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討10 FUNDAMENTALS OF RAPID SOLIDIFICATION PROCESSING

Massachusetts Institute of Technology   Merton C. Flemings

Massachusetts Institute of Technology
The Castings Research Lab., Waseda Univ.   Yuh Shiohara

INTRODUCTION

Solidification processes involving dendritic solidification are carried out commercially over a range of cooling rates of over 12 orders of magnitude - from 10^{-4} K/s for large ingots to nearly 10^{9} K/s for surface treatments. Dendrite tip velocities, or isotherm velocities, range from as little as 10^{-8} m/s to as much as 10^{2} m/s. Table 1, lists examples of the various solidification processes and their respective regimes of cooling rates.

At the lower ranges of cooling rates, we believe we understand the formation of dendritic structures and segregation in usual metal alloys fairly well. This understanding extends up to about 10^{3} cooling rate, or up to a dendrite tip velocity of about 10^{-2} m/s. It is based on two assumptions that are certainly valid in nonfaceting alloys at least up to these rates: that interface kinetics are very rapid, and that liquid composition is essentially uniform within interdendritic regions, except in the vicinity of the dendrite tips. In addition, except when thermal gradients are maintained artificially steep (as in crystal growing), temperature of the dendrite tips is close to the equilibrium liquidus.

As technical and commercial interest increases in products produced in solidification processes at rates of 10^{3} K/s and above, there is much impetus to extend our understanding of solidification mechanisms to the regime of these more rapid rates.

In this paper, a summary is first given of some aspects of structure, segregation, and properties of castings and ingots solidified at ordinary cooling rates (below about 10^{3} K/s). The paper then carries these ideas to rapid rates and to high undercoolings before nucleation, and considers other phenomena that become important in rapid solidification processing. Our experimental and conceptual understanding of solidification at rapid rates has improved significantly in the last few years but there is much left to be done before we understand solidification at these rates to the degree that we do at the lower rates of usual castings and ingots.

SOLIDIFICATION AT 10^{-4} TO 10^{3} K/s

At the relatively slow rates of solidification of castings and ingots, nucleation generally occurs with little undercooling. It has also long been known experimentally that dendrite tips grow into the melt with little undercooling so that the dendrite tip temperature is very close to the liquidus temperature. As a result of this, and the rapid interface kinetics and uniform interdendritic liquid mentioned above, the microsegregation and solidification behavior is then described by the widely used "local solute distribution equation", often referred to as the Scheil equation [1]. Figure 1 illustrates the solidification model schematically for an Al-4.5%Cu alloy.

The Scheil equation almost always predicts somewhat more microsegregation than is observed experimentally and this is due to three factors. One is diffusion in the solid. A second is "ripening" of secondary dendrite arms during solidification and the consequent more rapid growth of larger arms [1, 2, 3]; this is shown schematically in Figure 1 by the increasing coarseness of the dendrite arms as the eutectic isotherm is approached. A third is "temperature gradient migration" of arms (the dissolution and reprecipitation of solid as a result of the temperature gradient [4].

Figure 2 is a plot drawn for the same Al-4.5%Cu alloy discussed above, of dendrite tip temperature versus dendrite tip velocity on the lower horizontal scale. In this, as throughout most of the paper,

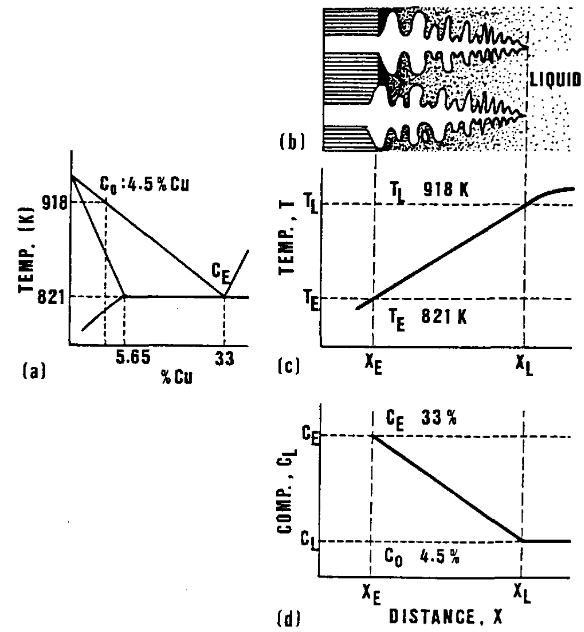

Figure 1. Solidification model for castings and ingots. Al-4.5%Cu alloy. (a) phase diagram, (b) schematic diagram of columnar dendritic growth showing growth of eutectic at T_E, (c) temperature versus distance; dendrite tips are at approximately the equilibrium liquidus, T_L, (d) liquid composition versus distance in the liquid and liquid-solid regions.

