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INFLUENCE OF FREEZING RATE OSCILLATIONS AND CONVECTION ON EUTECTIC MICROSTRUCTURE†

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Abstract—As discussed in our review paper (Wilcox, W. R. and Regel, L. L., *Microgravity Quarterly*, 1994, **4**, 147–156), the influence of microgravity on eutectic microstructure has been rather erratic and largely unexplained. Directional solidification in microgravity sometimes coarsened the structure, sometimes made it finer, and sometimes, even on the same system, had no measurable effect. Theoretical models predicted no influence of the weak buoyancy-driven convection that occurs in the vertical Bridgman technique on earth. Thus, we hypothesized that freezing rate fluctuations due to irregular convection might be responsible. For example, with a fibrous microstructure an increase in freezing rate must cause new fibers to form, either by branching or by nucleation. A decrease in freezing rate would cause fibers to terminate by overgrowth of the matrix phase. If the kinetics of fiber formation differs from that for fiber termination, an oscillatory freezing rate would cause the average fiber spacing to deviate from that at a steady freezing rate. We have been investigating this hypothesis both experimentally and theoretically. Vertical Bridgman experiments were performed on the MnBi–Bi eutectic with freezing rate oscillations caused by periodic electric current pulses passed through the material. With increased current amplitude, more and more grains exhibited irregular microstructures. Of the grains with continued quasi-regular rod structure, the microstructure became finer. This result was contrary to that expected from our hypothesis for this system. Numerical modeling also predicted that an oscillatory freezing rate should yield a finer microstructure. It was also predicted that freezing interface oscillations should cause the average melt composition at the freezing rate to deviate from the eutectic. This results in the formation of a composition boundary layer of sufficient thickness that it would become sensitive to convection. Hence we have arrived at a revised hypothesis. On earth, irregular convection causes freezing rate fluctuations that change the interfacial melt composition, leading to a thick composition boundary layer. Convection interacts with this boundary layer to change the interfacial melt composition, thereby altering the response of the system to freezing rate fluctuations. © 2001 Published by Elsevier Science Ltd.

1. INTRODUCTION

Directionally solidified MnBi/Bi eutectic has a quasi-regular MnBi rod structure at freezing rates above 9 mm/h (e.g. [1]). As with many other eutectics, the average rod spacing λ depends on the freezing rate V such that $\lambda^2 V = \text{constant}$. The influence of convection on the microstructure of the MnBi–Bi eutectic was reviewed in [2]. In microgravity experiments, Larson and Pirich (e.g. [3]) obtained λ about half of that from the vertical Bridgman technique on the ground under otherwise identical conditions. Smith [4], on the other hand, obtained the same λ in microgravity. Smith used a gradient freeze technique with the temperature increasing monotonically with height, while Larson and Pirich had a maximum in melt temperature versus height. Thus, the Smith furnace would have produced much less buoyancy-driven convection in the melt. Pirich [5] found that application of a magnetic field to reduce convection gave the same λ as in microgravity. Alternately starting and stopping rotation (ACRT) of the vertical ampoule during solidification increased λ [1]. These experiments all indicate that convection increases λ for the MnBi/Bi eutectic. However, extensive numerical modeling here (e.g. [6]) showed negligible influence of buoyancy-driven convection on

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eutectic microstructure. In this modeling, it was assumed that both the average interfacial composition and the bulk composition are at the eutectic composition. Favier and deGoer [7] hypothesized that an off-eutectic bulk melt composition could explain the observed influences of convection, but this was not supported either by theoretical considerations [2] or by experiments (e.g. [8]). Drevet et al. [9] proposed that if the eutectic does not freeze at the extremum, then the average interfacial composition deviates from the eutectic and the microstructure becomes sensitive to convection.

In all of the above, attention was focussed on the direct influence of convection on the composition field near the freezing interface. An alternative explanation is that convection acts indirectly by causing the freezing rate V to fluctuate [2]. When V is increased, one would expect λ to decrease, probably by nucleation of new rods. When V is decreased, λ would increase by the matrix growing over some of the rods. If the kinetics of fiber termination and nucleation differ, then one would expect an oscillatory freezing rate to change λ. Our objective here was to test this hypothesis both experimentally and theoretically.

