THE INFLUENCES OF CONVECTION ON DIRECTIONAL SOLIDIFICATION OF EUTECTIC Bi/MnBi

David J. Larson, Jr.
Grumman Corporate Research Center
Bethpage, NY 11714-3580

ABSTRACT- Eutectic alloys of Bi-Mn were directionally solidified using the Bridgman-Stockbarger technique to determine the influences of gravitationally-driven thermo-solutal convection on the Bi-MnBi rod eutectic. Experiments were conducted that varied the level of convection by varying the growth parameters (solidification velocity or applied temperature gradient) and growth orientation (relative to the terrestrial gravitational vector), by microgravity damping, by applied magnetic field damping, and by imposing forced convection. Peltier interface demarcation and in-situ thermocouple measurements were used to monitor interface velocity and thermal gradient and to evaluate interface planarity.

Rod diameter, in the regular faceted/non-faceted MnBi/Bi eutectic, was found to vary with solidification velocity. At high solidification velocities the rods appear circular in cross-section, but as the velocity is slowed the cross-section becomes more faceted changing to chevrons, then to hexagonal segments and finally to a platelet structure at very low velocities. Inter-rod spacing and mean rod diameter were found to vary as the inverse square root of the solidification velocity, as expected. Interface undercooling was found to vary as the square root of the solidification velocity , also as predicted by theory. Inter-rod spacing and mean rod diameter were not found to be influenced by the applied thermal gradient, in contradiction to suggestions that all eutectics with faceting at the interface should show a temperature gradient dependence.

Forced convection at the interface was found to have little effect within the cooperative growth regime, however, increased mixing substantially coarsened the low velocity platelet structure and promoted radial segregation. Damping of the natural thermal convection, using transverse applied magnetic fields or microgravity significantly increased interfacial undercooling and decreased both the mean rod diameter and the inter-rod spacing. Magnetic field damping and microgravity damping were found to be equally effective at damping the natural thermal convection. Magnetic field damping was ineffective at damping thermo-solutal convection during off-eutectic solidification, whereas microgravity damping was shown to be effective under similar growth conditions.

1.INTRODUCTION

Morphological control as a means of optimizing mechanical and physical properties has gained increased acceptance over the past several decades. Eutectic solidification reactions are attractive in this respect because substantial microstructural refinement (to sub-micron dimensions) and alignment can be achieved directly, by controlling the solidification parameters. Eutectic reactions are also of interest and importance because many of the most significant commercial materials, such as cast irons, solders, brazements, and Al-Si castable alloys, solidify via this reaction. Controlling the morphologies and microstructures of this class of alloys is thus highly significant.

This work reports on a study of the Bi/MnBi eutectic solidification

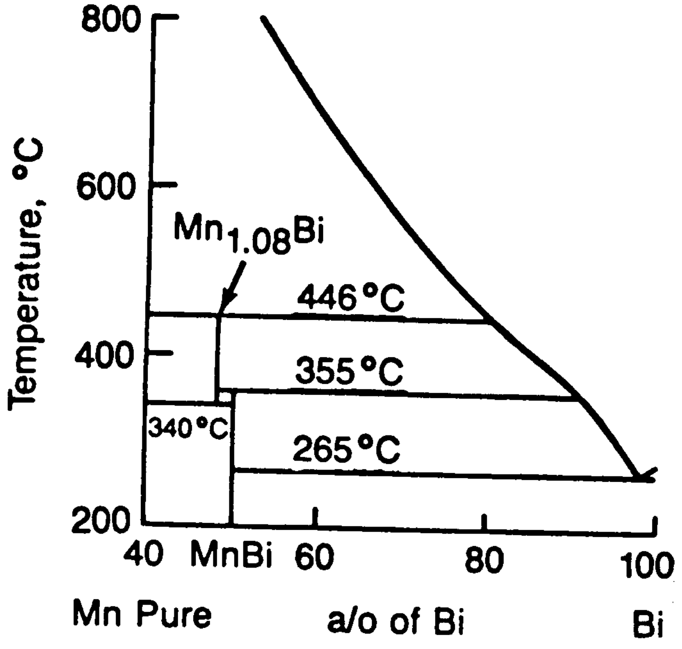


Figure 1a. Bi-MnBi region of the Bi-Mn phase diagram(1).

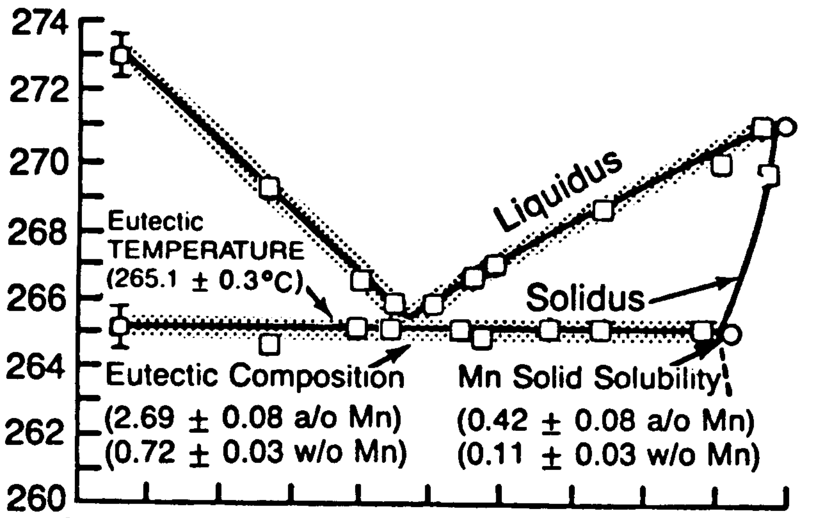


Figure 1b. Bi/MnBi eutectic region of the Bi-Mn phase diagram(2).

reactions using the Bridgman-Stockbarger directional solidification technique as a means of controlling solidification parameters. The Bi-Mn phase diagram (1) is shown in figure 1a, and the eutectic Bi/MnBi phase diagram segment (2) is shown in figure 1b. It is clear from the phase diagram that this is a highly asymmetric eutectic solidification reaction. The low volume fraction phase, MnBi, would be expected to be arrayed as a fiber within a matrix of terminal solid solution Bi. The MnBi phase might be expected to have a tendency to facet as it is a non-cubic intermetallic. Directional solidification of this rod eutectic results in the simultaneous growth of the MnBi faceted rod and Bi matrix phases in a regular array coupled by the diffusion field in the liquid ahead of the solidification interface.

The dependence of the inter-rod spacing, λ, and the rod diameter, d, on velocity is described by the well known Jackson-Hunt (3) theory for eutectics growing under diffusion controlled, plane-front, solidification conditions. This theory is well established for eutectic systems without faceting at the solidification interface. The relationship predicts that λ and d vary as the inverse square root of the solidification velocity and that interface undercooling, ΔT, varies as the square root of solidification velocity. The optimum growth velocity, undercooling, and wavelength is described as growth in extremum and, stated simply, demands that at a given solidification velocity the structure will grow at a minimum undercooling. Alternatively, a structure growing at a given undercooling will grow at a maximum velocity . The Bridgman-Stockbarger technique imposes a solidification velocity on the solidification interface, and thus growth occurs with minimum undercooling.

The Jackson-Hunt (3) theory was appended by Verhoeven et al (4) to include the influence of forced convection. It was concluded that the diffusional field ahead of the solidification interface was so tightly coupled to the interface that it was unlikely to be influenced by macroscopic fluid flow. Early experiments using microgravity as a means of damping convection suggested that, counter to theory, the damping of gravitationally driven convection refined both the inter-rod spacing and the mean rod diameter (5). Subsequent experiments in microgravity confirmed this finding and suggested that interface undercooling was increased under damped conditions (6-8). The present study was undertaken to better understand the origins of these discrepancies.