Table 1 Range of Cooling Rates in Solidification Processes

Range of Cooling Rate Limit (K/s)	Designation	Production Processes	Dendrite Arm Spacing* (μm)
10^{-4} to 10^{-2}	slow	Large castings and ingots	5000 to 200
10^{-2} to 10^{3}	medium	Small castings and ingots, continuous castings, strip, die castings, and coarse powder atomization.	200 to 5
10^{3} to 10^{9}	rapid	Fine powder atomization, melt spinning, spray deposition electron beam or laser surface melting.	5 to 0.05

e.g. for Al-4.5%Cu alloy.

dendrite growth is assumed to be columnar. In solidification of an alloy against a metal wall with no mold-metal resistance to heat transfer, G/R is a constant, where G is thermal gradient, K/m, and R is growth rate, m/s. For aluminum alloys, as will be seen later in this paper, $G/R = 1.5 \times 10^6$ Ksm^{-2}, and Figure 2 is constructed on that basis. The top horizontal scale shows cooling rate corresponding to the dendrite tip velocities below.

Figure 2 is based on a model which has developed from the studies of Bower et al [5], Jin and Purdy [6], Kurz and Fisher [7], and Trivedi [8] and has been given by Trivedi and Somboonsuk [9]. The result, as plotted here, incorporates effect of capillarity on melting point depression, as well as effect of solute build-up in front of the rapidly growing tips. An important aspect of this model is that it involves the marginal stability criterion to determine dendrite tip radius.

Note that in the range of tip velocities up to about 10^{-2} m/s (cooling rates up to about 10^3 K/s) dendrite tip temperature is not greatly reduced from the liquidus temperature, confirming the validity of the general applicability of the Scheil equation to solidification at these rates.

DENDRITE ARM SPACINGS

The most important single effect of increasing the cooling rate of usual castings and ingots is the resulting decrease in dendrite arm spacing. It has been recognized for over 20 years that the relation between arm spacing and cooling rate is a linear one on a log-log scale, with the slope being about minus one third [1, 5, 10]. Figure 3 shows this dendrite arm spacing, d_2, versus cooling rate for Al-4.5%Cu (and other aluminum alloys), based on experimental data.

It has been recognized over these last two decades that the factor governing this dendrite arm spacing is "ripening" or "coarsening" during solidification of the much finer dendrite structure that forms at the beginning of solidification. We are now able to make a first estimate of this on the basis of elegant studies of Glicksman and coworkers [11,12], and Trivedi and coworkers [9], in which modern dendritic growth theory incorporating stability theory is confirmed by observations on transparent model alloys (of succinonitrile).

Figure 3 shows this "initial secondary dendrite arm spacing", d_2^i, that forms just behind the dendrite tip [9]. This arm spacing is just twice the radius of the dendrite tip, r*, which is also shown in Figure 3. Comparison of the results for d_2^i and d_2 shows that the secondary dendrite arm spacing increases about an order of magnitude during solidification, a result which has been implied by many solidification studies on metals conducted over the last decades.

Stability theory, combined with a global diffusion model has also been used to calculate primary dendrite arm spacing [9]. This model, although perhaps less rigorous than the one for secondary dendrite arm spacing, provides reasonable results, and those results are also shown in Figure 3.

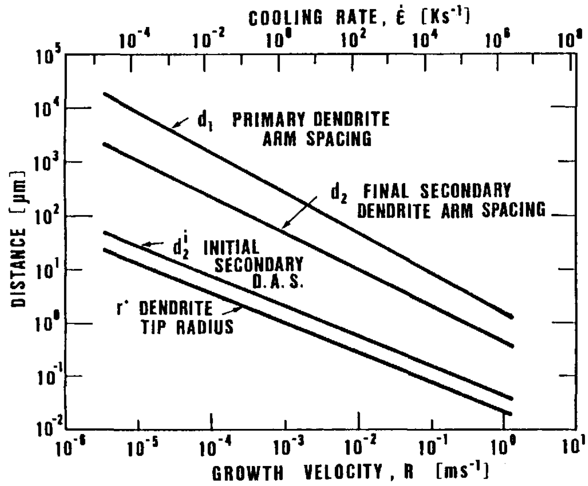

Figure 3. Dendrite arm spacings and dendrite tip radius versus tip velocity and cooling rate, Al-4.5%Cu alloy. Plot for D_2 is based on extensive experimental data from a number of investigations [1, 5, 10]; other plots are calculated from analyses of Trivedi and Somboonsuk [9].