2. EXPERIMENTS

MnBi/Bi eutectic (0.72 wt% Mn) was directionally solidified in a vertical Bridgman–Stockbarger furnace [10]. Five ingots were solidified at the same translation rate for each set of experiments, with the same freezing rate but different current pulsing conditions. For each current period, the current was suddenly turned on, held constant for time t, and then turned off.

2.1. *Types of microstructure*

Several types of microstructure were observed, depending on the freezing rate and current pulsing conditions. The usual quasi-regular MnBi rod structure consists mostly of triangular and chevron cross sections. Figure 1 shows regions with other microstructures. The MnBi in some regions was coarse and irregular, while other regions had large rods, broken lamellae, rod clusters, or no MnBi at all. As shown in Fig. 2, at freezing rates of 2.1 cm/h and above, the microstructure became less regular as the current density was increased. The opposite behavior occurred at a freezing rate of 1.1 cm/h, which is near the lowest rate at which a quasi-regular structure is normally observed. Note that the effect was much larger for positive current than for negative current pulses. Constant current had no effect.

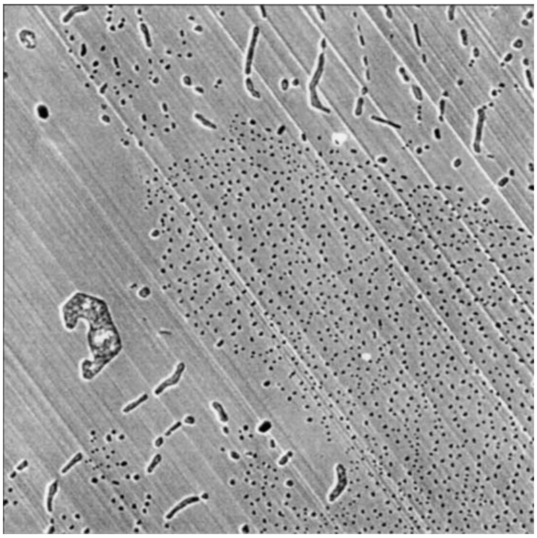

Fig. 1. Microstructures in MnBi/Bi eutectic solidified at $V = 4.3$ cm/h with $t = 3$ s positive current pulses of 72 A/cm^2 and a period of $T = 6$ s.

2.2. *Rod spacing*

The nearest-neighbor distance λ of each rod was calculated from the distance of the center of each rod to that of its nearest neighbor. The average λ, standard deviation, kurtosis, skewness, and 95% confidence limits were obtained. The standard deviation was almost one-third of λ. The 95% confidence limits for λ were about $\pm 1.5\%$ of the means. No trend with current pulsing or freezing rate could be discerned, except that a distribution with large kurtosis also tended to have large skewness. Within a given cross-sectional sample, the rod area tended to increase as the nearest-neighbor distance increased, although the correlation coefficient r was only about 0.44. A log–log plot of the average λ versus translation rate V for experiments performed both without electric current and with constant electric current (no pulsing) gave a straight line with a $-\frac{1}{2}$ slope, yielding $\lambda^2 V = 1.4 \times 10^{-16}$ m^3/s. The value of λ with constant current was essentially the same as that solidified without current.

Figure 3 shows λ for four sets of experiments with positive current. When the material was solidified with current pulses, λ decreased with increasing current amplitude.

