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TITLE: **PROBABILITY DISTRIBUTION FUNCTION EVOLUTION FOR BINARY ALLOY SOLIDIFICATION**

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PROBABILITY DISTRIBUTION FUNCTION EVOLUTION FOR BINARY ALLOY SOLIDIFICATION

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Abstract

The thermally controlled solidification of a binary alloy, nucleated at isolated sites, is described by the evolution of a probability distribution function, whose variables include grain size and distance to nearest neighbor, together with descriptors of shape, orientation, and such material properties as orientation of nonisotropic elastic modulus and coefficient of thermal expansion. The relevant Liouville equation is described and coupled with global equations for energy and solute transport. Applications are discussed for problems concerning nucleation and impingement and the consequences for final size and size distribution. The goal of this analysis is to characterize the grain structure of the solidified casting and to enable the description of its probable response to thermal treatment, machining, and the imposition of mechanical insults.

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 particular layout of dendrite arm structure if growth is unstable,

— The specific configuration for impingement with adjacent grains.

To examine the effect of these and other factors we use a Liouville formulation 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. In this paper we summarize the essence of our work; many more details and discussion are given by Steinzig [1].

In the analysis we solve coupled partial differential equations for the global transport of heat and solute. At the same time, a Liouville equation is used to evolve a PDF from prescribed initial conditions through grain nucleation and stable growth, to the possible transition to unstable growth and ultimately to impingement with neighbors. Instead of using a source to the Liouville equation for nucleation, as in a Johnson-Mehl type nucleation mode [2], we use a constant number of nucleation sites 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 law, and thus the number of "active" nucleation sites is dependent on the initial distribution in size and on the rate at which heat is extracted from an area. At this stage of our development, we consider the thermal transport to dominate the process, with local-scale solute transport in the liquid phase able to accommodate rapidly to the results of thermally controlled growth.

Impingement models described by other authors (Charbon and LeSar [3]) usually limit the growth-rate expression by including a factor that varies with local volume fraction of the solidified material. We follow a similar 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.

Previous PDF techniques have been applied to solidification processes controlled by either heat or solute transport. Lifshitz and Slyozov [4] performed an analysis to examine the self-similar evolution of the distribution of grain sizes. Chen and Voorhees [5] and other investigators have extended the technique, with particular attention to Ostwald ripening. Masumara [6] considered a Fokker-Plank diffusion of the PDF in size space in order to describe the final distribution of grain sizes.

Many investigators have described the solidification of a binary alloy in purely global terms, using various nucleation models and characterizing the process in terms of the evolving volume fraction of solidified grains (Swaminathan and Voller [7]). Boundary conditions at the grain boundaries are described in terms of latent heat removal and the Gibbs-Thomson jump conditions. Typically a Scheil or lever rule is invoked for describing the effects of solute transport within the grains. We use many features of these global approaches in the formulation of our transport equations for the PDF.

Direct numerical solution (DNS) techniques have been described by Charbon et al. [8, 9] and by Trygvasson and Juric [10]. The results furnish much detailed information on grain structure during growth and impingement. Voronoi tessellations and other geometric techniques are useful for showing some of the properties of final grain configuration and furnish useful comparisons with the results of our PDF evolution calculations.

We also examine the relationship of PDF moments to the spatial (regional) average properties in a specific realization. We wish, for example, to extract from the analysis the mean and variance of the regional elastic modulus resulting from the distribution of grains with significantly nonisotropic single-crystal moduli so as to anticipate response of the solidified material to mechanical and/or thermal insults. We also are interested in the regional consequences of local variations in nonisotropic thermal expansion coefficient, residual stress, material segregation. In our present formulation we ignore fluid motion in the mushy zone, which can be incorporated using the techniques of Ni and Beckerman [11].