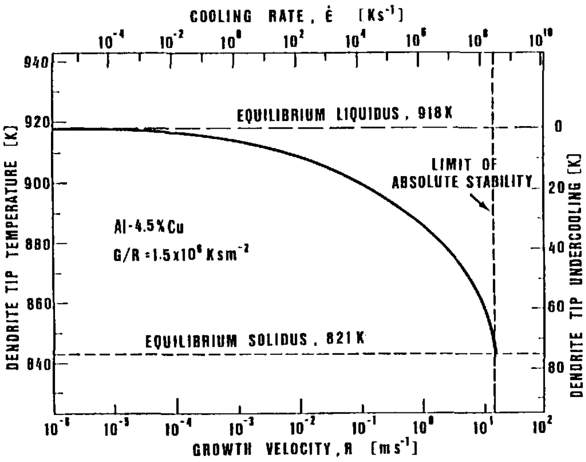

Figure 2. Dendrite tip temperature versus tip velocity and cooling rate, columnar growth of Al-4.5%Cu. Based on analysis of Trivedi and Somboonsuk [9].

HEAT FLOW AND MECHANICAL PROPERTIES

Solidification of the model alloy Al-4.5%Cu discussed herein has been studied analytically by Adams [13] and more recently, numerically, at MIT by Campagna [14]. Campagna's physical model is the "Scheil model" shown schematically in Figure 1. Figures 4 and 5 show two results of these calculations, for one dimensional heat flow - e.g. solidification of a strip or plate against a flat cold mold.

Figure 4 assumes no mold-metal resistance to heat transfer, and so places an upper limit on the solidification rate that can be achieved. Liquidus and solidus isotherms move so their distances from the chill are proportional to the square root of time (except that the solidus isotherm speeds up near the end of solidification when the metal plate no longer acts as if it were semi-infinite). One result of these calculations is that for this alloy the average thermal gradient in the liquid-solid "mushy" zone, divided by the dendrite tip velocity is 1.5×10^6 Ksm^{-2} and it is for this reason that Figure 2 has been plotted for $G/R = 1.5 \times 10^6$.

Figure 5 presents results of calculations similar to those of Figure 4 except for the case of a metal-mold heat transfer coefficient h such that the Biot Number, hL/k equals 0.6 where L is casting thickness if solidification is from one side only (or half thickness if from both sides) and k is thermal conductivity.

We may use Figure 5 to gain insight into the currently important industrial processes used in producing "premium quality castings". These cast-

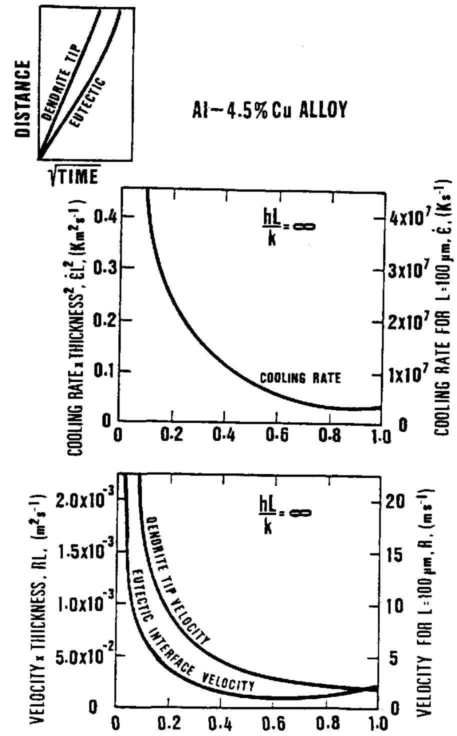

Figure 4. Heat flow and solidification of Al-4.5%Cu alloy against a water cooled chill; no mold. Metal resistance to heat transfer. (from Campagna [14])

