APPENDIX B

Directional Solidification of Pb-Sn Eutectic with Vibration

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ABSTRACT

Pb-Sn eutectic alloy was directionally solidified at 1.4 to 3.2 cm/hr with forced convection induced by axial vibration of the growth ampoule with a frequency of 10 Hz to 40 Hz and an amplitude of 0.5 to 1.0 mm. To determine the exact growth rate, an interface demarcation technique was applied. The lamellar spacing was increased 10% to 40% in ingots solidified with vibration compared to those solidified without vibration. The number of grain boundaries was increased by vibration.

The average intensity of convection in the melt under axial vibration of the ampoule was estimated by comparing the experimental results with a theoretical model.

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1. Introduction

In recent years, many theoretical and experimental investigations have been performed on the effect of convection on eutectic microstructure. The main motivation for these investigations was that directional solidification of eutectic alloys can produce high quality composites with interesting anisotropic properties.

A theory for diffusion-controlled eutectic growth was presented by Jackson and Hunt [1]. Assuming a linear velocity gradient in the flow of melt across the interface, Quenisset and Naslain [2], followed later by Baskaran and Wilcox [3] and Chandrasekhar et al. [4] calculated numerically the interfacial composition during lamellar growth. The variation of composition at the solid/liquid interface was converted to changes of the undercooling at the interface. Using the extremum criterion, a relationship was derived between lamellar spacing and convection. Employing the same strategy with two different directions of flow relative to microstructure, Caram et al. [5] determined the influence of convection on rod growth. These theoretical investigations led to the conclusion that convection increases the lamellar and rod spacing during eutectic solidification.

Eisa and Wilcox [6] and Chandrasekhar [7] experimentally studied solidification of the MnBi-Bi eutectic with the accelerated crucible rotation technique (ACRT). The MnBi rod spacing was increased by using ACRT.

Popov and Wilcox [8] directionally solidified the Pb-Sn eutectic at 1.0 and 4.6 cm/hr with ACRT using a vertical Bridgman - Stockbarger technique. Application of ACRT did not change the lamellar spacing, although this did influence the rate of rotation of the spiral structures observed by Mourer and Verhoeven [9].

Another approach to enhance convection in the melt during directional solidification is application of vibration. Vibrational mixing has been utilized in melt growth by many researchers [10-19], with a wide range of amplitudes and frequencies of vibration. For example, ultrasonic vibration at 10 KHz with micron range amplitudes was used in the Czochralski growth of Te-doped InSb [10-12] and $In_xGa_{1-x}Sb$ [13]. The grain size of the Bi_2Te_3-Bi_2Se_3 eutectic system was reduced by ultrasonic agitation of the melt during directional solidification [14]. Vibration at frequencies of 10 - 100 Hz and an amplitude of 0.05 to 5 cm resulted in better grain selection in GaAs [15], CdTe [16-18], and $In_xGa_{1-x}Sb$ [19] crystals directionally solidified by zone melting and Bridgman techniques. Even though the vibration enhanced grain selection, the number of twin boundaries in CdTe [16-18] and $In_{0.2}Ga_{0.8}Sb$ [19] increased. The mechanism for modification of microstructure is not yet known.

The main objective of this work was to investigate the influence of axial vibration of the growth ampoule on the lamellar growth of Pb-Sn eutectic using a vertical Bridgman - Stockbarger technique.

2. Experimental Methods

The experimental set-up consisted of a vertical Bridgman-Stockbarger crystal growth apparatus with provision for axial vibration of the growth ampoule, as shown in figure 1. The hot and cold zones were made of Kanthal heating elements embedded in Fibrothal insulation, separated by 5 cm of zirconia insulation as an adiabatic zone. The ampoule was translated from the hot zone to the cold zone to promote solidification.

The vibration unit consisted of a Bruel Kjaer vibrator connected to a power amplifier and HP function generator. With this arrangement the ampoule could be oscillated in the axial direction, parallel to gravity, at a frequency of 0.1 to 100 Hz and an amplitude up to 1.5 mm. The acceleration due to vibration was measured using an accelerometer connected to a power amplifier and data acquisition system. Figure 2 shows a dynamic acceleration measurement during axial vibration of the ampoule at a frequency of 20 Hz and 0.5 mm amplitude. An acceleration of $\pm 0.1g$ to $\pm 0.15g$ ($g=9.81\ m/s^2$) was measured for the range of frequencies and amplitudes utilized for our experiments.