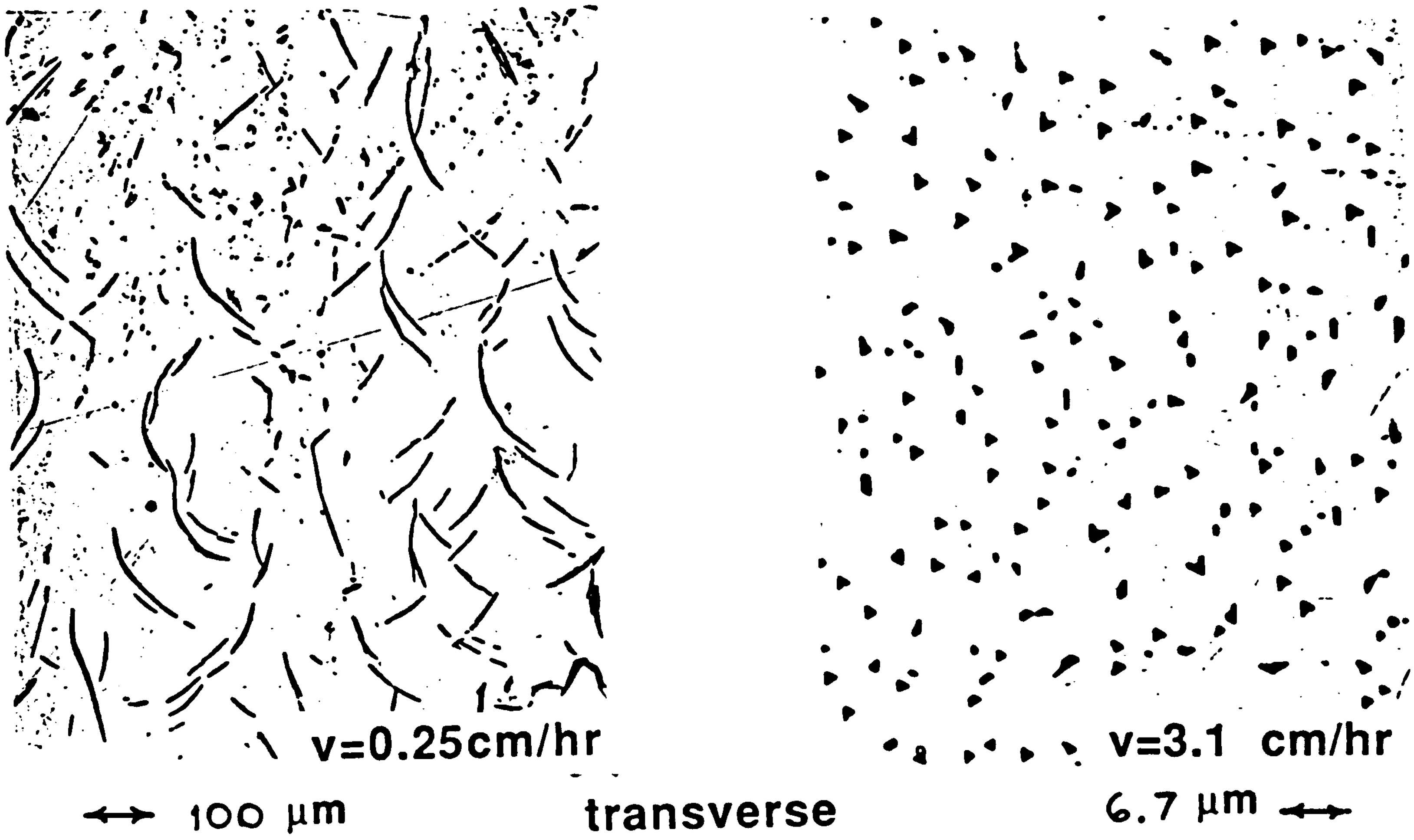
2. EXPERIMENTAL TECHNIQUE

Experiments were conducted over a wide range of solidification velocities (0.5 to 50 cm/h) and thermal gradients (5 to 125 °C/cm). Growth orientation relative to the terrestrial gravity vector was varied, some experiments conducted vertically upwards (thermally stabilized) and some vertically downwards (thermally destabilized). It was assumed that for compositions on the eutectic that there was no solutal component to the gravitationally-driven convection. Additional experiments were conducted in the suborbital microgravity environment on sounding rockets flying Keplerian trajectories, and another was conducted in the microgravity orbital environment of the space shuttle. Applied transverse magnetic fields were also used to damp the natural thermal convection. Lastly, forced convection was imposed on the solidification interface by conducting spin-up/spin-down experiments while directional solidification was taking place. Peltier interface demarcation was used to monitor the solidification velocity and the interface shape and in-situ ultrafine thermocouples were used to monitor the cooling rate and thermal gradient within the samples. Sample velocity, V, and thermal gradient, G, in the liquid ahead of the interface were used as experiment parameters, as previously noted, whereas radial thermal gradients were minimized by using a thermal model of the Bridgman-Stockbarger process and Peltier interface demarcation to adjust the growth conditions until a near-planar interface was achieved. Our experimental techniques have been previously described (9,10).

3. EXPERIMENTAL RESULTS AND DISCUSSION

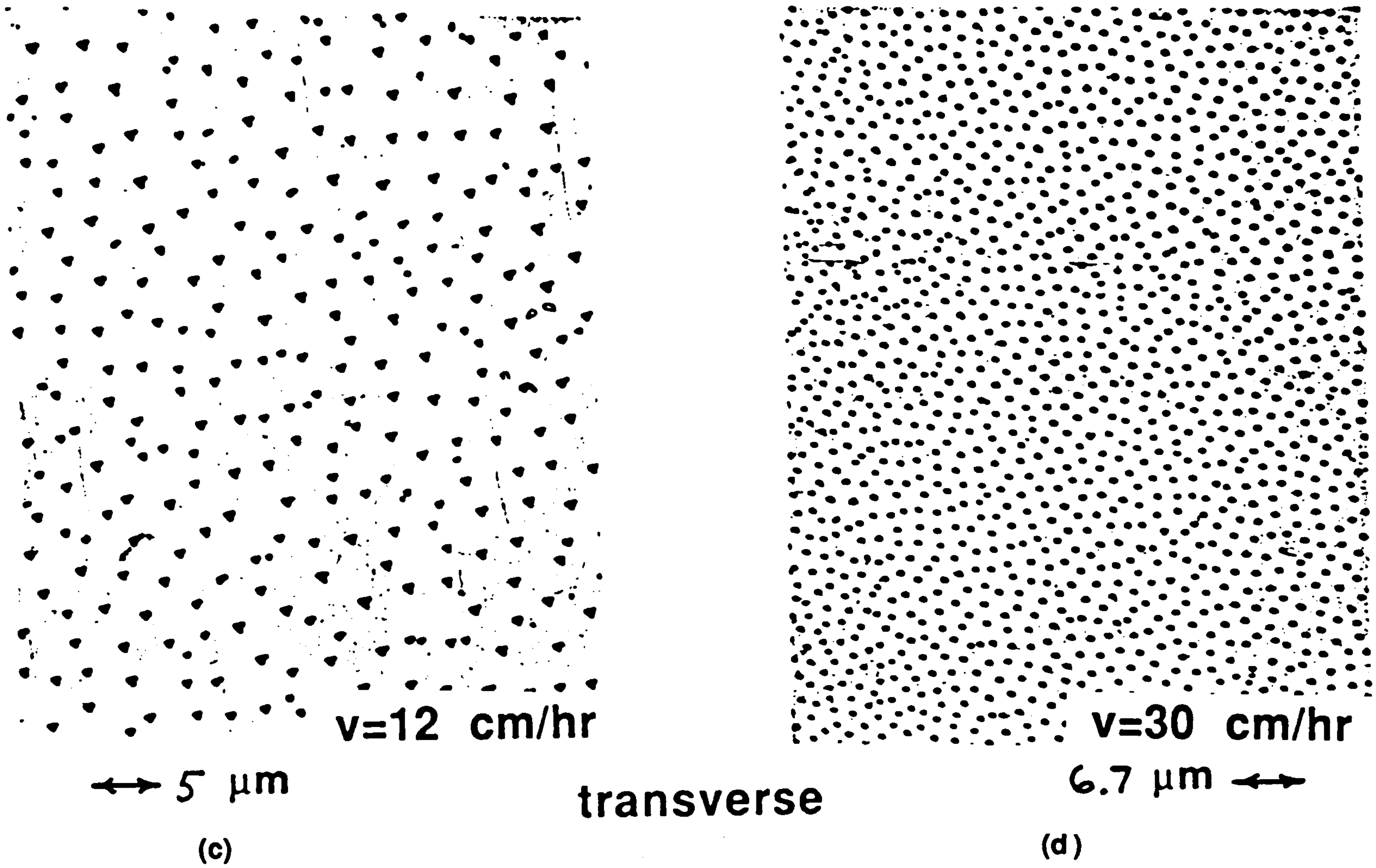
The solidification morphology of the dispersed MnBi rods was found to be a regular array of high aspect ratio fibers whose growth axis coincided with the 'c' direction of the equilibrium MnBi phase, which is hexagonal. The rod-cross-section was found to vary in morphology as a function of solidification velocity and to coincide with the basal plane of the hexagonal cell. Typical examples of the rod cross-sections as a function of solidification velocity are shown in figures 2a-d. At the highest solidification velocities, Fig. 2d, the rods become chevron-like and then appear as degenerate hexagonal segments that confirm that the growth planes that define the shape are the hexagonal prismatic planes. For velocities in excess of 2 cm/hr the structure is properly described as a regular faceted (MnBi)/non-faceted (Bi) eutectic, and the growth is cooperative.