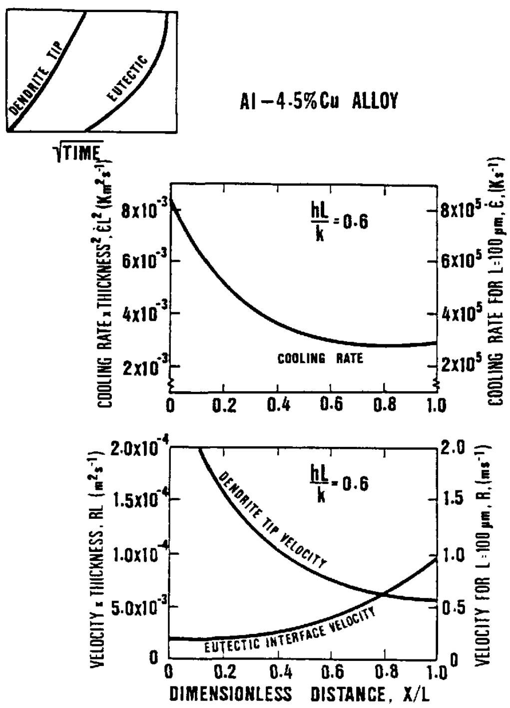

Figure 5. Solidification of Al-4.5%Cu alloy against a water cooled chill, with mold-metal heat transfer coefficient such that the Biot Number is 0.6. (from Campagna [14])

ings are ones in which mechanical properties and reliability are substantially higher than those of usual commercial castings. An essential feature of producing them is increasing the cooling rate to achieve a fine dendrite arm spacing. This is usually done by inserting extensive metal "chills" in otherwise conventional refractory molds. Consider as example a 100 mm thick section of an aluminum casting that is chilled on both sides. Mold-metal interface coefficient is such that the Biot Number is 0.6 so Figure 5 applies. From this figure it is seen that cooling rate is approximately 3.0 K/s at the surface and 1.0 K/s at the centerline. From Figure 3, the resulting dendrite arm spacing is therefore 30 microns at the surface and 50 microns at the center - a suitable range for good mechanical properties as seen by the experimental data in Figure 6.

Many studies over the last few decades have also shown that reducing dendrite arm spacings of ingots and continuous castings to a range below about 50 microns results in improvements in workability of the cast structure and improvements in properties of the wrought materials produced. At higher solidification rates, we see from Figure 5 that if mold-metal interface resistance is held to a very low value we may achieve cooling rates of 10^3 K/s or higher throughout a plate of thickness 2L in excess of 10 mm. The dendrite arm spacing in this plate would be no higher than a few microns. Surely this is an important direction for future rapid solidification processing - to achieve very fine structures in cast strip of usable thickness.

SOLIDIFICATION AT RATES GREATER THAN 10^3 K/s

At these rates, tip temperature is reduced greatly from the equilibrium liquidus temperature, as shown by Figure 2. In this region we expect microsegregation to be reduced from the amount predicted by the Scheil equation, because of build-up of solute in front of the growing dendrite tips. There is another reason also that may result in reduced segregation, at least as measured by amount of eutectic. That is that nucleation or growth of the second phase may be limited, resulting in growth of the supersaturated primary phase at temperatures below the equilibrium eutectic temperature.

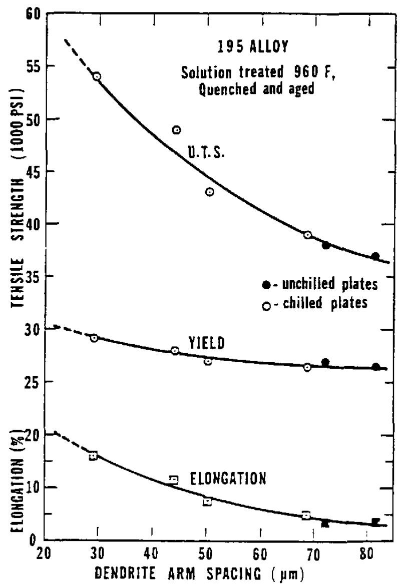

Figure 6. Mechanical properties of Al-4.5%Cu alloy versus dendrite arm spacing in chilled and unchilled plates. (From data in Ref 15)