The growth material was prepared by weighing a proper amount of 99.9999% purity Pb and Sn shots, corresponding to 61.1wt% Pb and 38.9wt% Sn. Quartz ampoules containing these shots were purged with argon and sealed under a vacuum of 10^{-6} torr. The materials were alloyed in a rocking furnace at 500°C for 6 hours. Then the ampoule was transferred to the vertical Bridgman-Stockbarger furnace for directional solidification experiments. Ingots 7 to 12 cm long and 0.6 cm in diameter were directionally solidified at an ampoule lowering rate of 1.0 cm/hr rate and an axial temperature gradient 40° C/cm (measured using a K-type thermocouple in an empty ampoule). The heater and cooler settings were 300°C and 25°C, respectively.

Cross sectional samples were taken from several locations along the ingot. The samples were cast in a resin mold and mechanically polished. The samples were electrochemically polished in a solution of 800 ml of absolute ethanol, 140 ml of distilled water and 60 ml of percloric acid for 60 sec at room temperature. In order to reveal the microstructure, the samples were chemically etched in a solution of 1 part of glycerol, 1 part of acetic acid and 4 parts of nitric acid for 30 sec at room temperature. Using such a procedure, the grain boundaries and the lamellar structure were revealed. The lamellar structure of cross-sectional and longitudinal samples was examined using optical and scanning electron microscopy.

3. Results and Discussion

To measure the lamellar spacing, cross-sectional samples were utilized. Since the eutectic growth develops with several grains at different orientations, the use of longitudinal samples would lead to a mismeasurement of the smaller spacing. Figure 3 presents a longitudinal slice. The lamellar spacing appear to be different in each grain because of the different orientations relative to the surface. The location of a change in the direction of lamella was taken as a grain boundary.

An intriguing result was obtained from the preliminary experiments performed without axial vibration. In these experiments, the solidification was carried out by moving the ampoule at a constant rate of 1.0 cm/h. The lamellar spacing, λ, was different from values obtained by others at the same velocity [20-23]. It was suspected that the difference between the values of lamellar spacing was due to a deviation of the growth rate from the ampoule lowering rate. Sukanek [24] showed that the freezing rate may deviate significantly from the lowering rate for directional solidification in a Bridgman - Stockbarger furnace, especially near the ends and with a large insulation zone (as used here). In our experiments, the sample was not very long (ampoule length/ampoule diameter = 12 to 15) and the insulation thickness was high (insulation zone/ampoule diameter $\approx$ 8). Therefore, we concluded that the deviation of the freezing rate from the translation rate might have been considerable.

To assess the deviation of the growth rate from the ampoule lowering rate, a technique was used to demarcate the liquid-solid interface periodically during the growth period. The growth ampoule was abruptly lowered 0.15 cm every one hour. This rapid movement disrupted the structure and enabled the interface shape and position to be seen in longitudinal slices. The average macroscopic freezing rate was determined by measuring the distance between these interface demarcations and knowing the frequency of suddenly lowering the ampoule. Figure 4 shows the growth rate versus length fraction solidified in ingots 7.0 to 10 cm long. The freezing rate was higher at the first to freeze section of the ingots, decreased halfway through the growth, and increased at the end of solidification. These result are in qualitative agreement with Sukanek's prediction [24].

Since the growth velocity varied, the lamellar spacing should have also varied along the ingots. Figure 5 shows the variation of the lamellar spacing versus the fraction solidified. For all vibration conditions, the lamellar spacing was smaller near the ends and increased in the center of the ingot, as shown in figure 5. For the growth with vibration, the lamellar spacing was larger than without vibration.

Depending on the intensity of vibration, the use of axial vibration during directional solidification is anticipated to enhance convection in the melt. The increased convection would be expected to cause a change in the lamellar spacing. The analysis of solidified samples in this work combined with the lamellar spacing obtained by solidification without any forced convection was in perfect agreement with the experiments conducted by Davies [20], Mollard and Flemings [21] and Chadwick [23], as well with the equation suggested by Hunt and Chilton [22]. Figure 6 shows a comparison of our results with and without vibration applied during solidification. The freezing rate is the actual growth rate obtained from the interface demarcation technique. This figure shows that the lamellar spacing was increased 10 to 45% by vibration as compared to the ingot solidified without vibration, depending on the freezing rate. However, comparison of the ingots solidified under different vibrational conditions (amplitudes up to 1.0 mm and frequency of 10 to 40 Hz) shows 5% changes in the lamellar spacing.