At velocities below 0.75 cm/hr, Fig. 2a, the morphology has changed to a platelet structure reminiscent of graphite in cast iron. The reason for this is evident when the relative stability of rods and lamellae are considered,



(a) (b)

Figures 2. Typical Bi/MnBi microstructures photographed normal to the solidification direction as a function of solidification velocity. (a) V = 0.25 cm/hr, (b) V = 6.7 cm/hr.



Figures 2. Typical Bi/MnBi microstructures photographed normal to the solidification direction as a function of solidification velocity. (c) V = 12.0 cm/hr, (d) V = 30.0 cm/hr.

following arguements presented by Jackson-Hunt (3). They calculate, for a system with isotropic interfacial free energies, that the minimum undercooling for growth of rods is lower than for lamellae when a critical surface energy ratio is less than unity. Substituting our experimental data into their equation results in the ratio approaching unity (0.996) when the morphological transition that we note takes place. At velocities greater than 0.75cm/hr, the rod structure will grow with the smaller undercooling and thus will grow ahead of, and ultimately eliminate the lamellar structure which grows with larger undercooling, and vice versa.

The sensitivity of the platelet and rod regimes to convection was tested by conducting spin-up/spin-down tests in the course of the Bridgman-Stockbarger directional solidification. This imposed forced convection at the solidification interface. Figure 3 shows the results of this study(9). It is clear that the platelet regime is extrememly sensitive to the increased convection, whereas the rod regime is relatively insensitive. The reason for the platelet sensitivity to convection is probably due to a non-isothermal interface which is sensitive to the fluid flow and to changes in the thermal gradient ahead of the solidification interface. The insensitivity of the rod growth is probably due to its coupled nature and to a moderatley high level of laminar convection which exists in the melt even without the forced convection. This natural convection has already affected the solidification conditions, particularly the interface undercooling, and further mixing has little effect. This will be discussed further after the damping experiments are described.

The eutectic mean rod diameter and mean inter-rod spacing and standard

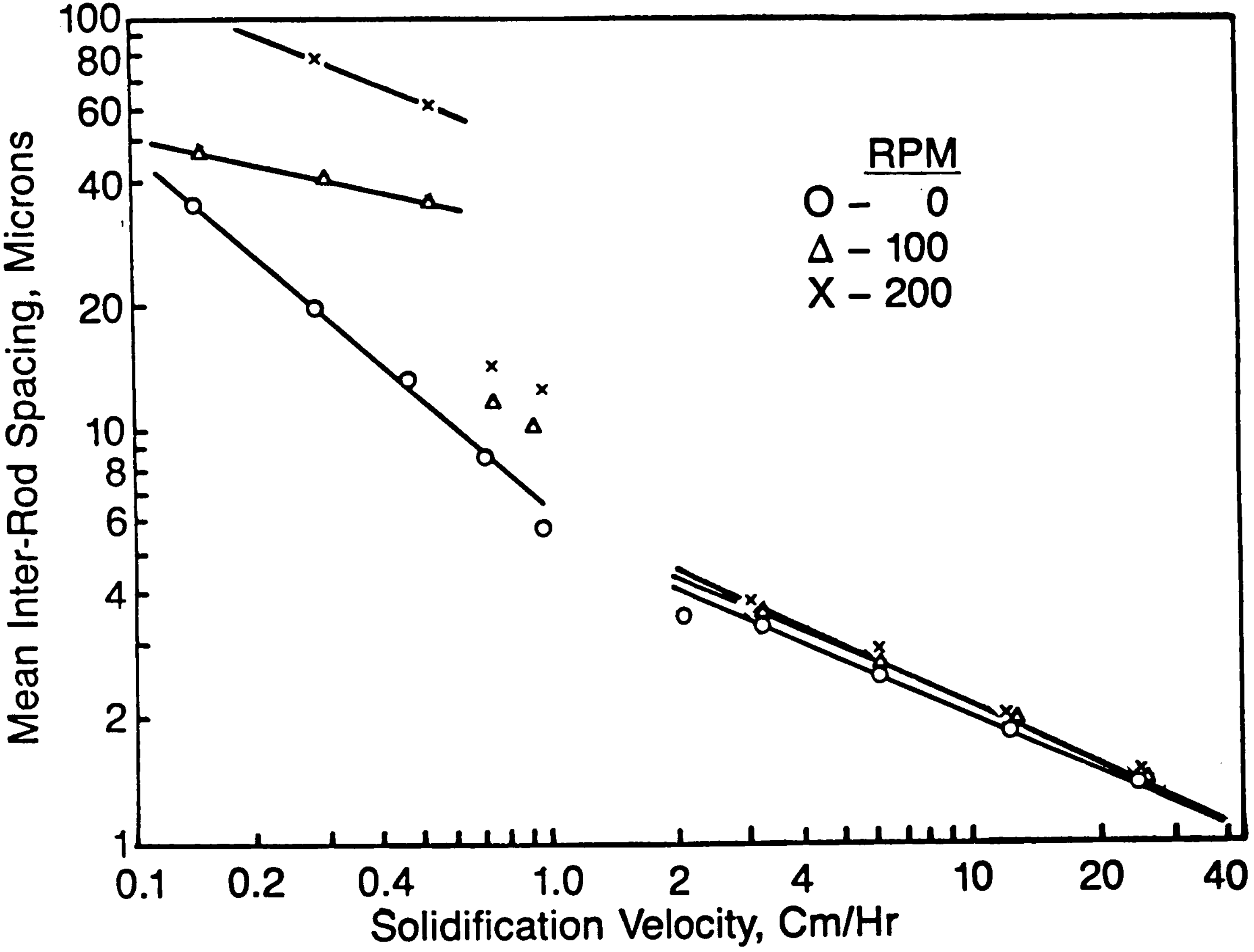


Figure 3. Mean Bi/MnBi inter-rod spacing as a function of solidification velocity, with forced convection imposed on the solidification interface.