The total amount of MnBi in areas with a quasi-regular structure tended to increase with increasing current density and increasing amount

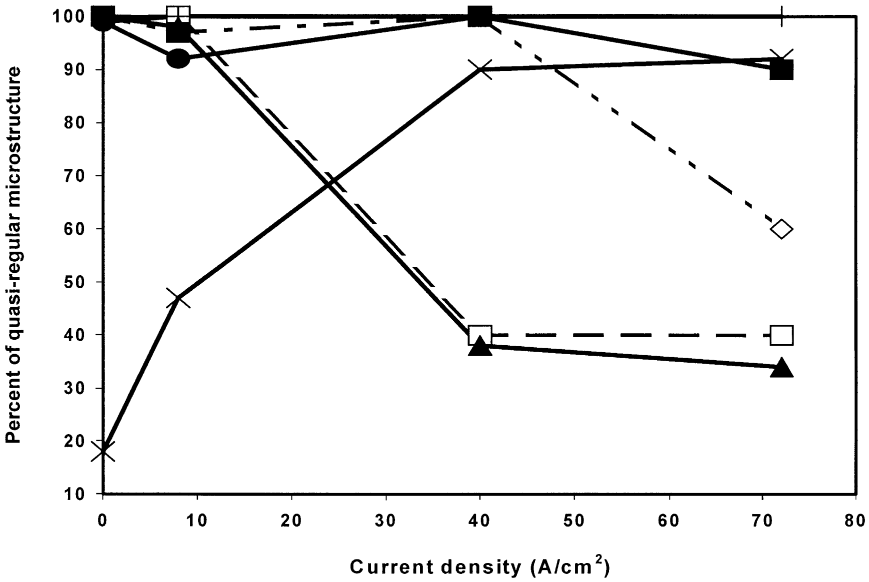

Fig. 2. Percent of quasi-regular microstructure versus current density: (◇) $V = 2.1$ cm/h, positive current pulses, $t = 0.75$ s, $T = 6$ s; (□) $V = 4.3$ cm/h, positive pulses, $t = 3$ s, $T = 6$ s; (▲) $V = 2.1$ cm/h, positive pulses, $t = 4.5$ s, $T = 18$ s; (×) $V = 1.1$ cm/h, positive pulses, $t = 0.25$ s, $T = 2$ s; (■) $V = 4.4$ cm/h, negative pulses, t=3 s, T=6 s; (●) V=5.5 cm/h, negative pulses, t=3 s, T=6 s; (+) V=8.0 cm/h, negative pulses, t=3 s, T=6 s.

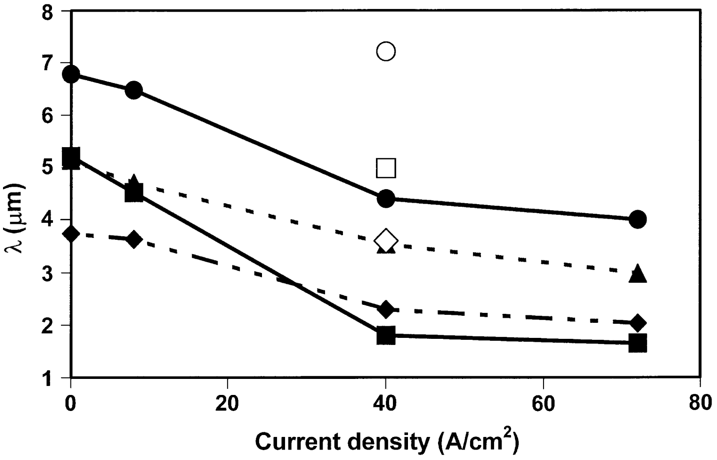

Fig. 3. Average rod spacing λ versus positive current density. Open symbols are with continuous current: (●) $V = 1.1$ cm/h, $t = 0.25$ s, $T = 2$ s; (○) same, continuous; (▲) $V = 2.1$ cm/h, $t = 0.75$ s, $T = 6$ s; (■) $V = 2.1$ cm/h, $t = 4.5$ s, $T = 18$ s; (□) same, continuous; (◆) $V = 4.3$ cm/h, $t = 3$ s, $T = 6$ s; (◇) same, continuous.

of material with no MnBi. The %MnBi did not depend on the percent of the cross section with a quasi-regular structure.

2.3. The effect of current polarity

Three sets of experiments were performed with negative electric current, i.e. current going through the interface from the melt to the solid. As with continuous positive current, continuous negative electric current had negligible effect on the fraction quasi-regular or on rod spacing. Current pulsing decreased λ and the fraction quasi-regular, but less so than with positive current.