Instability of the solid/liquid interface might be expected due to the oscillatory displacement of interface position according to the frequency and amplitude of vibration [25]. In a eutectic solidification, this might influence interface stability, for example causing a transition from lamellar to rod or even the cessation of regular growth. Also vibration might cause nucleation at the interface and increase the number of eutectic grains. Such a process could lead to ingot with a more refined microstructure.

In this work, the use of several values of amplitude and frequency did not result in rod eutectic growth or a broken eutectic. In all the cases, the microstructures remained lamellar. No separation of Pb or Sn was observed, as in the ACRT experiments [8]. However, in all the experiments with vibration, independent of its amplitude and frequency, the ingots showed an increase in the eutectic grain boundaries. That is, the average grain size decreased compared to growth under the same conditions without agitation of the melt. The examination of samples in the center of the ingot showed an increase in the number of grain boundaries. The surface spiral structure observed by Popov and Wilcox [8] and Mourer and Verhoeven [9] was not present in any ingot solidifed in this work, either with or without vibration.

The average fluid flow across the solid/liquid interface during the experiments with vibration was estimated by using Chandrasekhar et al.'s theoretical results [4]. They calculated the change in lamellar spacing for eutectic compositions of 10%, 30%, and 50% as a function of convection intensity. Interpolating their results, the change for the eutectic composition of Pb- Sn (38.9wt%) can be estimated. For an average increase of 10% in the lamellar spacing obtained in this work with application of vibration , the use of Chandrasekhar's results led to an intensity of convection, Γ, close to 20. This value is significantly greater than the flow due to natural convection ($\Gamma \approx 0.0065$).

4. Conclusions

The influence of axial vibration of the ampoule on lamellar growth of Pb-Sn eutectics was investigated. An interface demarcation technique was used to determine the average macroscopic freezing rate along the ingot. Up to 0.15g (g=9.81 m/s^2) variation in acceleration was measured during axial vibration of the ampoule. Such gravitational modulations would be expected to change the fluid flow in the melt and at the interface. Axial vibration of the ampoule has increased the lamellar spacing in Pb-Sn eutectics by 10% to 45%, depending on the freezing rate. For different vibrational conditions the lamellar spacing was changed by less than 5%. Under these applied vibrational conditions, the eutectic microstructure did not change from lamellar to rod growth or irregular growth. The microstructure in all the experiments remained regular lamellar. The number of eutectic grains was increased by vibration.

Acknowledgement

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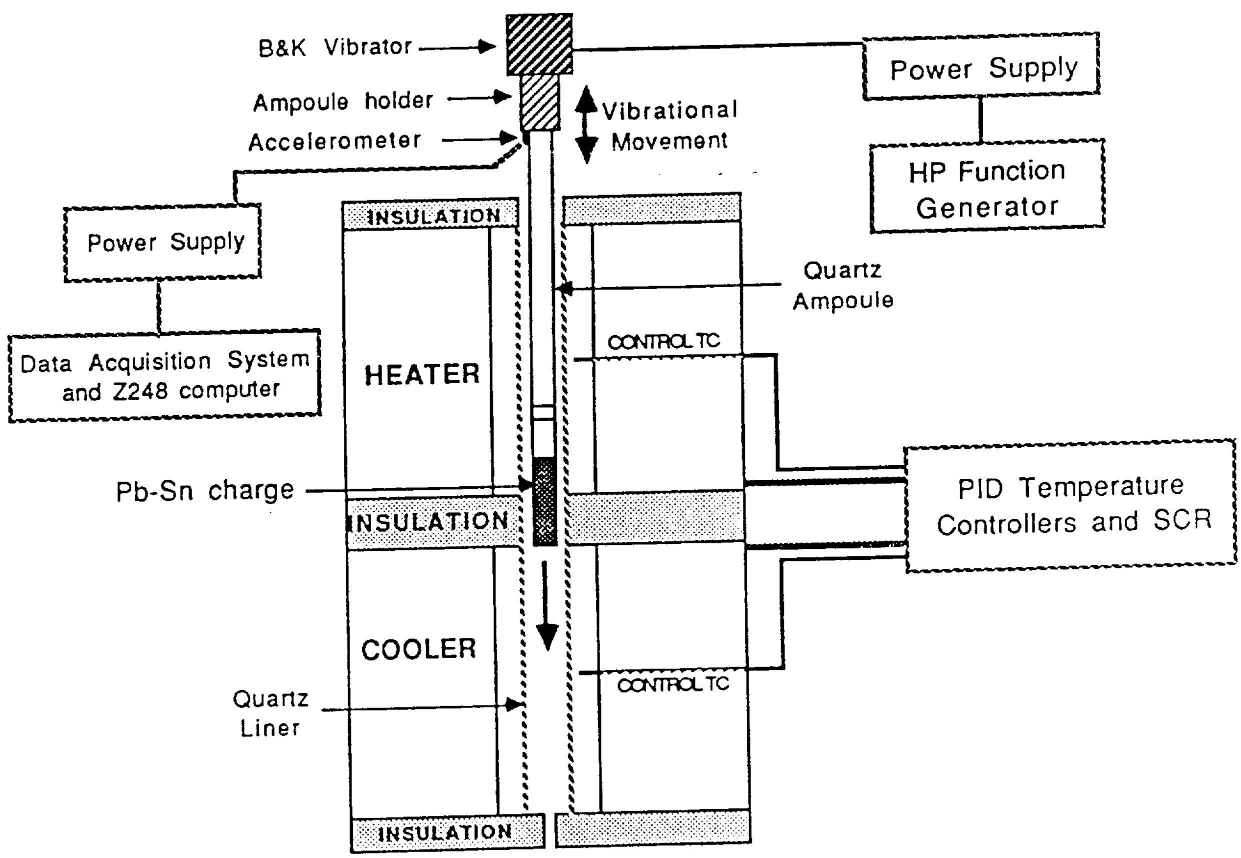