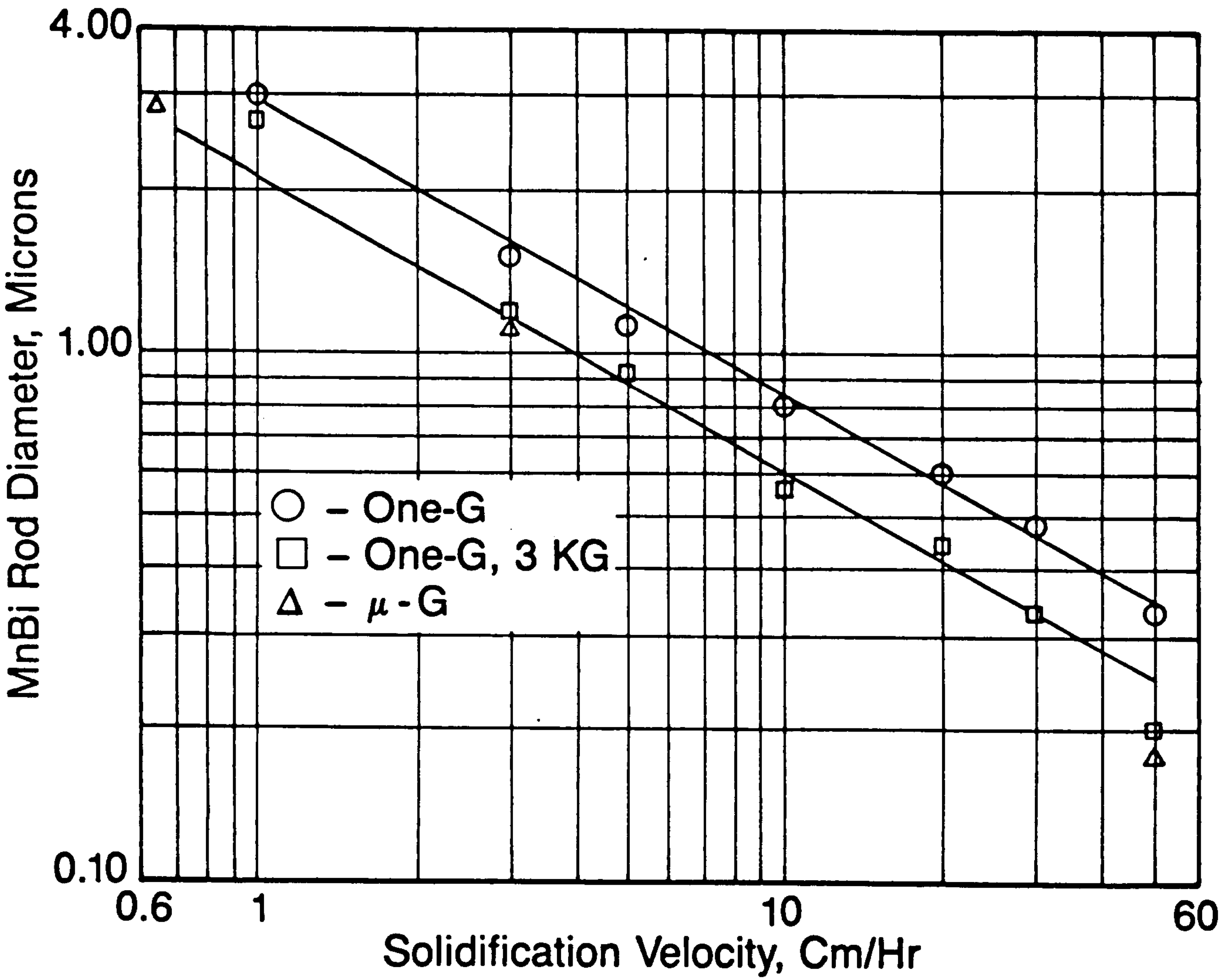


Figure 4b. Mean MnBi rod diameter as a function of solidification velocity, with and without convection damping imposed on the sample.

deviations were determined from metallographic sections taken normal to the solidification direction using a Leitz Texture Analyzer System (TAS). Data for the mean rod diameter and inter-rod spacing versus solidification velocity are present in Figures 4a and 4b, respectively. Data for samples processed in one-g, without damping, are shown as circles. The line fitting these data is drawn with the anticipated $V^{-1/2}$ dependence and serves to confirm this dependence for both the mean rod diameter and the inter-rod spacing. Samples grown at differing growth orientations relative to the gravity vector could not be distinguished and as a consequence only a single curve is presented.

Figures 4a and 4b also show the mean rod diameter and the mean inter-rod spacings for samples processed in one-g using applied magnetic field damping (squares) and samples processed in orbit using microgravity damping (triangles). It may be seen that the microgravity damped and applied magnetic field damped results are statistically distinct from the one-g undamped results. It is apparent that the reduction of the level of convection has served to decrease both the inter-rod spacing and the mean rod diameter significantly. It is clear, too, that magnetic field damping and microgravity damping are equally effective at damping the gravitationally-driven thermal convection present in the eutectic melts

The reason for the structural refinement is not so apparent, and as a consequence a series of experiments were conducted to investigate whether the applied thermal gradient in the melt ahead of the solidification interface was responsible for refinement. This concept stemmed from suggestions (10,11) that the presence of faceting at the eutectic solidification interface should invariably lead to non-isothermal interfaces that should show a

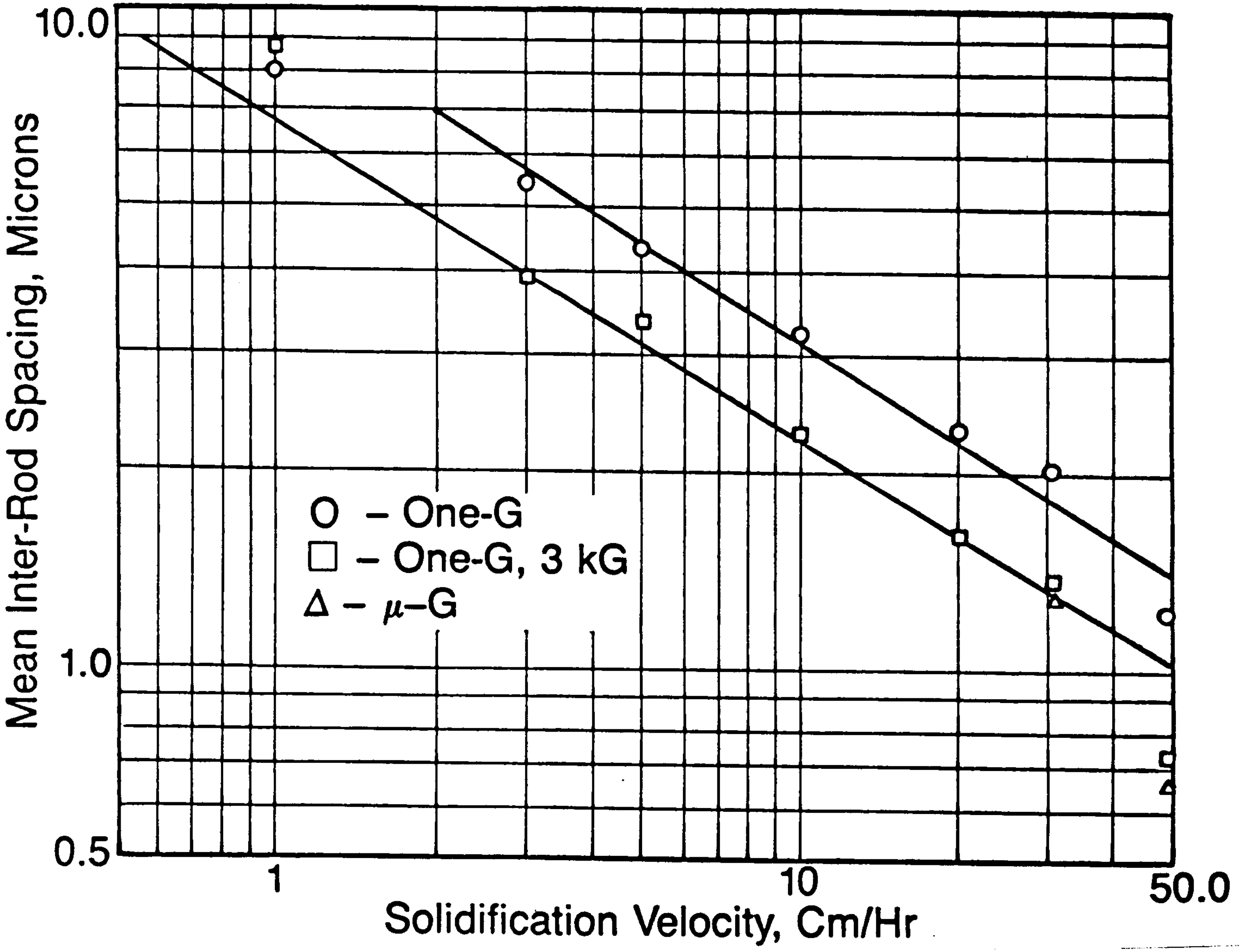


Figure 4a. Mean Bi/MnBi inter-rod spacing as a function of solidification velocity, with and without convection damping imposed on the sample.

gradient sensitivity. The non-isothermal interface was a natural consequence of the faceted phases' inability to respond quickly to a perturbation, and thus, the diffusional coupling at the solidification interface was disturbed. This resulted in one phase leading or lagging (non-isothermal) and the establishment of a solutal boundary layer of the same order as those encountered during off-eutectic solidification or during solid solution crystal growth. The latter condition introduces the possibility of convection sensitivity, though this line of reasoning was not pursued.