2.4. Rod roundness

As freezing rate and current pulsing amplitude increased, the MnBi rods tended to become less triangular and more rounded. The image analysis software permitted a quantitative characterization

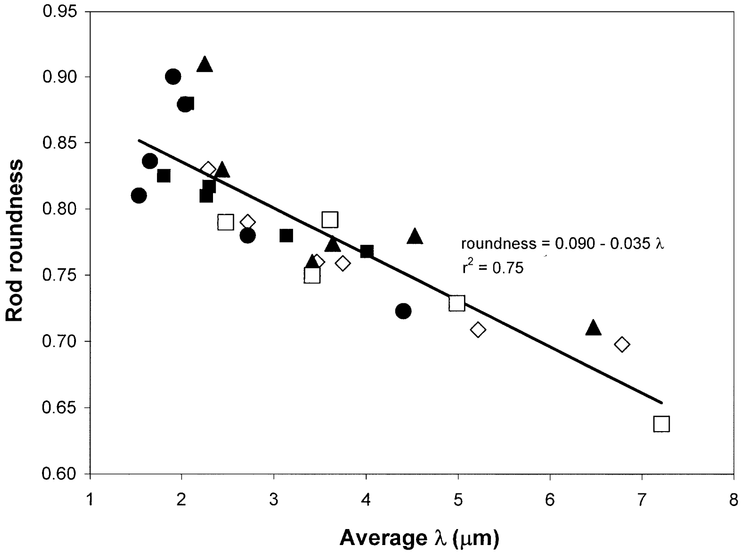

Fig. 4. MnBi rod roundness versus λ: (↓) no current; (□) 40 A/cm^2 continuous current; (▲) 8 A/cm^2 pulses; (′) 40 A/cm^2 pulses; (□) 72 A/cm^2.

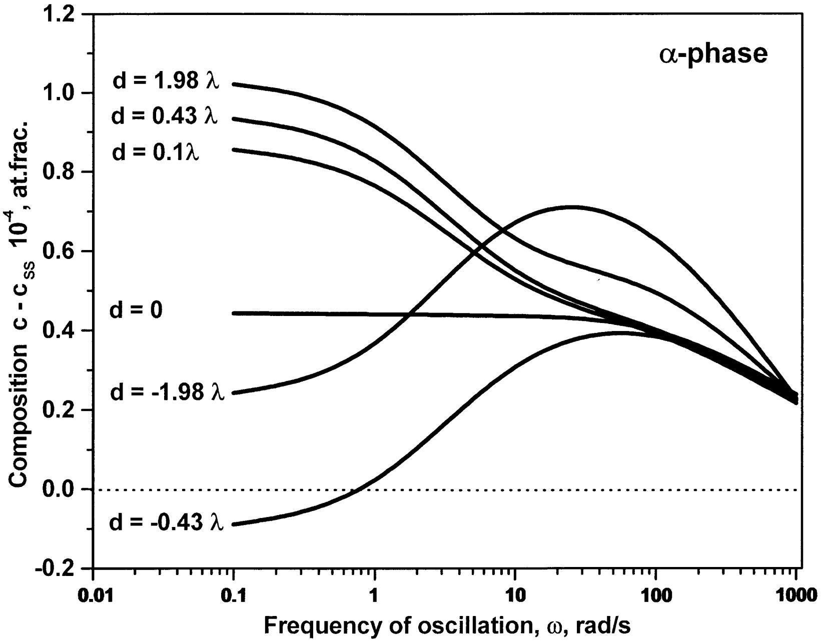

Fig. 5. Frequency dependence of the spatially averaged deviation of the composition from eutectic at the freezing interface of the α phase for different lead distances d of α in front of phase β. The volume fraction of α is 0.645.

of rod shape via the roundness.§ Figure 4 shows that roundness increased as λ decreased. This trend was true regardless of whether λ decreased due to increasing the freezing rate or increasing the current amplitude, and did not depend on current polarity.