Figure 1: Schematic diagram of the experimental setup including vertical Bridgman Stockbarger furnace and a provision for axial vibration of the growth ampoule.

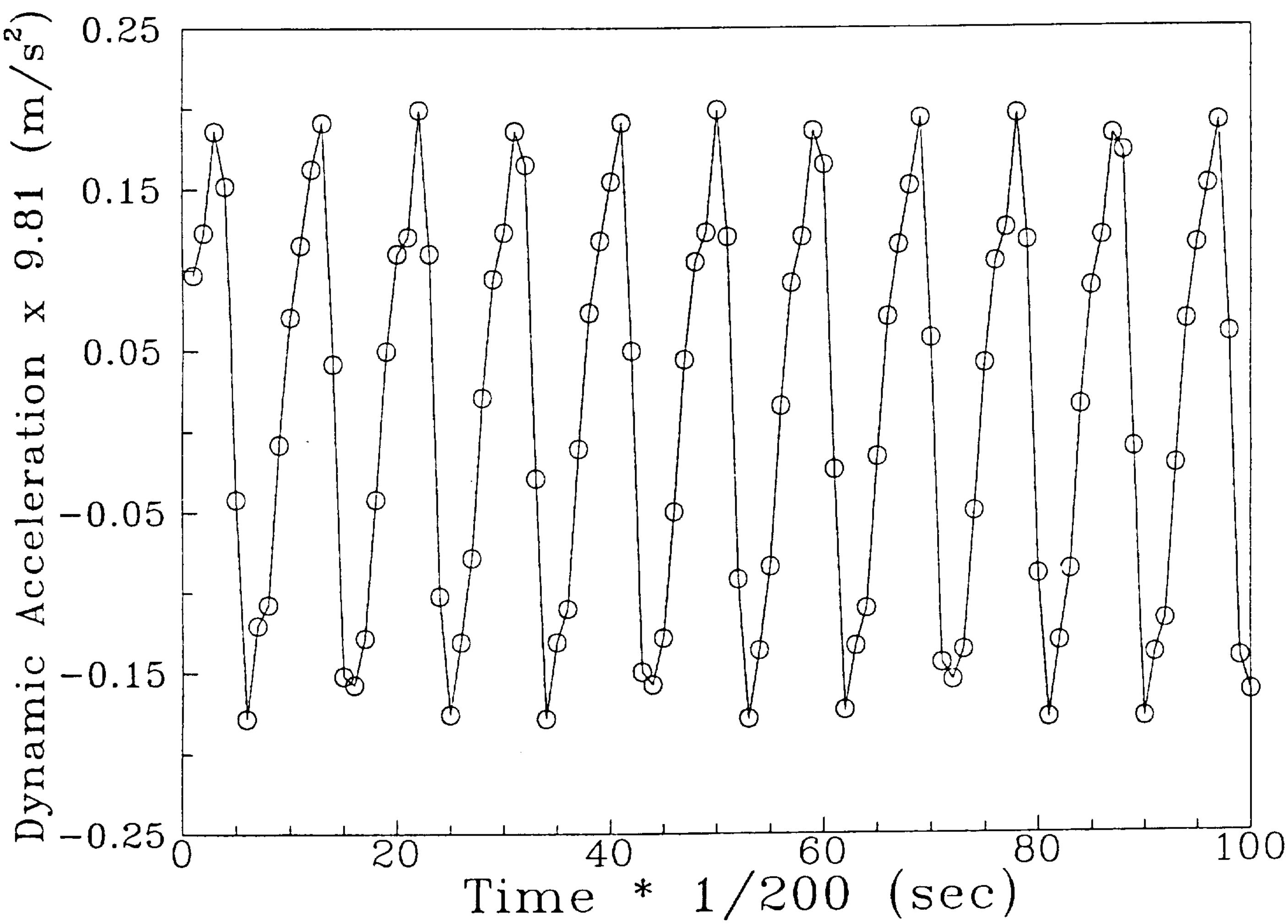
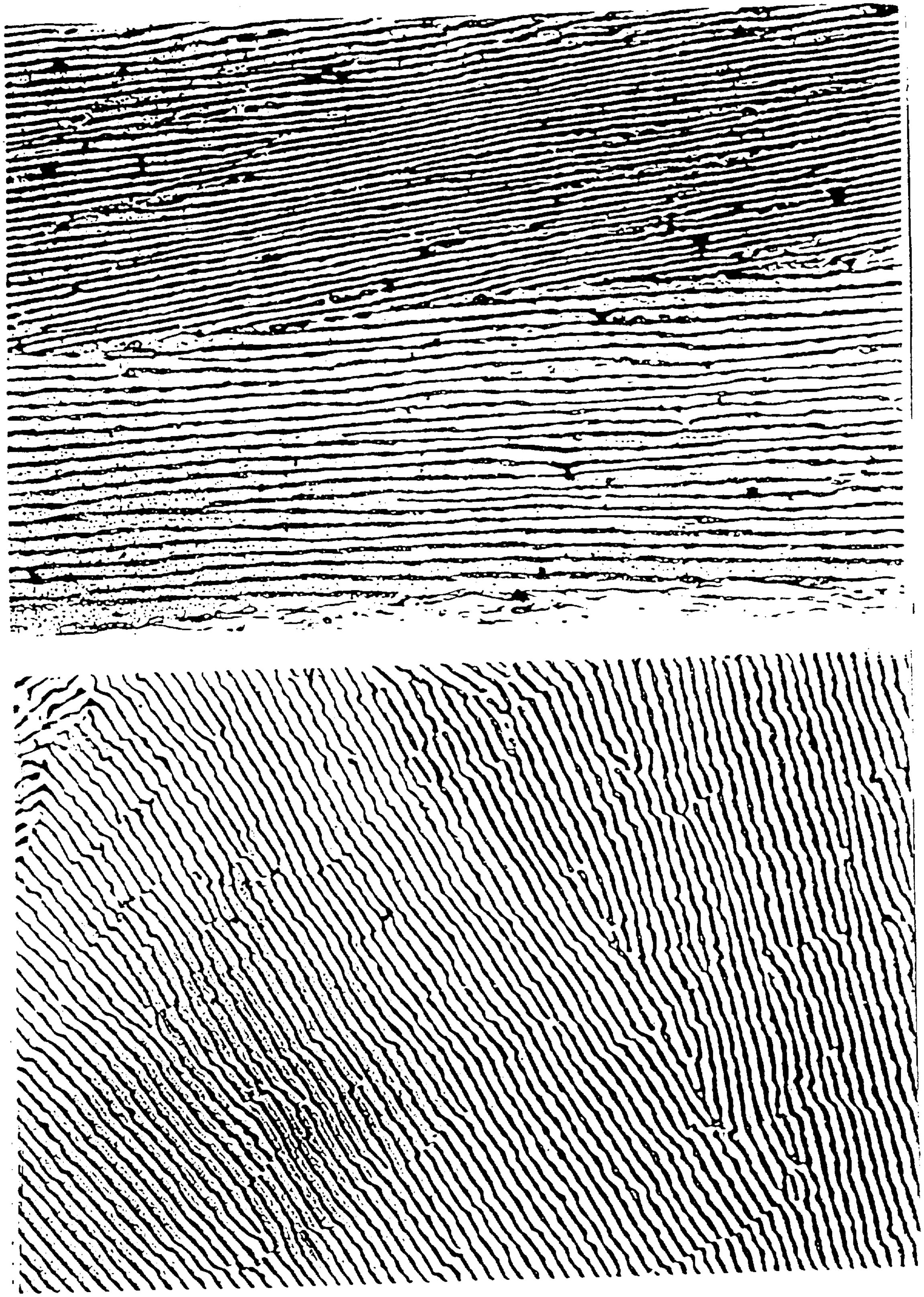