Evolution of the Probability Distribution Function

The probable nature of the local grain structure at each point in space and time is described by a PDF of the form such that

$$P\left(\mathbf{R}, \mathbf{n}, c_m, \mathbf{s}, \cdots, \mathbf{x}, t\right) d\mathbf{R}\, d\mathbf{n}\, dc\, ds \cdots \tag{1}$$

is the probable number of grains with size $\mathbf{R}$ in the interval $d\mathbf{R}$, crystal-plane orientation $\mathbf{n}$ in $d\mathbf{n}$, coring nonhomogeneity c_m in dc_m, with nearest neighbor at a distance $\mathbf{s}$ in $d\mathbf{s}$, etc., at position $\mathbf{x}$ and time t. The size vector, $\mathbf{R}$, describes the variations of radius with directions; the unit vector $\mathbf{n}$ relates to the orientation of crystal structure; the variable c_m is a measure of solute nonhomogeneity (coring) in the grain. Additional descriptor variables can also be included, relating to nonisotropic orientation of elastic modulus, nonisotropic thermal conductivity, nonisotropic bulk modulus for thermal expansion, residual state of stress in the grain, and dislocation and/or impurity density.

Although some alloys solidify with grain-growth rates that depend on the orientation of $\mathbf{R}$ with $\mathbf{n}$ and with $\mathbf{s}$, for which unique correlations can be postulated (neglecting the effects of large gradients of global temperature or solute), we here illustrate our technique with the assumption of purely spherical growth. The description thus contains the mathematical peculiarity of allowing grains to "overlap" after impingement, with complete solidification (when the volume-fraction moment of the PDF reaches unity) being adjusted geometrically (e.g., with a Voronoi-like tessellation) to give an "after-the-fact" description of the overall configuration of grains.

Moments of the PDF describe the expected average properties of the solidifying material over an ensemble of many individual realizations of the "casting" process. For example, the ensemble average grain size as a function of position and time is given by

$$\overline{R} = \int_0^\infty RP(R, S, s, x, t)\, dR\, ds/N \, . \tag{2}$$

Often, however, the investigator is more interested in the expected regional average within a single casting, together with the probable variance from one casting to another. Invoking an appropriate ergodic hypothesis, we can make the correspondence between an ensemble and regional average directly as a result of the PDF analysis.

We can write the Liouville equation in the form

$$\frac{\partial P}{\partial t} + \frac{\partial \dot{R} P}{\partial R} + \frac{\partial \dot{s} P}{\partial s} = 0 \tag{3}$$

in which for the example in this paper we have excluded bulk motion and have included only two scalar variables, R (spherical radius) and s (distance to nearest neighbor). The functions $\dot{R}$ and $\dot{s}$ are dependent variables that describe the growth rate and nearest-neighbor migration that is expected for any arbitrary specification of the current state of each individual grain. To illustrate, consider the case in which impingement does not result in pushing nearest neighbors apart, so that $\dot{s} \equiv 0$. Despite the vanishing of $\dot{s}$, the inclusion of s in the PDF is a crucial part of the formulation for its description of final grain-size distribution, as described in the section on impingement.

Spherical Growth of an Isolated Grain

The functional form for $\dot{R}$ depends upon material parameters,

$$K_1 \equiv \frac{k}{L} \, , \tag{4}$$

$$K_2 \equiv \frac{2\sigma}{L} \, , \tag{5}$$

the undercooling

$$\Delta T \equiv T_s - T_b \, , \tag{6}$$

and the phase-diagram form of the liquidus line, which, if linear, is described by

$$T = T_s + m_\ell C_+ \, . \tag{7}$$

In these equations, k is thermal conductivity, L is the latent heat per unit mass, σ is the surface tension coefficient, T_s is the solidification temperature for the metal in the absence of solute, m_ℓ is the slope of the liquidus line, and C_+ is the solute concentration in the liquid just outside the grain. Because diffusion times are small compared with local heat-extraction times, C_+ is the same for every grain. With a critical radius for grain-growth activation defined by

$$R_c \equiv \frac{K_2}{\Delta T + m_\ell C_+} \tag{8}$$

and a Laplace assumption for the temperature variations outside the grain, the growth-rate formula is

$$\dot{R} = \frac{K_1 K_2}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right) \tag{9}$$