At the "Absolute Stability Limit" given by Mullins and Sekerka [16], dendrites can no longer grow, and we again expect a plane front. That limit, shown in Figure 2, has been calculated as occurring at 13 m/s, based on equilibrium interface kinetics. We have, however, no assurance that interface kinetics remain infinite at these higher velocities and in fact have reason to believe that significant departure from equilibrium may occur at somewhat lower velocities. Kinetic analyses of solute redistribution indicate that a critical growth velocity in metal alloys, R_c, occurs at [17]:

$$R_c \approx \frac{D}{\lambda}$$

where λ is the atomic spacing. At growth velocities well below this value of R_c, the equilibrium kinetic models discussed above apply. At much higher velocities, "solute trapping" occurs to such extent that the partition ratio approaches unity. Interface temperature must be at or below the thermodynamic "T_o" temperature for complete solute trapping [18, 19, 20]. This transition occurs within an order of magnitude of R_c. Taking D as 3×10^{-9} m^2/s and λ as 3×10^{-10} m, the critical velocity is 10 m/s, or just about the absolute stability limit calculated for equilibrium interface kinetics. However, this numerical value of R_c is only an estimate and we as yet have no experimental verification of its value in any aluminum alloy.

Whether or not solute trapping takes place, we expect substantial reduction in segregation at these cooling rates in the range of 10^3 to 10^8 K/s, for reasons mentioned above. Metastable phases often form as well at these cooling rates. And of course dendrite structure is extremely fine, with dendrite arm spacing in aluminum alloys ranging from 5 microns at 10^3 K/s down to 0.1 microns at 10^8 K/s cooling rate.

Figure 7, from work at Allied Chemical Corporation is one example of the important practical benefits to be obtained from rapid solidification processing. This figure shows the significant increase in elevated temperature strength that can be obtained in aluminum alloys by combining rapid solidification processing with the development of new alloys specially tailored for this mode of processing.

SOLIDIFICATION AT HIGH DEGREES OF UNDERCOOLING

Extensive "undercooling" ("supercooling") can occur in metal alloys even at very slow cooling rates, in the absence of heterogeneous nuclei [1, 17, 21-25]. Achievable undercoolings are in the

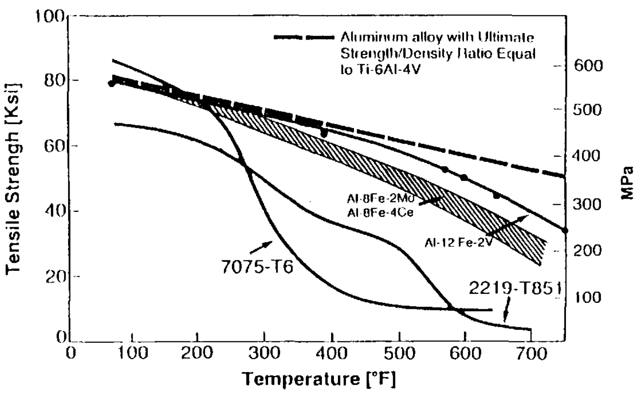

Figure 7. Elevated temperature strength of some rapidly solidified aluminum alloys, compared with conventional aluminum alloys (7075-T6 and 2219-T851) and with Ti-6Al-4V. Courtesy C. Adam, Allied Corporation.

range of 0.2 to 0.3 times the absolute melting point, and undercoolings of 200-300 K are readily obtained in iron and nickel base alloys in bulk specimens as well as in fine droplets.

When nucleation occurs in undercooled specimens, growth is very rapid, with heat flow from the growing dendrite tips into the supercooled liquid. For all but very fine droplets, initial growth and recalescence occur adiabatically. From stability theory as we understand it today, solidification of such melts should always be dendritic. Above the equilibrium solidus, once tip velocity is low enough that solute trapping is low, growth is limited by solute transport alone and dendrites of exceedingly fine tip radius grow into the melt at a velocity that can be calculated by a mathematical approach similar to that used to calculate tip undercooling in Figure 2. The result is a plot of dendrite tip velocity versus tip undercooling that is quantitatively nearly identical to Figure 2 [11].

Our quantitative understanding of solidification of undercooled metal alloy melts, remains poor, primarily because of the great difficulty of making experimental measurements during the progress of this extremely rapid event, and also because of the major effect of coarsening in altering the structure that originally forms. From a fundamental point of view, we seek an understanding of (1) nucleation behavior of stable or metastable phases, (2) dendrite shape, size and growth velocities at different undercoolings, (3) solute redistribution occurring during recalescence, (4) recalescence rate, and (5) remelting and coarsening effects occurring during and after recalescence.