Figure 2: Dynamic acceleration measured using an accelerometer during axial vibration of the ampoule at a frequency of 20 Hz and 0.5 mm amplitude.



(a)

(b)

Figure 3: Lamellar eutectic microstructure. Growth without vibration at 1.8 cm/hr (a) longitudinal view; (b) radial view. The lamellar spacing in the radial sample was 2.5 microns. Magnification 1000x.

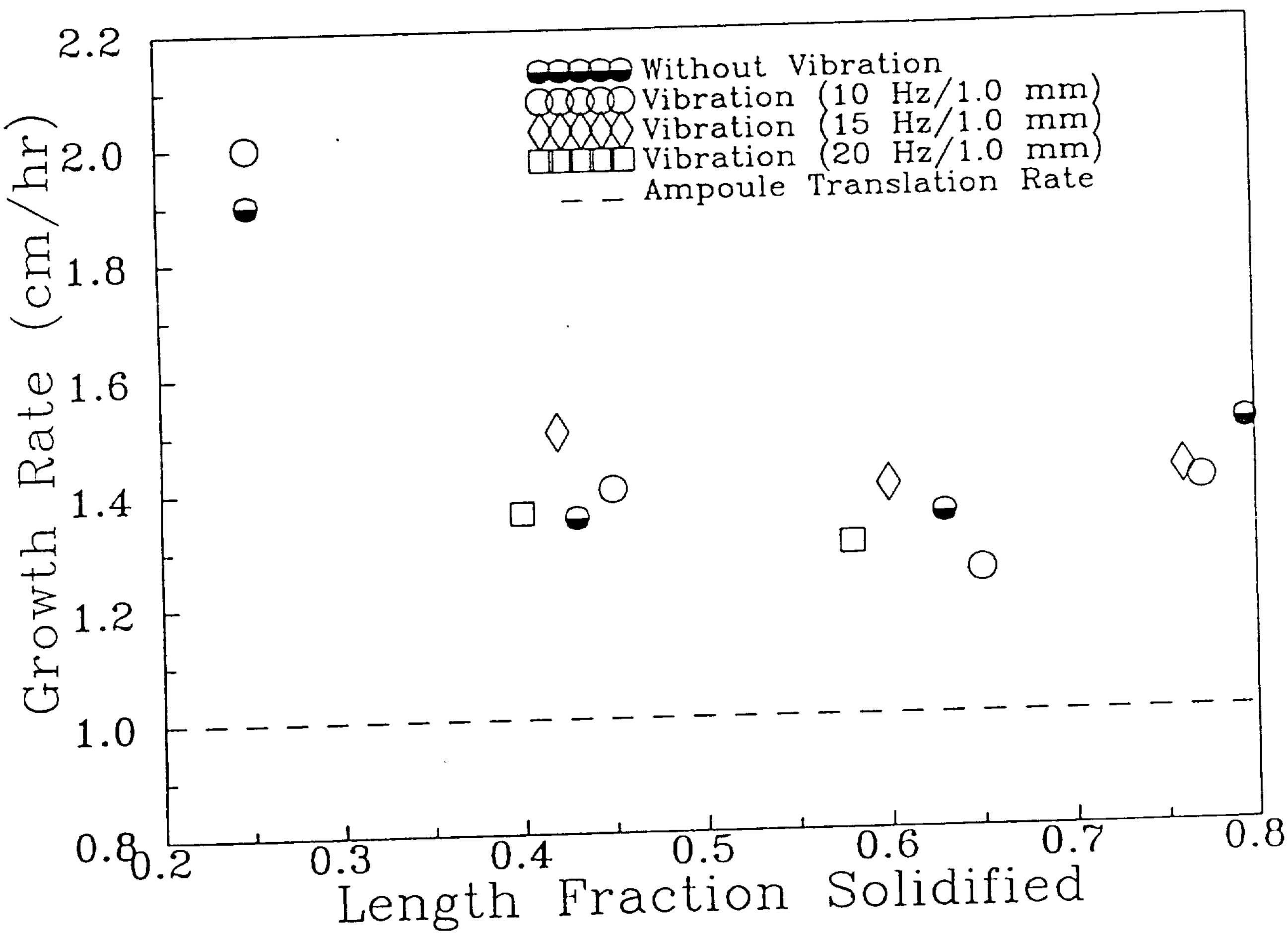


Figure 4: Growth rate versus length fraction solidified. The growth rate was obtained by the interface demarcation technique.

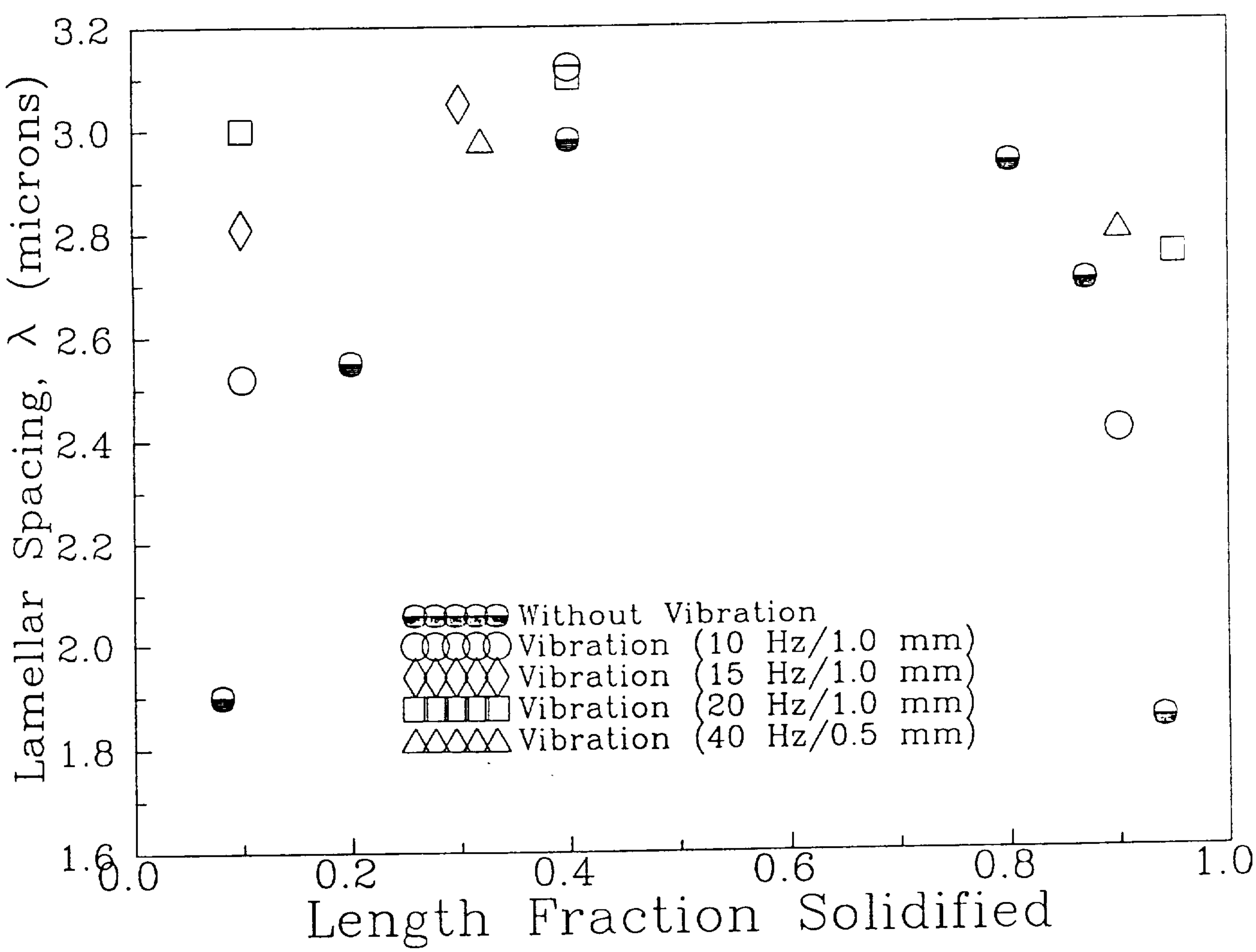


Figure 5: Lamellar spacing as a function of length fraction solidified.