3. THEORY

Three methods were used to model the influence of an oscillatory freezing rate on eutectic microstructure in the absence of convection [11–15].

3.1. *Sharp interface model*

A sharp interface model of lamellar growth [12] showed that if both phases nucleate (high amplitude of oscillations), there is a decrease of the

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§The roundness is defined as 4π (area)/(perimeter)^2, which has a value of 1 for a circle and 0.60 for an equilateral traingle.

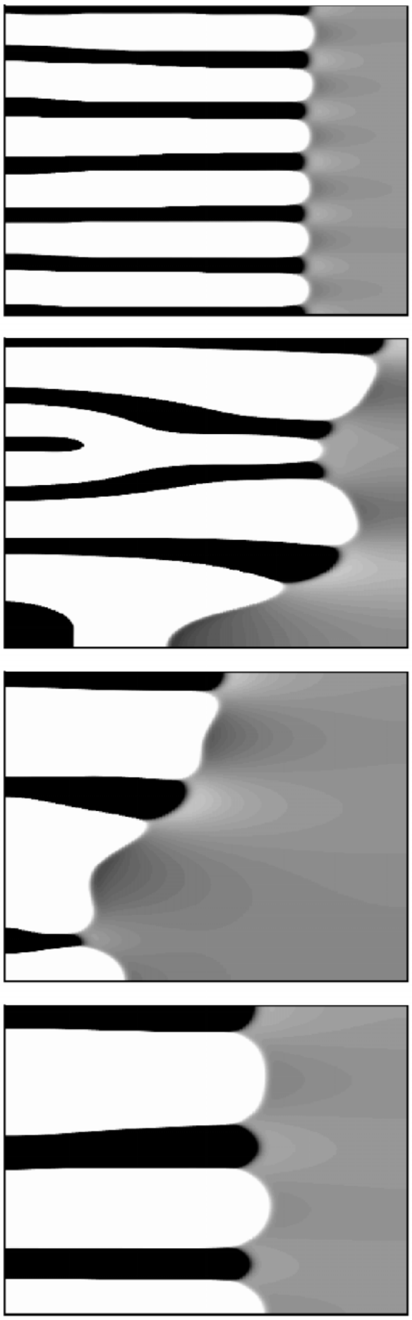

Fig. 6. Phase-field simulation of the evolution of a lamellar microstructure caused by decreasing the freezing rate (top to bottom).

microstructure parameter λ, making the eutectic finer. If nucleation is prohibited (the amplitude of oscillations is low), and the interfacial composition becomes off-eutectic as shown in Fig. 5. This departure from the eutectic composition would cause the composition field, and hence the microstructure, to become sensitive to convection. The influence of oscillations on interfacial composition is more pronounced for a large difference in volume fractions.

