PDF must be converted from a description of three-dimensional grain radii to a description of two-dimensional radii, which is the common method of reporting experimental results from a cut and polished microstructure sample. To make the conversion, consider a spherical grain of radius R ; a random slice through this sphere produces a disk of

Figure 6.1: Terminology for mapping 3D simulation results to 2D experimental results

any radius from $0 \Rightarrow R$, depending on where the slice is taken. We describe the distance from the centerline of the sphere to the location of the slice as x , and the radius of the cut disk at that point by r , as in Fig. 6.1.

For this configuration, the probable number per volume in r space is equal to the probable number per volume in x space, i.e.

$$P_R(r)dr = P_R(x)dx$$

With the relation for a circle, $x^2 + r^2 = R^2$, the probability of a slice creating a disk of radius r from a sphere of radius R is

$$P_R(r) = P_R(x) \frac{2r}{\sqrt{R^2 - r^2}}.$$

For a distribution of grains in R , the probability of generating a disk of size r

from a random slice through all the grains is given by

$$P(r) = \int P(R) P_R(r) dR:$$

From Eq. 6.7 and Eq. 6.8,

$$P(R) = 4\pi R^2 N e^{-\frac{4}{3}\pi R^3 N}.$$

Thus.

$$P(r) = \int_r^\infty C_1 R^2 e^{-aR^3} \frac{r}{\sqrt{R^2 - r^2}} dR,$$

in which $C_1 = 8\pi N P_R(x)$ and $a = \frac{4}{3}\pi N$. With equal probability for any value of x , and a change of variable, $\xi^2 = R^2 - r^2$, the equation reduces to

$$P(r) = C_1 r \int_0^\infty (\xi^2 + r^2)^{\frac{1}{2}} e^{-a(\xi^2 + r^2)^{\frac{3}{2}}} d\xi.$$

With an average disk size $\bar{r}$ such that $\frac{4}{3}\pi \bar{r}^3 N = 1$, the equation can be manipulated to give $P(r)$ as a function of normalized radius $\frac{r}{\bar{r}}$, i.e.

$$P(r) = C_1 \bar{r}^3 \left[\frac{r}{\bar{r}} \int_0^\infty \left[\omega^2 + \left(\frac{r}{\bar{r}} \right)^2 \right]^{\frac{1}{2}} e^{-\left[\omega^2 + \left(\frac{r}{\bar{r}} \right)^2 \right]^{\frac{3}{2}}} d\omega \right],$$

in which $\omega^2 = \left(\frac{\xi}{\bar{r}} \right)^2$. With the entire probability distribution normalized to give a value of 1 for the integration, $C_1 \bar{r}^3 = 1$.

In a like manner, we can generate an equation to give $P(A)$ as a function of normalized cross-sectional area, $\frac{A}{\bar{A}}$, i.e.

$$P(A) = \int_0^\infty \left(\omega^2 + \frac{A}{\bar{A}} \right)^{\frac{1}{2}} e^{-\left(\omega^2 + \frac{A}{\bar{A}} \right)^{\frac{3}{2}}} d\omega.$$

Several experimental results of the final distribution in grain size are available, and previous analyses to describe these distributions with computer simulations have been presented in the literature. The experimental results of Scheil and Wurst [39] concerning the distribution of grain size in recrystallized Armco iron were investigated by Johnson and Mehl [11], who described this microstructure with geometrical constructions, and obtained an approximate form for the distribution of grain diameters that compares well with the experimental results. Mahin et al. [13] point out other sets of experimental data on microstructures that appear to compare favorably with computer-generated simulations based on a Johnson-Mehl nucleation model with isotropic growth. Saetre et al. [15] compared these experimental results from an iron silicon alloy of aluminum with computer simulations using a variety of nucleation models, from cellular to modified Johnson-Mehl. Their conclusion is that what appears to be good agreement between experimental data and Johnson-Mehl simulations is not so good when plotted on a log-normal scale. All of the predictive results are essentially geometric in their calculations.

In our analysis, Section 6.2, an analytical solution is derived for the special case of all nucleation sites initially the same size. The result of the analytical solution is that, for a delta function distribution of initial nucleation-site sizes, the final distribution in grain size is only a function of the initial distribution in space of the positions of the nucleation sites, as manifested in the position of the

nearest neighbor to each. An experimental and analytical comparison is shown in Fig. 6.2.