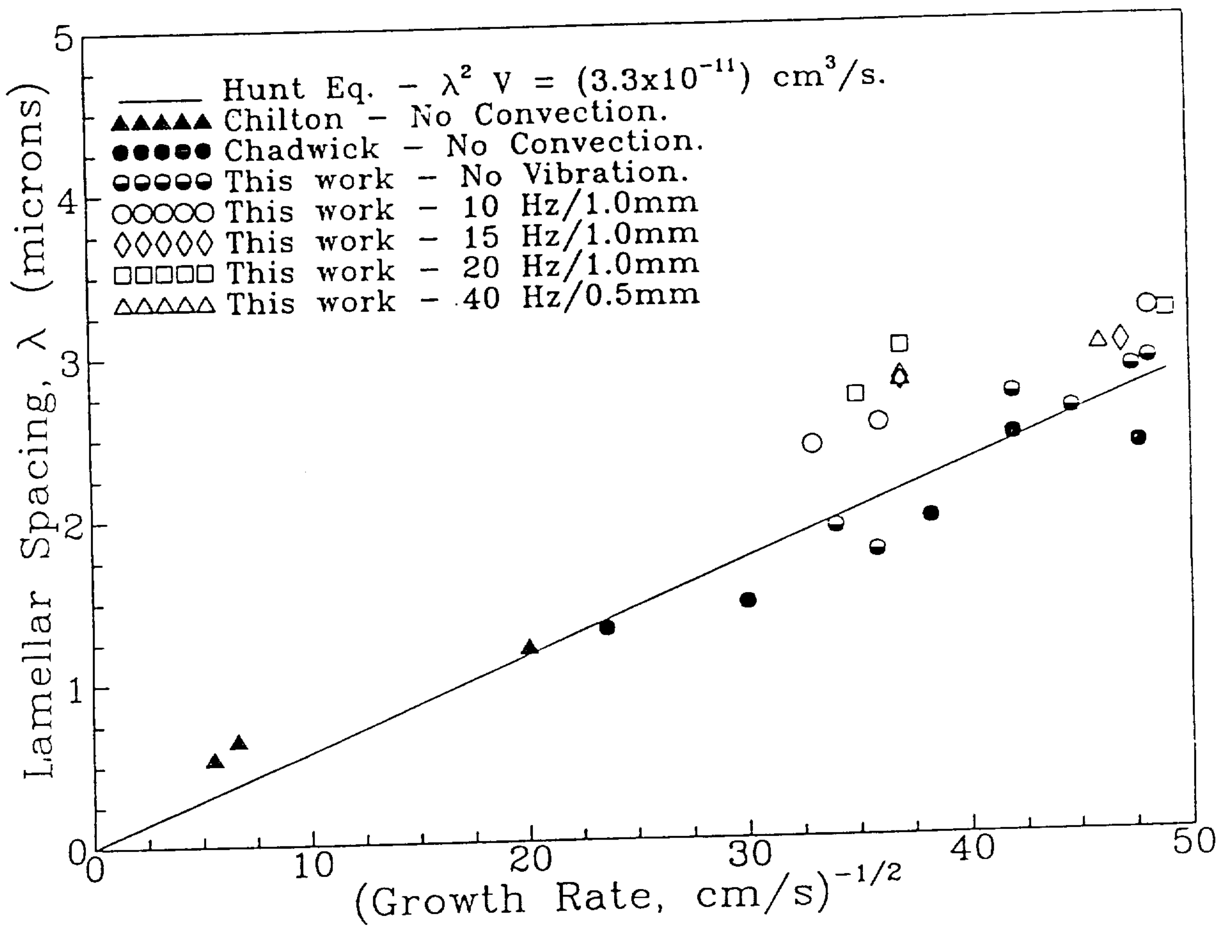


Figure 6: Lamellar eutectic spacing obtained during this work, for several vibration conditions, compared to the results obtained by Davies [20], Mollard and Flemings [21], Hunt and Chilton [22], Chadwick [23]. The growth rate was obtained by the interface demarcation technique.