Another reason for suspecting that the applied thermal gradient was the origin of the structural refinement was experimental evidence which showed that thermal gradients ahead of the solidification interface increased from approximately 100 °C/cm in one-g to about 120 °C/cm under damped conditions (12,7,8). Since it was reported that increased thermal gradients decreased rod diameter and inter-rod spacing (10), it was logical to assume that the thermal gradient was the gravitationally dependent (flow dependent) cause for the effect.

Figure 5 shows the results of the present investigation (13). The thermal gradient was varied from approximately 5°C/cm to 120°C/cm and a least squares fit to the data confirms the $V^{-1/2}$ dependence predicted, but does not support a dependence of the spacing on temperature gradient. If G^n was that the thermal gradient dependent function, the exponent determined from the structural data by linear regression analysis was 0.027. This is within the experimental error and it may be concluded that no such dependence exists for the Bi/MnBi rod eutectic.

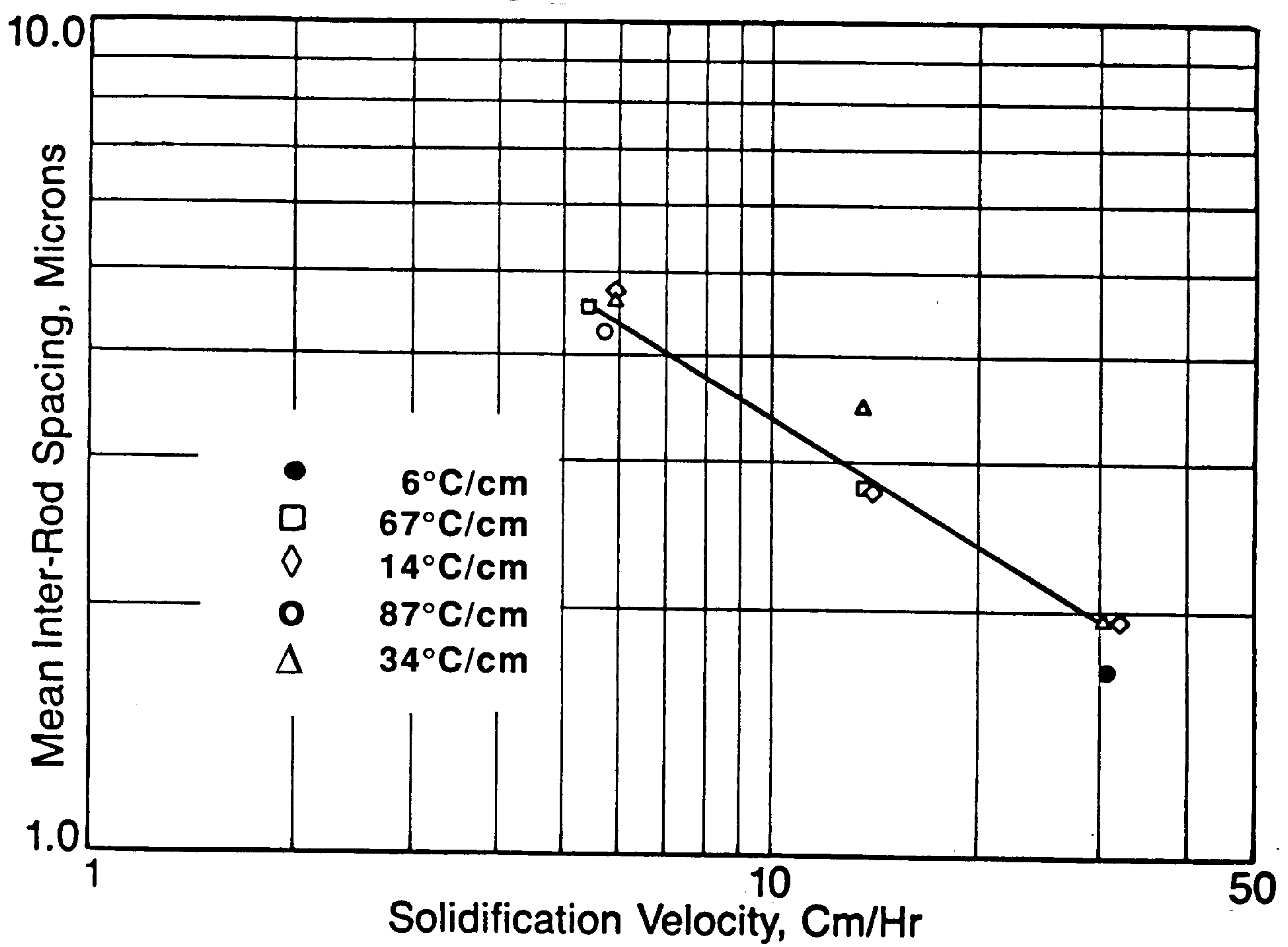


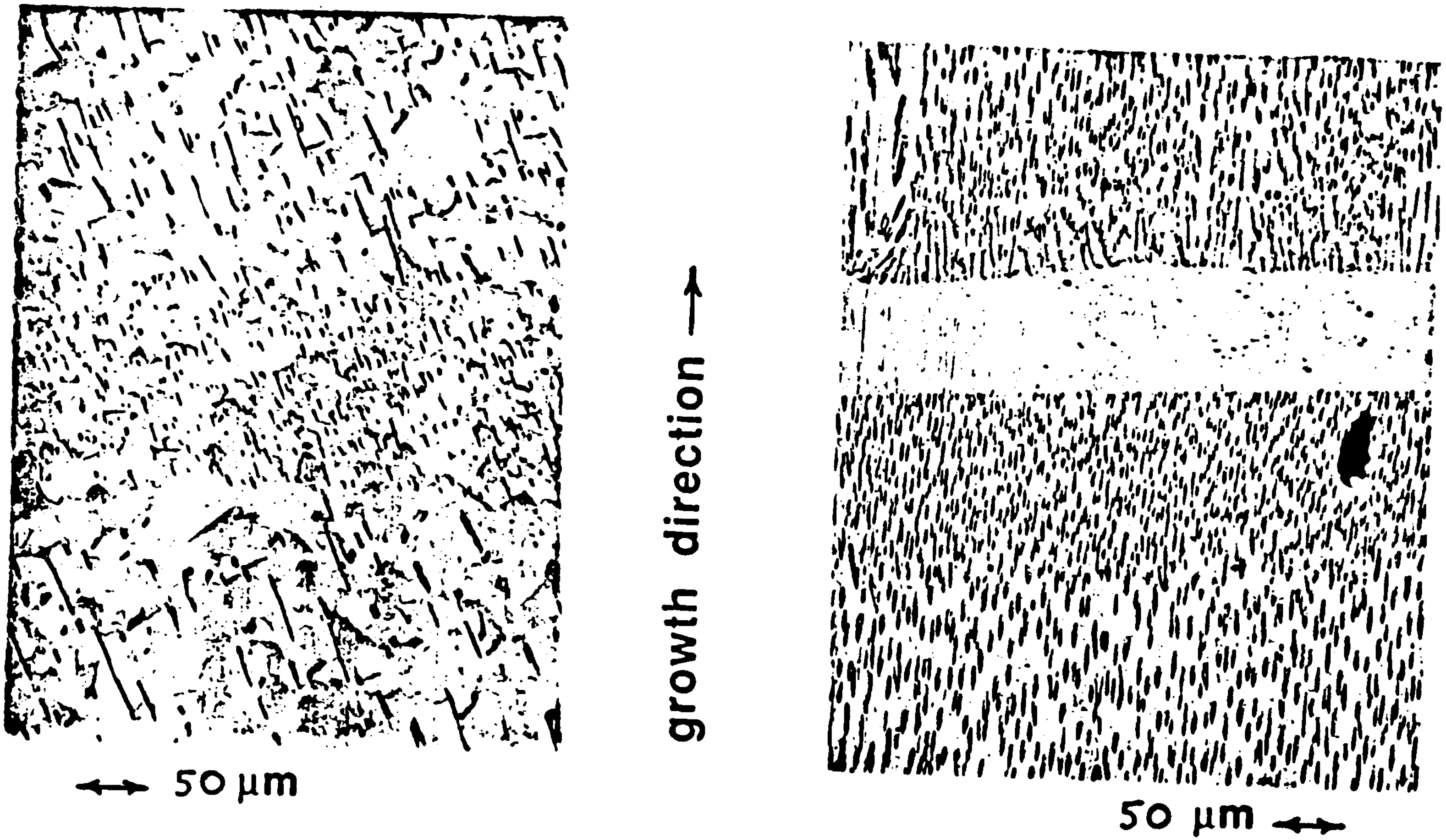
Figure 5. Mean Bi/MnBi inter-rod spacing as a function of solidification velocity showing the dependence on applied thermal gradient.