Figure 6.2: Distribution in grain area; experimental data of Saetre et al. (histogram) and analytical PDF (solid line)

A second comparison with experimental data is shown in Fig. 6.3. This is the experimental data of Scheil and Wurst [39] as replotted by Mahin et al. [13]. The shape of the distribution curve is quite different from that of Saetre, et al., because one is plotted as a function of grain area and the other is plotted as a function of grains radius.

Figure 6.3: Distribution in grain radius; experimental data of Scheil and Wurst (dashed curve) and analytical PDF (solid curve)

In Fig. 6.2. our theoretical distribution is wider than the experimental distribution; in Fig. 6.3 it is narrower. There are several possible sources for these discrepancies, which are not currently resolved. Nevertheless, the conclusion of this section is that the final distribution in grain size is strongly influenced by the initial distribution in distance to nearest neighbor.

7. CONCLUSIONS

We conclude that for many types of granular solidification, the final average nondimensionalized grain size can be characterized by a dimensionless formula.

$$\tilde{R}_f = \frac{5.08}{\sigma_1^{0.33} \sigma_2^{0.22}}.$$

This result was derived with a specific distribution of nucleation sizes and the idealization of hard impingement; it is nevertheless able to match closely the experimental data from four separate experiments investigating three different alloys. In a computer-code simulation of metal casting, it enables the determination of final grain size as a function of cooling rate near the leading edge of the mushy zone. Because the formula depends (weakly) on initial nucleation-site parameters, these quantities would have to be measured for use in the correlation. When the cooling rate and final average grain size can be measured in an experiment, the formula may also prove useful in determining the nucleation parameters P_o and R_m by an inverse method. Parameterization of nucleation properties could then lead to a tabular format for grain size calculations by industry.

The second major conclusion of this work is that the PDF evolution is able to show analytically the effects of impingement, by relating the initial distribution of nucleation site location to the final distribution of grain size. We draw this conclusion because the analysis of Chapter 6 ignores other sources that contribute to widening the distribution in size, and nevertheless captures a significant part of the distribution seen in experimental data.

APPENDIX A Numerical Simulation Code

```

PROGRAM LAGRANGE
C2345678901234567890123456789012345678901234567890123456789012
C   program to calculate growth in r space and include s space
C   potential variability.

    PARAMETER (NR=60,
*RH0=17.,CP=4.01E6,THK=2.09E6,RLH=2.83E10,SIGMA=535.,
*RML=3000.,RMS=2000.,CINIT=0.01,
*TOTIME=3.1,IRR=6)
    DOUBLE PRECISION RE(0:NR),RC(0:NR),REDOT(0:NR),
*ANC(0:NR),CRIT(NR),TBI,
*DT,DT2,TIME,TS,TB,CB,RM,FSS,RCRIT,RCRITM,STCR,RMAX,RMIN,ANV,
*DR,RLENGTH,SWITCH

    OPEN(UNIT=10,FILE='lag.o',STATUS='unknown')
    OPEN(UNIT=9,FILE='lagcc.o',STATUS='unknown')
    DT=0.00001
    DT2=0.01
    SWITCH=3.
    MAXC=(SWITCH/DT) + (TOTIME-SWITCH)/DT2
    IF(SWITCH.GE.TOTIME)MAXC=TOTIME/DT
    WRITE(6,*)MAXC
    PINT=.001
    PINT2=.5
    TS=640.

    RMAX=1E-4      !.0001
    RLENGTH=.14E-5
    DR=RLENGTH/REAL(NR)
    RMIN=RMAX-RLENGTH

    ANV=1E8
    EDOT=-4.26E6
    PI=4.*ATAN(1.)
    FTPI=4./3.*PI
    RM=RML/RMS
    C1=THK/RLH
    C2=2.*SIGMA*TS/RLH !2.4E-5

c
c   Initial temperature for pure material, alloy at Rm, or alloy

c   TBI=TS - C2/RMAX
    TBI=TS + RML*CINIT - C2/RMAX - dt
c   TBI=TS + RML*CINIT - dt
    TB=TBI
    CB=CINIT