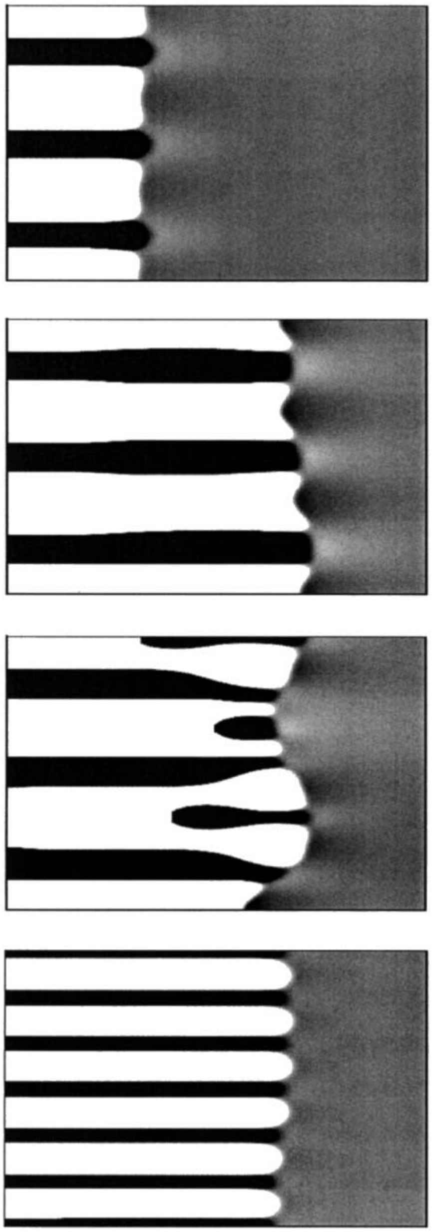

Fig. 7. Phase-field simulation of the evolution of a lamellar microstructure caused by increasing the freezing rate (top to bottom).

If only one phase nucleates, the result depends on the departure of the interface from planarity and the supersaturation necessary for nucleation.

3.2. *Phase-field model*

Phase-field models have proven their usefulness in modeling time-dependent pattern formation during phase transitions (e.g. [16–22]). Rather than being taken as atomically sharp, phase boundaries are assumed to occupy some finite width. This