The reason for the absence of the thermal gradient dependence in this case is due to two factors, which were confirmed by Peltier interface demarcation experiments. Figure 6 shows the results of these experiments (14,15). The photomicrograph shown was taken from a polished section of the sample cut parallel to the growth direction. The polarity of the current pulse applied was negative, causing cooling at the solidification interface. The interface was thus 'instantaneously advanced' resulting in a refinement of the structure. However, what should be noted is that the structure has had no difficulty adjusting to this severe perturbation and so the primary hypothesis for suspecting a non-isothermal interface must be rejected. In addition, the interface immediately preceding the band of pro-eutectic single phase Bi is seen to be very nearly planar. Considering the thermal conductivities of the respective phases, the interface must grow very nearly isothermally.

Evaluation of thermal data demonstrated that in one-g the sample experienced a small but reproducible interface undercooling; however, the damped samples experienced a much greater degree of undercooling. This was unexpected, and the data are shown in Figure 7. These data may be fit with the expected $V^{1/2}$ functionality (3), and they raise the possibility that the undercooling is the origin of the structural refinement. This hypothesis suggests that since the Bi/MnBi eutectic is highly asymmetric the extrapolated liquidus and solidus lines defining the undercooled phase relations might be significantly different from the phase relations prescribed by the equilibrium phase diagram. In the case of a eutectic alloy of Bi-Mn, undercooling of approximately 6°C (the maximum noted), would reduce the expected volume fraction of the dispersed MnBi phase by an amount comparable to that measured

PELTIER INTERFACE DEMARCATION

negative polarity



Eutectic Bi-Mn

Figure 6. Photomicrograph of a longitudinal section of a Bi/MnBi sample directionally solidified showing a Peltier interface demaracation. The refinement of the Bi/MnBi structure during the pulse should be noted.

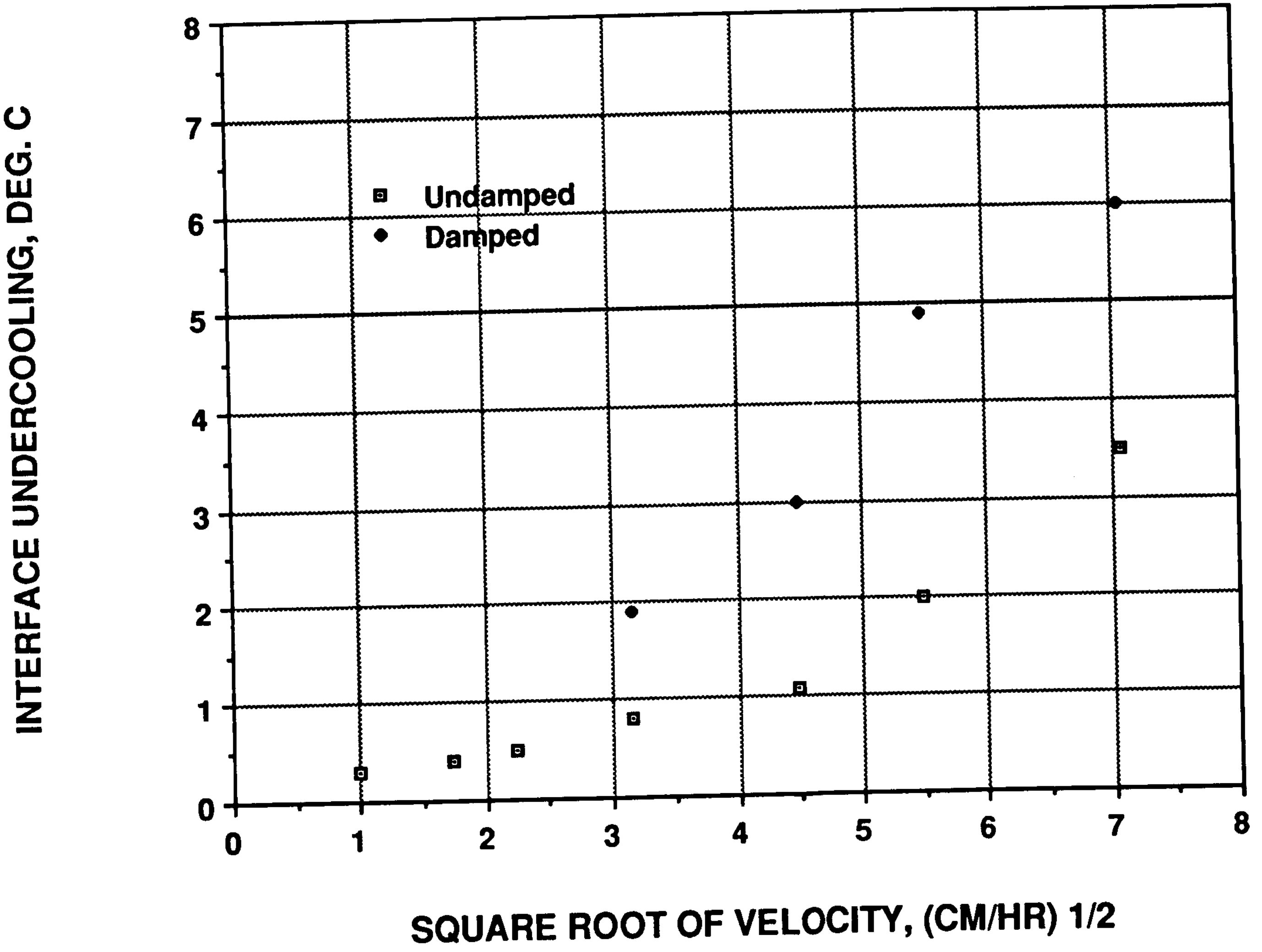


Figure 7. Interface undercooling as a function of the square root of the solidification velocity, for samples solidified with and without convection damping.

within the damped sample undercooled 6^{o}c. Figure 8 shows the result of volume fraction calculations based on the measured rod and inter-rod dimensions of both the undamped and damped samples. It is clear that there is a strong velocity dependence, however, there is no statistically significant difference between the curves. This is critically important to note since the damped and undamped cases experienced significantly different undercooling conditions. The evidence suggests that even though the phase diagram is asymmetric, this factor is not the cause of the structural refinement. Actually, in one microgravity processed sample, the terminal solid solubility of Mn in Bi was noted to be almost twice what the equilibrium solubility was determined to be, 0.21 wt.% Mn. This is consistent with an extended solubility due to the undercooling. It has been reported that compositional adjustments within the Bi/MnBi eutectic are made by varying the inter-rod spacing and maintaining the rod diameter essentially constant during a constant velocity test. This would suggest that a decreased volume fraction of MnBi would be accommodated by maintaining the rod diameter constant and increasing the inter-rod spacing. This is entirely inconsistent with our experimental finding.