```

```

      RHOC=RH0*CP
c      RCRIT=-C2/(TBI-TS-RML*CINIT)

      RE(0)=RMIN
      RC(0)=RE(0) - DR/2.
      DO 30 J=1,NR
        RE(J)=RE(J-1) + DR
        RC(J)=RC(J-1) + DR
30      CONTINUE

      TOTAN=0.
      DO 34 J=1,NR
        ANC(J)=ANV*DR
        TOTAN=TOTAN + ANC(J)
34      CONTINUE
      WRITE(6,*)'TOTAL NUCLEATION SITES IN ALL R= ',TOTAN
      WRITE(6,7)(RC(J),J=0,NR,IRR)
      WRITE(6,7)(RE(J),J=0,NR,IRR)
      WRITE(6,*)
7      FORMAT(1X,50(F8.7,1X))

      MST=0
      PTIME=0.
      PTIME2=0.
      TIME=0.
      TSW=0.
      RCRITM=1.

      DO 40 IT=1,MAXC
        TIME=TIME+DT
        RNA=0.
        DO 44 J=1,NR
          IF(RE(J).GT.RMAX+.005*RMAX)RNA=RNA + ANC(J)
44      CONTINUE
          IF(TIME.GT.SWITCH.AND.TIME.LT.SWITCH+DT)THEN
            WRITE(6,*)TIME,RNA
            DT=DT2
            PINT=PINT2
          ENDIF
          RCRIT=C2/(TS - TB + RML*CB)
          IF(RCRIT.LT.RCRITM)RCRITM=RCRIT
          DO 50 J=0,NR
            STCR=RE(J)/RCRIT
            IF(STCR.LE.1.0)THEN
              REDOT(J)=0.
              CRIT(J)=2.
            ELSEIF(STCR.LT.7.)THEN
              REDOT(J)=C1*C2/RE(J)*(1./RCRIT - 1./RE(J))
c              REDOT(J)=C1*C2*(1./RCRIT - 1./RE(J))/(RE(J)+.0001)
              CRIT(J)=0.

```

```

        ELSE
          REDOT(J)=0.8*C1*C2/(4.*(RCRIT)**2)
c          REDOT(J)=0.8*(C1*C2/(4.*RCRIT)/(RCRIT+.00005))
          CRIT(J)=1.
        ENDIF
        RE(J)=RE(J) + REDOT(J)*DT
50      CONTINUE

        DO 51 I=MST,0
          IF(RE(NR)/RCRIT.GT.7)THEN
            TSW=TIME
            MST=1
          ENDIF
51      CONTINUE
          FSS=0.
          DO 52 J=1,NR
            RC(J)=(RE(J) + RE(J-1))/2.
            FSS=FSS + FTPI*RC(J)**3*ANC(J)
52      CONTINUE

          IF(TIME.GT.PTIME)THEN
            WRITE(6,15)TIME,FSS,TB,RE(NR)/RCRIT,RNA,TSW,RCRITM
            WRITE(9,16)TIME,TB,RE(NR)/RCRIT
8          FORMAT(1x,f11.3,1x,f4.2,1x,f8.4,1x,F11.8,1x,f9.1,1X,2(F7.6,1X))
9          FORMAT(1X,100(F3.1,1X))
11         FORMAT(1X,50(F8.7,1X))
15        FORMAT(1x,f12.5,1x,f4.2,1x,f9.5,1x,F11.8,1x,f10.0,1X,2(F12.7,1X))
14        FORMAT(1X,50(F3.1,1X))
16        FORMAT(1X,F10.5,1X,F9.4,1X,F7.4)
        PTIME=PTIME + PINT
        ENDIF
        TB=TBI + (EDOT*TIME + RLH*FSS)/RHOC
        CB=CINIT/(1. + FSS*(RM - 1.))
        IF(FSS.GE.1.)THEN
          WRITE(6,*)FSS,' SOLIDIFIED AT TIME = ',TIME
        GOTO 100
        ENDIF
40      CONTINUE

100     WRITE(10,8)TIME,FSS,TB,RE(NR)/RCRIT,RNA
        WRITE(10,12)(RE(J),J=1,NR,IRR)
        WRITE(10,12)(RE(J),J=NR-10,NR)
        WRITE(10,12)(REDOT(J),J=1,NR,IRR)
12      FORMAT(1X,50(F5.4,1X))
13      FORMAT(1X,f11.3,1x,f4.2,1x,f7.3,1x,f8.6)
        STOP
        END

```

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