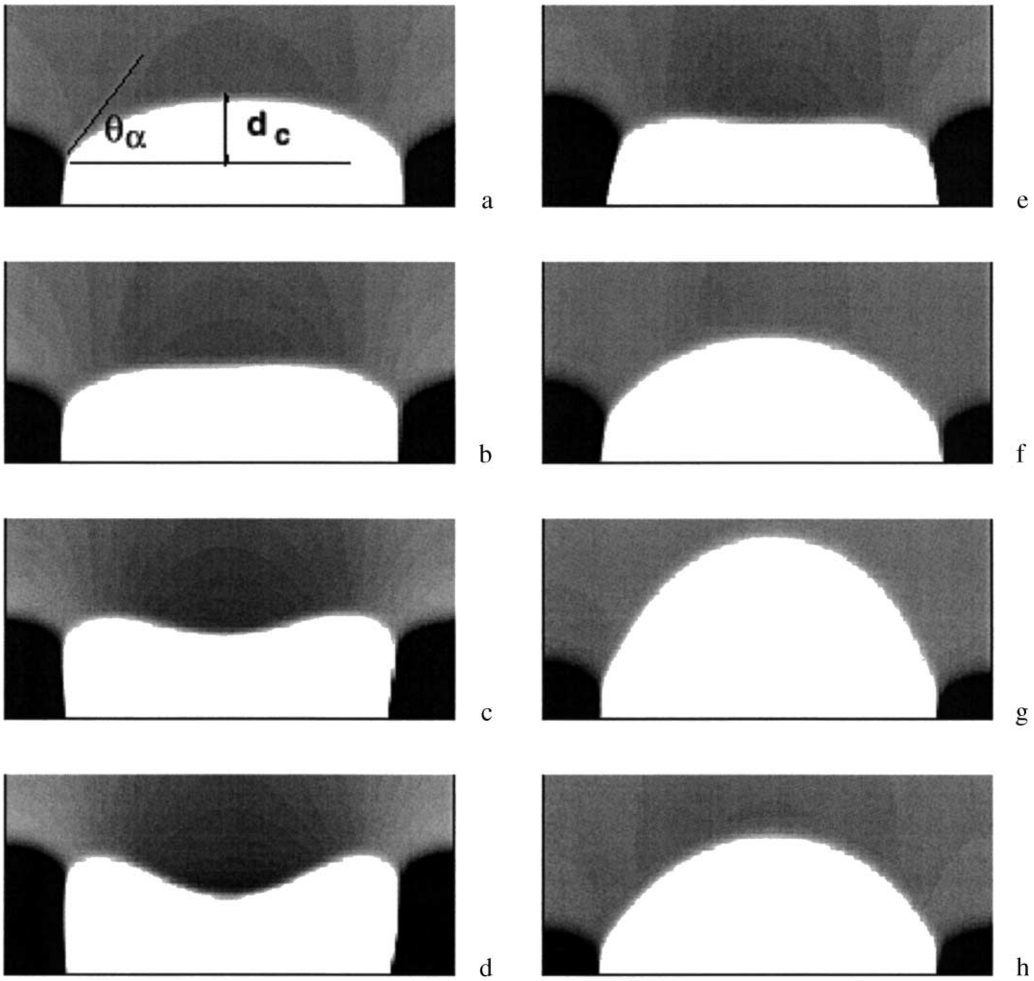

Fig. 8. Evolution of the interface shape when the freezing rate oscillates with insufficient amplitude to nucleate or terminate lamellae. Note that the angles at which the phases meet at the tri-junctions remain constant while the volume fractions of the two phases change slightly. Here (d) corresponds to the maximum freezing rate and (g) the minimum freezing rate.

permits easy tracking of the position of a phase boundary in numerical computation, at the expense of a fine mesh and considerable computation time. We were fortunate in being permitted to use the supercomputer at NASA's Marshall Space Flight Center in Huntsville, Alabama via the Internet.

In order to check our methods, we first developed a one-dimensional phase-field model [13]. This gave accurate solutions for the equilibrium partition of a single-phase alloy and the volume fractions and compositions of a two-phase solid binary alloy at equilibrium. Oscillatory solidification produced solute striations in the resulting single-phase solid.

A powerful phase-field method was developed for evolution of lamellar eutectic microstructures [14]. Nucleation, phase termination, and volume fraction adjustment were observed. Some examples are shown in Figs. 6–8, with black representing one component, white the other component, and gray a mixture. Thus the two solid phases may be seen along with the composition field in the melt. When the freezing rate is increased, the supersaturation in front of lamellae increases, causing formation of a deep depression, followed by nucleation, instability, and volume fraction adjustment that eventually stabilizes the freezing interface. Vice versa, with a decrease in freezing rate, an instability develops that changes the local growth direction and provokes volume fraction adjustment with subsequent elimination of lamellae. With freezing rate oscillations, backmelting becomes important, especially for large lamellar spacings.

Irregular structures, not shown here, were produced via some freezing rate changes. It is noteworthy that the behavior in these simulations duplicates those observed in films of organic eutectics held between glass slides [23].

3.3. *Entropy minimization model*

The results from the sharp interface and phase-field models were incorporated into a computation of the entropy production rate during solidification [15]. It is assumed that the microstructure adjusts such that the entropy production rate is a minimum. For a constant freezing rate, this is equivalent to the traditional "extremum" assumption that the interfacial undercooling is a minimum for a given freezing rate, or that the freezing rate is a maximum at a given undercooling. Here the traditional result of Jackson and Hunt [24] was obtained at a constant freezing rate. An oscillatory freezing rate was predicted to decrease the inter-phase spacing λ, but not by a large amount. It was assumed that the amplitude was insufficient to nucleate or terminate lamellae.

4. CONCLUSIONS

When we set out to do this research, we expected that current pulsing would increase λ because this would confirm the hypothesis [1] that a fluctuating freezing rate caused the increases in λ observed with increased convection. The opposite results were obtained. Thus we are forced to consider the hypothesis of Drevet et al. [9] that the average interfacial composition deviates from the eutectic because the system does not freeze at the extremum. This composition deviation extends the region of concentration change to a distance on the order of D/V into the melt, making it much more sensitive to convection. (Here D is the diffusion coefficient and V is the freezing rate.) Furthermore, our theoretical modeling indicates that an oscillatory freezing rate can also cause the interfacial composition to deviate from the eutectic, even when the extremum condition is satisfied.