Recently, a new theory has been proposed by Magnin and Kurz (16) that purports to describe the solidification behavior of faceted/non-faceted eutectics. This theory is really an extension of the Jackson-Hunt (3) theory, incorporating and adjusting the Fisher-Kurz (11) theory. Figure 9 is a plot using this theory and shows the undercooling versus inter-rod spacing for an envelope of curves, each for a constant velocity and showing the anticipated gradient dependence. It is clear that although a gradient dependence is predicted, it occurs at very low velocities, below that of the present work. Figure 10 shows how these parameters would change at constant velocity if the

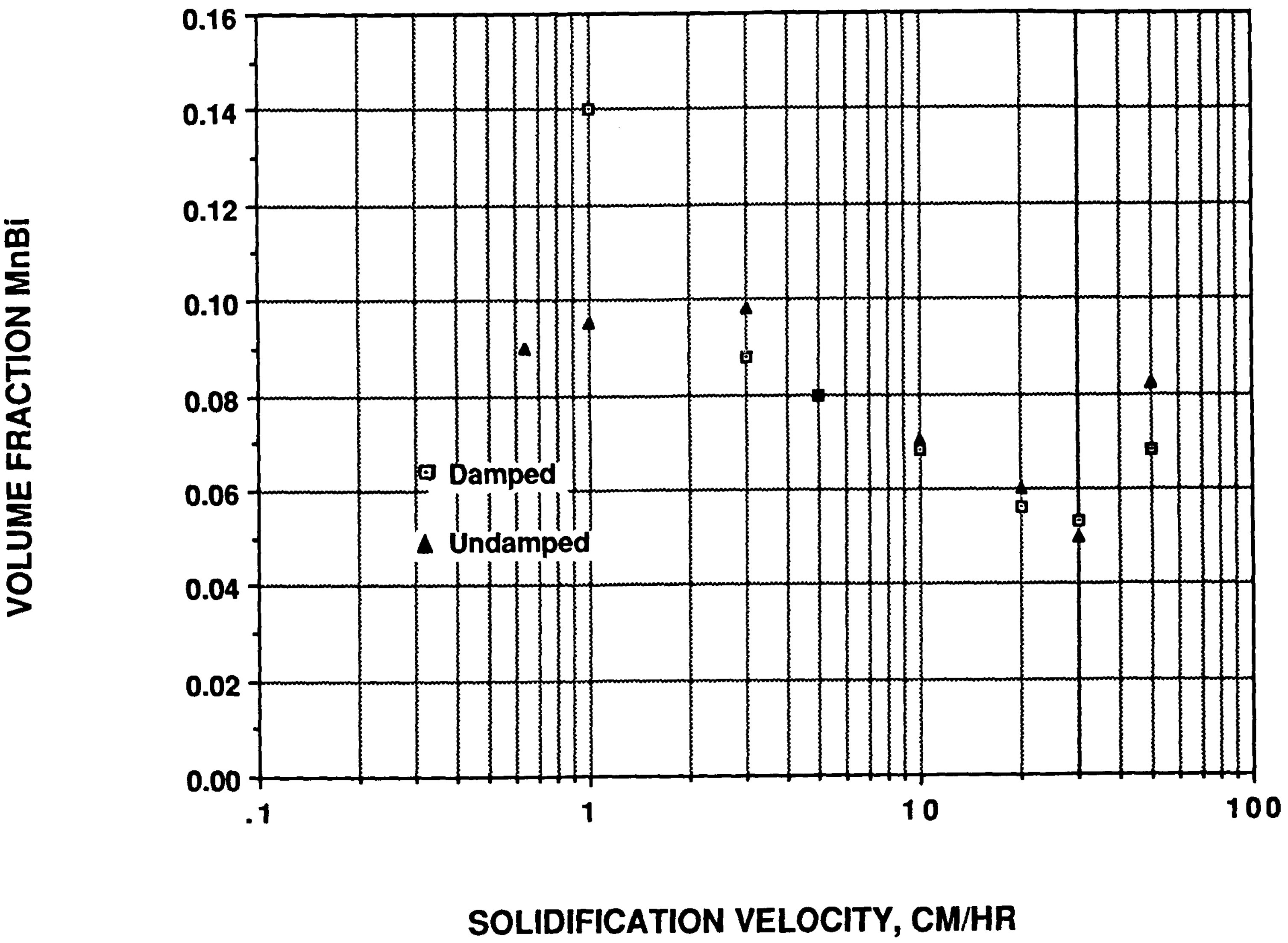


Figure 8. Volume fraction of the dispersed MnBi phase as a function of the solidification velocity, for samples solidified with and without convection damping.

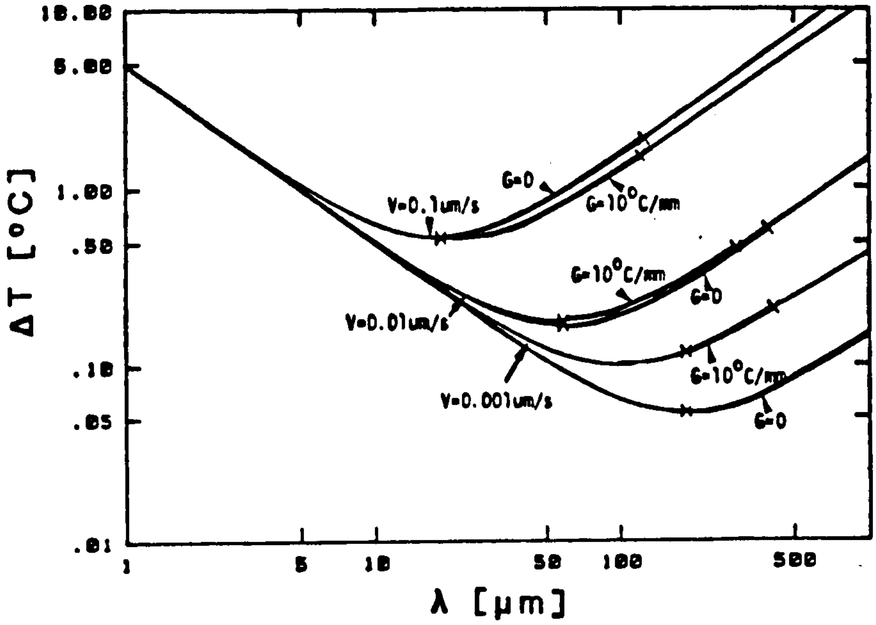


Figure 9. Interface undercooling as a function of eutectic spacing(16), showing the sensitivity to solidification velocity and to the applied thermal gradient.

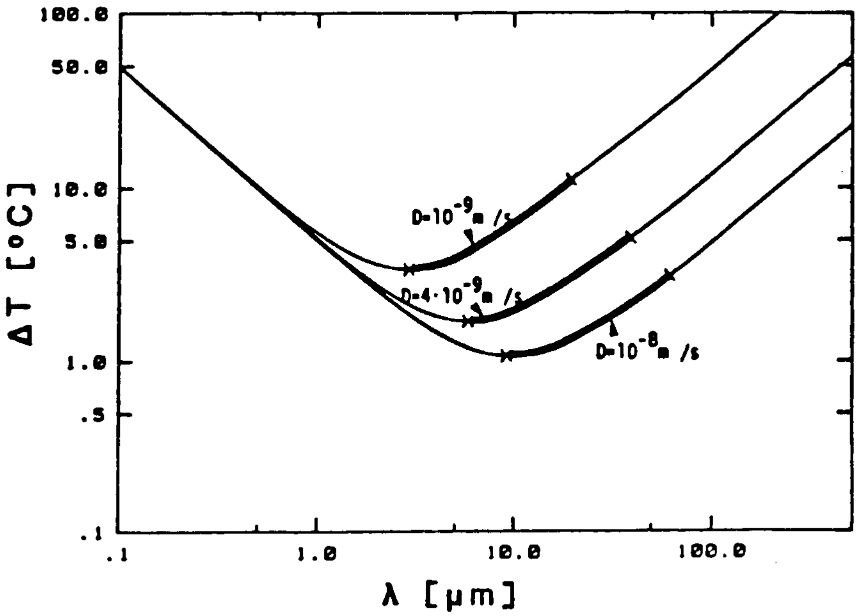


Figure 10. Interface undercooling versus eutectic spacing(16) showing the sensitivity to a varying inter-diffusion coefficient, at constant velocity.

interdiffusion coefficient within the liquid were varied. It is clear from their results that the interdiffusion coefficient has much greater potential impact on undercooling and/or microstructure than any other.