One example of the difficulty in conducting such experiments is illustrated by work to be discussed in detail by Dr. Shiohara later in this conference. Figure 8 is a high speed optical measurement of recalescence in a 9 mm diameter levitation melted droplet of Ni-25%Sn [26]. Recalescence occurs in about .005 seconds and, remarkably, it proceeds within that time to a temperature at which solid and liquid are at their equilibrium compositions and temperature. The compositions are given by the equilibrium liquidus and solidus, and the temperature is determined by equating the specific heat associated with the undercooling to the heat of fusion plus any heat lost to the surroundings. If, as may be presumed, initial dendritic growth proceeds with a solid composition at or approaching C_o, then substantial solute redistribution must take place in the solid during recalescence, probably with fine scale remelting.

A practical conclusion that can be drawn from the above is that if structural benefits are to be

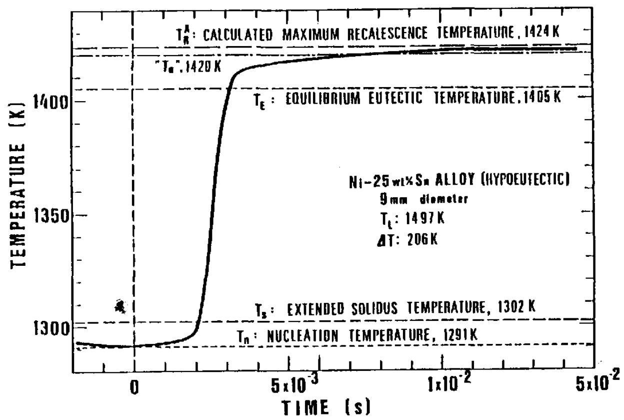

Figure 8. Optically measured recalescence curve for a 9 mm droplet of Ni-24wt%Sn undercooled 206K [26].

obtained from undercooling, recalescence must be held to some temperature below the T_o and perhaps below the extrapolated equilibrium solidus, by a combination of high initial undercooling and rapid heat extraction during recalescence.

FUTURE OPPORTUNITIES FOR RAPID SOLIDIFICATION PROCESSING

There remain many ripe opportunities in rapid solidification processing, both for the fundamental researcher and for the technologist.

In the area of development of theory, there is much room left for refinement of the analyses presented herein, including prediction of morphology and combination of stability theory with global diffusion (i.e., with aspects of the solute diffusion problem other than at the immediate dendrite tip). But these theories will be able to proceed only to a limited extent without continuing and close correlation with experiment. Such correlations have been made in various ways for metals and non-metals at slower cooling rates. The work now needs to be carried to higher interface velocities and to higher undercoolings. Real time measurements will be an essential part of such experiments, because of the impossibility in many cases of extrapolating backwards in time from the observed final structures. Such measurements might be of temperature, sample dimensions and surface structure, dendrite shape and velocity (in transparent systems), or structure of solid phases forming (by x-ray or TEM).

On the technological side, a clear opportunity is to develop improved processes for achieving high solidification rates in near net shape processing. One example is the development of improved strip casting processes to achieve high cooling rates (e.g. > 10^3 K/s) in strips of usable thickness. Another example is surface melting and re-solidification (perhaps with simultaneous alloying). Also on the technological side is the opportunity for development of new alloys uniquely suitable to rapid solidification processing. We have seen already new tool steels, new high temperature aluminum alloys, and new superalloys which can be produced best, or only, by rapid solidification processing.

CLOSURE

In closure, this paper has attempted to illustrate the continuous change that occurs in solidification behavior of non-undercooled melts as cooling rate increases from 10^{-4} K/s to about 10^3 K/s. At higher cooling rates, more significant changes occur as dendrite tip temperature begins to drop significantly from the equilibrium liquidus. Discontinuous change in solidification behavior occurs if absolute stability is reached (with or without solute trapping), if a metastable phase forms, or if solidification is to a glass rather than to a crystalline solid. Discontinuous change in solidification behavior also occurs if undercooling before nucleation is significant. There is much left to be discovered and developed in rapid solidification processing and exciting opportunities abound for workers in the field.

ACKNOWLEDGMENTS

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