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REFERENCES

1. Eisa, G. F., Wilcox, W. R. and Busch, G., Effect of convection on the microstructure of the MnBi/Bi eutectic. *Journal of Crystal Growth*, 1986, **78**, 159–174.
2. Wilcox, W. R. and Regel, L. L., Influence of gravity on the microstructure of fibrous eutectics. *Microgravity Quarterly*, 1994, **4**, 147–156.
3. Pirich, R. G. and Larson, D. J., Influence of gravity driven convection on the directional solidification of MnBi/Bi eutectic composition. In *Materials Processing in the Reduced Gravity Environment of Space*, ed. G. E. Rindone. Elsevier, New York, 1982, pp. 523–533.
4. Smith, R., The influence of microgravity on the microstructure and properties of eutectics. Queens University, Kingston, Ont., 1992.
5. DeCarlo, J. L. and Pirich, R. G., Effect of applied magnetic fields during directional solidification of eutectic Bi–Mn. *Metal Transactions*, 1984, **15A**, 2155–2161.
6. Caram, R., Chandrasekhar, S. and Wilcox, W. R., Influence of convection on rod spacing of eutectics. *Journal of Crystal Growth*, 1990, **106**, 194–302.
7. Favier, J. J. and de Goer, J., Directional solidification of eutectic alloys. In *Proceedings of the Fifth European Symposium on Materials Science under Microgravity*, ESA SP-222, European Space Agency, Paris, 1984, pp. 127–133.
8. Rydzewski, J. H., Effect of slight deviations from the eutectic composition on the microstructure of MnBi/Bi. M.S. Thesis, Clarkson University, Potsdam, NY, 1993.
9. Drevet, B., Camel, D. and Favier, J. J., Solute boundary layer and convection in solidification of eutectic alloy. In *Proceedings of the Seventh European Symposium on Materials and Fluid Sciences in Microgravity*, ESA SP-295, 1990, pp. 101–108.
10. Li, F. C., Regel, L. L. and Wilcox, W. R., The influence of electric current pulses on the microstructure of the MnBi/Bi eutectic. *Journal of Crystal Growth*, in press.
11. Popov, D. I., Ph.D. Thesis, Clarkson University, 1999.
12. Popov, D. I., Regel, L. L. and Wilcox, W. R., Eutectic solidification with a fluctuating freezing rate: sharp interface model. *Journal of Crystal Growth*, submitted for publication.
13. Popov, D. I., Regel, L. L. and Wilcox, W. R., One-dimensional phase-field model for binary alloys. *Journal of Crystal Growth*, 2000, **212**, 574–583.
14. Popov, D. I., Regel, L. L. and Wilcox, W. R., Phase-field model of unsteady and oscillatory eutectic solidification. *Journal of Crystal Growth*, 2000, **209**, 181–197.
15. Popov, D. I., Regel, L. L. and Wilcox, W. R., Application of the theorem of minimum entropy production to growth of lamellar eutectics with an oscillating freezing rate. *Journal of Crystal Growth*, in press.
16. Caginalp, G. and Jones, J., A derivation and analysis of phase-field model of thermal alloys. *Annals of Physics*, 1995, **237**, 66–107.
17. Langer, J. S., Models of pattern formation in first-order phase transitions. In *Directions in Condensed Matter Physics.* ed. G. Grinstein and G. Mazenko. World Scientific Publ. Co., Singapore, 1986, vol. 1, pp. 165–186.
18. Caginalp, G. and Xie, W., Phase-field and sharp-interface alloy models. *Physical Review* E, 1993, **48**, 1897–1909.
19. Karma, A., Phase-field model of eutectic growth. *Physics Reviews* E, 1994, **49**, 2245–2250.

20. Elder, K. R., Drolet, F., Kosterlitz, J. M. and Grant, M., Stochastic eutectic growth, *Physical Review Letters* 1994, **72**, 677–680.
21. Wheeler, A. A., McFadden, G. B. and Boettinger, W. J., Phase-field model for solidification of a eutectic alloy. *Proceedings of the Royal Society of London* 1996, **A452**, 495–525.
22. Caginalp, G., An analysis of a phase-field model of a free boundary. *Archive for Rational Mechanics and Analysis*, 1986, **92**, 205–245.
23. Jackson, K. A. and Hunt, J. D., Eutectic solidification in transparent materials. 16 mm movie from Bell Telephone Laboratories (*ca* 1966).
24. Jackson, K. A. and Hunt, J., Lamellar and Rod Eutectic Growth, *AIME Transactions*, 1966, **236**, 1129.