for as long as the growth process is stable. Mullins and Sekerka [12] show, with various assumptions that the growth becomes unstable when $R > 7R_c$, leading to dendritic growth. A few dendritic tips lead the growth, with lateral fill-in that gives a nominal effective radius growing at a rate proportional to the tip propagation rate. As a simple approximation, we assume that the dendrite tips grow at a rate equal to that of a spherical grain with radius $2R_c$ (the maximum growth rate), which, substituted in Eq. (8) gives

$$\dot{R} \approx \frac{K_1 K_2}{4R_c^2} = \frac{K_1}{4K_2}\Delta T^2 \, . \tag{10}$$

This is the form used by many investigators, e.g., Rappaz et al. [13], and observed in the DNS calculations of Juric and Trygvasson [10].

With R specified as a function of T_b, C_+, and R, it becomes necessary to use the global transport equations that describe the evolution of T_b, C_+, and the volume fraction, f_s, of all the solidified grains per unit volume at each instant. We note that

$$f_s \equiv \int \frac{4\pi}{3} R^2 P(R,s)\, dR\, ds \tag{11}$$

is a moment of the PDF over the entire domain of R and s. From the Liouville equation with $\dot{s} = 0$, it is easily shown that

$$\frac{\partial f_s}{\partial t} = \int 4\pi R^2 \dot{R} P(R,s)\, dR\, ds \, . \tag{12}$$

Let the global diffusive rate of energy transport per unit volume be described by

$$\dot{E} \equiv \frac{\partial}{\partial x_i}\left(k \frac{\partial T_b}{\partial x_i}\right) \tag{13}$$

and let the global diffusive rate of solute lying transport outside of grains be described by

$$\dot{G} \equiv \frac{\partial}{\partial x_i}\left\{\left[\rho_\ell D_\ell (1 - f_s)\right] \frac{\partial C}{\partial x_i}\right\} \tag{14}$$

in which k is the thermal conductivity in both liquid and solid, ρ_ℓ is liquid density, and D_ℓ is the solute diffusivity (here neglected within the grain). C is the solute concentration, which varies on some multi-grain global scale but is assumed to be uniform within the region about a grain, where $C = C_+$. With these identifications the global-heat transport equation becomes

$$\frac{\partial}{\partial t}(\rho C_p T) = \dot{E} + L \frac{\partial f_s}{\partial t} \, . \tag{15}$$

in which the density, ρ. and specific heat, C_p, are considered for this discussion to be the same for liquid and solid. The global solute transport equation can be written in a similar form, which is often simplified by assuming that the solute diffusion coefficient in the solid is zero (Scheil rule) or very large (lever rule), with the respective results

$$C_+ = (1 - f_s)^{(\kappa-1)} \left[A + \int \frac{\dot{G}}{\rho(1 - f_s)^\kappa} \right] \tag{16}$$

$$C_+ = [1 + (\kappa - 1)f_s]^{-1} \left[A + \int \frac{\dot{G}}{\rho} \, dt \right] \tag{17}$$

where κ is the partition coefficient, and A depends on initial conditions.

Nucleation

The process of nucleation is calculated by solving the Liouville equation, coupled to the global energy transport equation, for PDF evolution from a prescribed initial distribution of nucleation-site radii. Consider for example a Heaviside distribution extending from $R = 0$ to $R = R_m$. Neglecting for this purpose the structure in s space, the analysis evolves the PDF from this initial state through the process of growth activation to a final state of complete solidification in which the final average grain size, R_f, can be estimated from the number per unit volume that are activated, N_a, by the formula

$$\frac{4\pi}{3} R_f^3 N_a = 1 \, . \tag{18}$$

The number that are activated is determined by the results of a competition between the latent heat release of the growing grains and the heat extraction rate from the region. The temperature drops from some initial value of T_b, with a consequent drop in R_c until $R_c = R_m$. Any further decrease in T_b (thus R_c) activates the growth of grains, which continue to enlarge as long as R exceeds R_c. The growth of grains, however, liberates latent heat, which slows the decrease of T_b (and R_c) until R_c reaches a minimum, then thereafter increases. Any growing grain for which R_c later exceeds R ceases its growth and, indeed, commences melting back to liquid, absorbing latent heat. Thus there is a continuing feed-back interaction among solidification, melting, and the consequent effects on T_b. By complete solidification there has been established a distribution of final grain sizes whose mean is estimated as described above.