If we take our data and consider the three invarient relationships predicted by the Jackson-Hunt (3) theory, that is

$$\lambda^2 V = K_1 \qquad (1a)$$

$$\Delta T \lambda = K_2 \qquad (1b)$$

$$\Delta T^2/V = K_2^2/K_1 \qquad (1c)$$

We find that although the data may fit the correct functional dependencies, the constants do not cross-correlate. This indicates that at least one of the terms that we are considering a constant may, in fact, be varying. Evaluation of the various possibilities indicates that the inter-diffusion coefficient is a most likely candidate, and should be considered to be a mass transport coefficient that may have a convective contribution incorporated within it. As convection is damped, the transport coefficient decreases. The alternative possibility is that the interdiffusion coefficient in the liquid is sensitive to the temperature depression associated with the interfacial undercooling and decreases as a function of interface temperature. The calculated interdiffusional coefficient for our damped samples is illustrated in Figure 11 and the corresponding adjustments to Figures 9 and 10, using our data, are presented as Figure 12. This plot successfully incorporates all of our relevant data and offers a concise summary of these complex interaction parameters.

4. SUMMARY

Data have been presented which demonstrate that the presence of

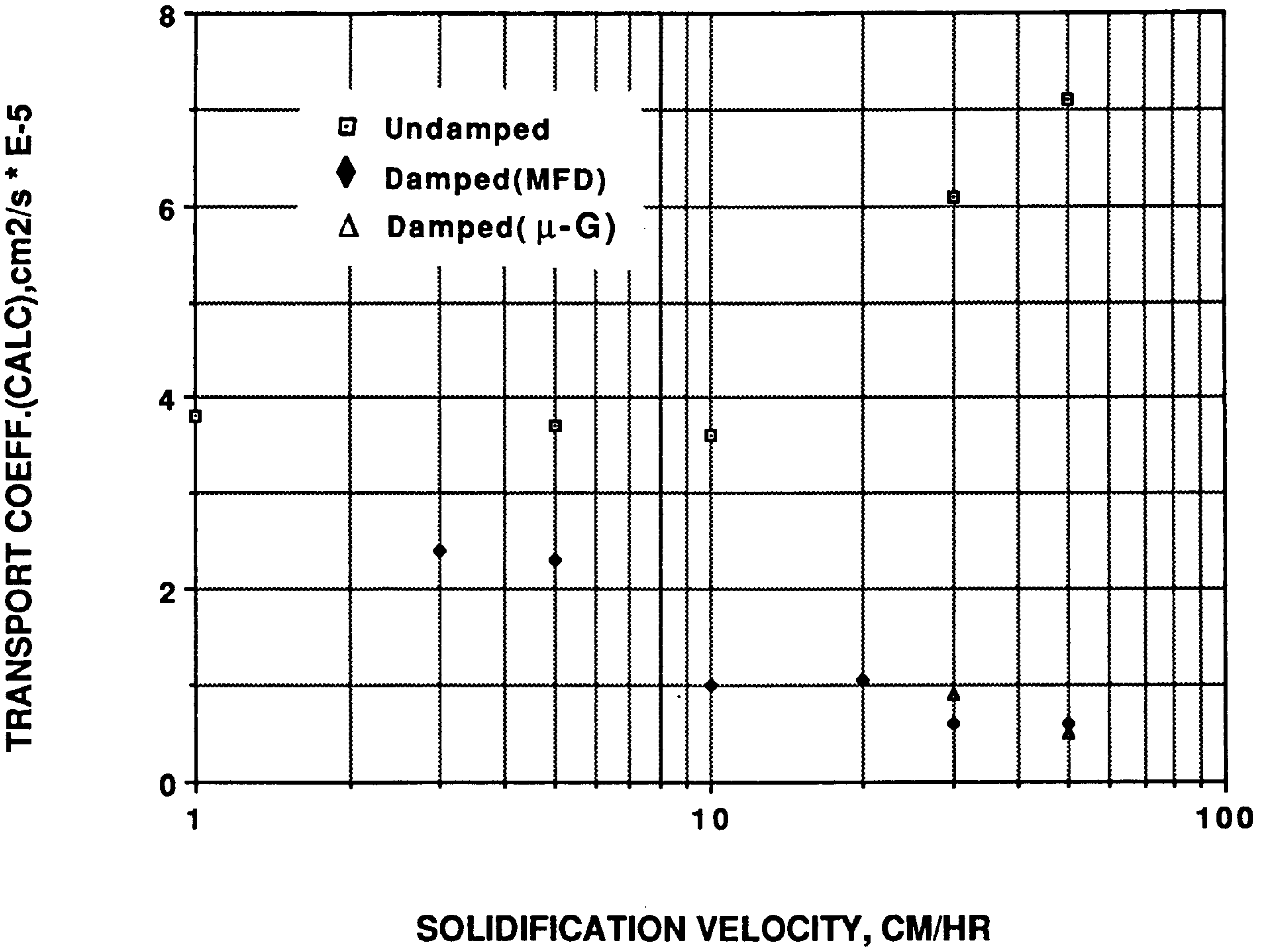


Figure 11. Calculated mass transport coefficient$^{(3)}$ as a function of solidification velocity for samples solidified with and without convection damping, eutectic Bi/MnBi.

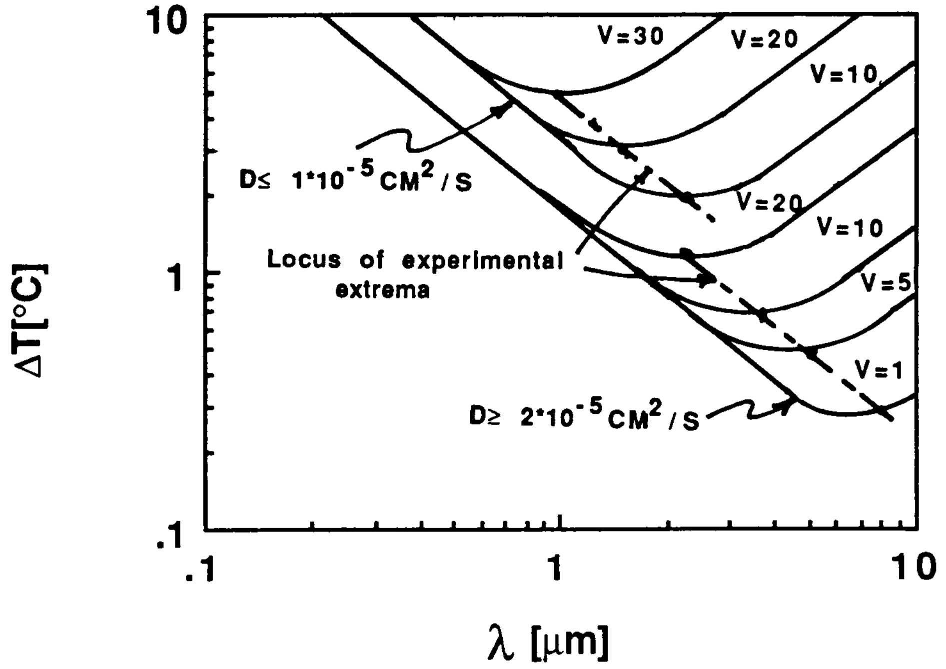


Figure 12. Interface undercooling as a function of the mean inter-rod spacing for eutectic Bi/MnBi showing the sensitivity to solidification velocity and convection damping.

convection during the directional solidification of faceted/non-faceted eutectic Bi/MnBi serves to significantly increase the mean rod-diameter and inter-rod spacing and to substantially decrease the interface undercooling. Alternatively, damping the natural, gravitationally-driven, convection normally encountered during directional solidification terrestrially, either by using applied magnetic field damping or microgravity damping, serves to decrease the spatial dimensions of the eutectic structure and to significantly increase the interfacial undercooling. The Jackson-Hunt and Magnin-Kurz theories have been used to explain these results. Microgravity damping and applied magnetic field damping of the natural thermal convection were both shown to be effective.

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