These interactive processes can be calculated in detail for any initial size distribution and variation of heat extraction rate with time. The examples described in [1] for tin and for the binary alloy of plutonium with small amounts of gallium show a linear relation between R_f and $(\dot{E})^{-1/2}$ for constant $\dot{E}$, over a large range of $\dot{E}$ values. These results are in agreement with the experimental results reported by Gardner [14] for Pu-Ga.

More realistic are the results for variable $\dot{E}$, as calculated for the proximity to a cold wall. Coupling the global heat transport to the PDF evolution, it has been confirmed [1] by comparison to the experiments of several investigators, that application of the PDF to nucleation does, indeed, do well in describing the variations of R_f with distance from the wall, despite uncertainties associated with Heaviside initialization for the PDF.

Impingement

Impingement models based on modifications to the formulas for $\dot{R}$ are accomplished by many investigators through the inclusion of a factor that depends on f_s, going to zero as $f_s \rightarrow 1.0$. A goal of impingement modeling is to describe the final distribution of grain sizes when solidification is complete. As noted by many investigators, there are two principal contributions to the establishment of final size distribution, nucleation and impingement of grains with neighbors.

Masumara [6] simulated impingement using a Fokker-Plank variant of the Liouville equation to represent diffusion of $P(R)$ in R space during grain growth and thereby obtained a final distribution of grain sizes. Our approach is based on the premise that probable nearest-neighbor proximity is a dominant contributor to the distribution of final grain sizes about the mean. To examine the consequences of this idea, we follow the evolution of $P(R,s)$ from prescribed initial conditions in which the distribution in s space is completely random. (With progressive activation, the evolving distribution in s space is still random in our model, being based on the current number of activated grains.) With stationary grains $\dot{s}$ vanishes and Eq. (3) becomes

$$\frac{\partial P}{\partial t} + \frac{\partial P\dot{R}}{\partial r} = 0. \tag{19}$$

To illustrate this process, we consider an initial distribution of nucleation sites that is monodispersed in size and random in nearest-neighbor distance:

$$P_0(R,s) = N\delta(R - \overline{R})G_0(s) \tag{20}$$

in which $\overline{R}$ is the initial size of all nucleation sites, N is the total number per unit volume, and G_0 is derived from the Poisson distribution for random spatial placement.

$$G_0(s) = 4\pi s^2 N \exp\left(-\frac{4\pi}{3}s^3 N\right). \tag{21}$$

The impingement factor we have chosen for our $\dot{R}$ formula is

$$\left(1 - \frac{R}{s}\right)^n \tag{22}$$

in which n is constrained to be less than 1.0.

The Liouville equation can be partially solved analytically for the case of unstable (tipled) growth with $\dot{E}$ constant. The partial solution is sufficient for the extraction of the PDF at solidification, which when integrated over s space is

$$P_f(R) = NG_0(R) \tag{23}$$

independent of n. This result shows that the final distribution of grain size is a direct mapping from the initial distribution of nearest neighbors. It is also possible to show that the time for complete solidification is

$$t_f = \frac{4R_c^2}{(1-n)N^{1/3}K_1K_2}, \tag{24}$$

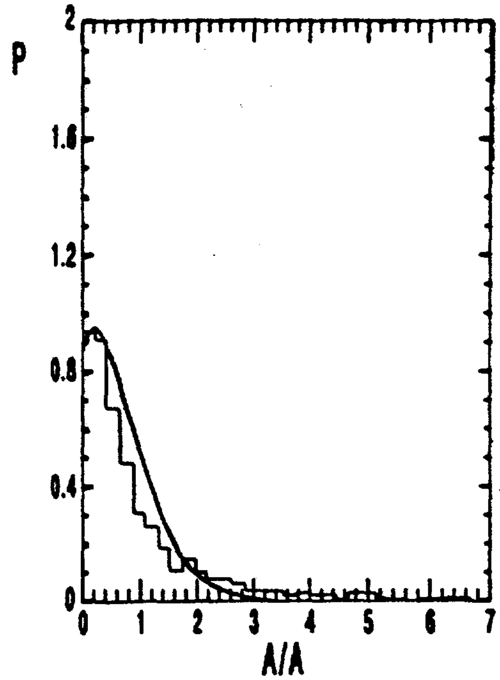

Figure 1: Distribution of grain sizes about the mean.

which shows why $n < 1$ is required. (The complete Liouville solution for $n = 1$ is given in [1] and arrives at the above conclusion for $P_f(R)$, but suffers from the necessity for infinite solidification time.)

To confirm the result, which has no adjustable parameters in its formulation, we compared the final distribution with experimental results given by Saetre et al [15]. The good agreement shown in Fig. 1 suggests that random nearest-neighbor placement is, indeed, a major contributor to final grain size distribution.

Evolution of the Full PDF

The distribution of probability in R space forms the core from which the entire PDF can be constructed, at least approximately. The basis for this assertion lies in the premise of strong correlations of probability among the various independent variables. Nonspherical grain shape is closely related in its orientation to the directions of the crystal structure, which is set at the inception of growth by vagaries of nucleation site configuration with possible influence of strong temperature gradients and perhaps other factors. Also strongly correlated with probability for crystal-plane orientation are the nonisotropic aspects of elastic modulus, thermal coefficient of expansion, and other material properties of concern for the description of probable regional response to thermal and/or mechanical insults. Density changes during the phase transition (omitted from the above discussion) are crucial for the determination of residual stresses in and around each grain, and indeed a complete description requires that P have functional dependence on the state of both internal strain and stress.

For practical implementation of material-characterization models into computer codes for metal casting analysis, we take considerable advantage of the strong correlations of probability. Many useful inferences can be extracted by use of a PDF that has been transported in R space and extended to the construction of a full PDF in the space of all the variables for which there is strong correlation to the crystal-plane orientation at inception. Even with grain rotation during solidification, there is little directional effect if the inception is random.

Extraction of Regional Properties

Properties like mean elastic modulus can be extracted from the PDF by appropriate moments:

$$N\overline{M} = \int PMd\cdots , \tag{25}$$

in which M is a nonisotropic material property of a single grain, being probabilistic only in its angular distribution. Two points of care must be taken with regard to the application of $\overline{M}$ to response analysis of an individual casting. The first is the potential variability from one casting to another, which can be described in terms of the probable number of grains in a region of the casting (defined by structural homogeneity across that region). PDF moments extend across the members of an ensemble of castings; application to an individual casting requires an ergodic hypothesis for equivalence between ensemble and spatial averaging, which can be tested by extraction of the probable variance derived from the PDF analysis.

The second caveat regarding application of mean properties to material response analysis is associated with the existence of important correlations among grain-to-grain fluctuations. Thus, for example, an average of the product of elastic modulus with strain has two parts; one is the product of mean quantities and the other is the mean of the product of fluctuations from mean. This issue has been discussed by Romero and Harlow [16] for the crenulative behavior of a material with local-scale fluctuations in kinematic-viscosity coefficient.

Discussion

Applications of the PDF technique for metal solidification problems will usually require implementation of the discretized equations into numerical codes for large computers. In addition to characterizing the probable grain structure of the finished casting, the resulting PDF finds use in the examination of heat treatment effects, machining processes (with the release of residual stresses and its configurational consequences), and the response to externally applied stresses at both low and high strain rates.

The PDF techniques discussed here are described in considerably more detail in [1] and are being implemented into the three-dimensional TELLURIDE metal-casting code of the Los Alamos National Laboratory.

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