Directional Solidification of Bi-Sn on USMP-4

Reza Abbaschian[1], H. de Groh III[2], E. Leonardi, V. Timchenko, and G. de Vahl Davis[3],

[1]Materials Science and Engineering
University of Florida, Gainesville, FL 32611

[2]NASA/Lewis Research Center
Cleveland, OH 44135

[3]University of New South Wales, Sydney, Australia 2052

The experiments used MEPHISTO hardware to study the solidification and melting behavior of bismuth alloyed with 1 at% tin. Three samples, each approximately 900 mm long and 6mm in diameter, were used. A portion of each sample also included a 2 mm diameter growth capillary, to assist in the formation of a single grain. One sample provided the Seebeck voltage generated during melting and freezing processes. Another provided temperature data and Peltier pulsed demarcation of the interface shape for post flight analysis. The third sample provided resistance and growth velocity measurements, as well as additional thermal data. The third sample was also quenched at the end of the mission to preserve the composition of the liquid near the interface for post flight determination. A total of 450mm of directionally solidified samples were preserved for post mission structural and compositional characterization. Substantial differences were observed in the Seebeck signal between the ground-based experiments and the space-based experiments. The temperature gradient in the liquid for the ground-based experiments was significantly lower than the temperature gradient in the liquid for the space-based experiments.

Introduction

The formation of dendrites generally follows morphological instability of a planar solid/liquid interface [1]. The morphological stability criterion of Mullins and Sekerka [2] can be used to predict the onset of instability in planar interfaces. The criterion determines the conditions for the growth or decay of a perturbation on a planar interface under a given steady state condition. More recent theoretical models indicate that anisotropic interfacial properties play a role in the morphological stability of planar interfaces, as well as the evolution of cellular and dendritic structures. This has been predicted theoretically by Coriell and Sekerka [3] and Coriell et al. [4] by extending the linear stability analysis of Mullins and Sekerka [2], and by Young et al. [5] in the weakly nonlinear regime. These treatments indicate that such anisotropies tend to stabilize the growth of a planar interface. Experimental observations reported by Tiller and Rutter [6] for lead-tin alloys and by Trivedi et al. [7,8] for transparent organic systems have been found to be generally consistent with the theoretical predictions.

The influence of anisotropic interfacial kinetics on the morphological stability threshold was recently demonstrated by the present investigators for solidification of Bismuth alloyed with 0.1% Sn [9,10]. The experiments were conducted under microgravity conditions during NASA's STS-62 flight of the Space Shuttle Columbia, using the MEPHISTO [11] directional solidification facility. The microstructural evaluation of the space grown samples indicated that for 1.85, 3.4 and 6.7 μm/s interface velocities, the growth occurred in a planar mode. At a higher velocity of 13.3 μm/s the microstructures were found to be cellular in one grain and planar in another. For 26.9 and 40 μm/s velocities, cellular/dendritic morphologies were observed in both grains. An important aspect of the planar-cellular transition at 26.9μm/s velocity was that one grain became cellular approximately 0.6 mm after the

initiation of growth, forming cells which were tilted about 6.5° with respect to the heat flow and growth directions, while the neighboring grain continued with planar growth for about 12.2 mm until it became cellular, with cells parallel to the growth direction. The cell spacing within the two grains were approximately the same; 265 and 276 μm, respectively.

The USMP-4 flight experiments were intended to build on the findings of the USMP-2 flight. In particular, to provide additional data on the role of interfacial kinetics on the morphological instability of facet forming materials. Since the interfacial kinetics and morphological instabilities also depend on the solute concentration, obtaining additional data at a higher solute concentration was also another aim of the experiment. As such, the Sn concentration for the USMP-4 flight was selected as 1 at% Sn instead of the 0.1 at% used for the USMP-2 flight.

Experimental Facility and Techniques
The MEPHISTO hardware is shown schematically in Figure 1, and described in more details elsewhere [9,12]. The central part of MEPHISTO consists of two furnaces each with a neighboring heat sink which is cooled by a refrigerant. One of the furnace-heat sink structures is stationary, while the other is on a moving platform. For the present experiments, the furnaces were heated to 750° C, while the cold zones were kept near 50° C. When the movable furnace-heat sink structure was translated away from the fixed furnace, the extent of the hot zone was lengthened, increasing the extent of the molten zone in the sample. The apparatus simultaneously processed three rod shaped samples, each of which was approximately 900 mm in length and 6mm in diameter. A 2mm ID, 3 mm OD quartz capillary was located on the moving furnace side, which extended about 250 mm into the sample.

Each of the three samples, which will be referred to as the "Quenching", "Peltier", and "Seebeck", has a special purpose in the study. The Quenching sample was used to measure the rate of solidification using the resistance change across the sample during processing and to quench a short section of sample around the interface at the end of the experiments. The Peltier sample had connections to allow marking the sample with short electrical pulses at desired times. The Seebeck sample was used to measure the difference between the temperature of the stationary and moving solid-liquid interfaces. The relationship between the measured Seebeck signal and the temperature of the moving and stationary interfaces can be found elsewhere [13]. The entire flight experiments were commanded and controlled via telemetry from the NASA-Marshall Payload Operations and Control Center. Approximately 0.5 Gb of data was gathered for 35 Seebeck solidification and melting cycles, with a range of velocities as low as 2.67 mm/hr to as high as 144 mm/hr (0.1-55 inches per hour). The alloy used for the experiments was Bi with 1 atomic %Sn. Bi and Sn form a simple eutectic diagram, with a maximum solubility of 1.63 atomic %Sn at the eutectic temperature of 140° C. The distribution coefficient for Sn in Bi was measured to be approximately 0.03.

Results
An overview of the microstructure of the Seebeck sample is shown in Figure 2(a)-(b). The micrographs show the successive development of the microstructure as a function of the distance and the growth velocity for the Seebeck sample. For solidification at velocities below V2, the growth occurs in a planer mode, while cellular morphology is seen at V3 through V6 velocities. The development of a plane-front microstructure, Figures 2(a), from the faceted cellular/dendritic structure of the Earth-grown portion of the samples showed that only a few dominant orientations emerge from the initial
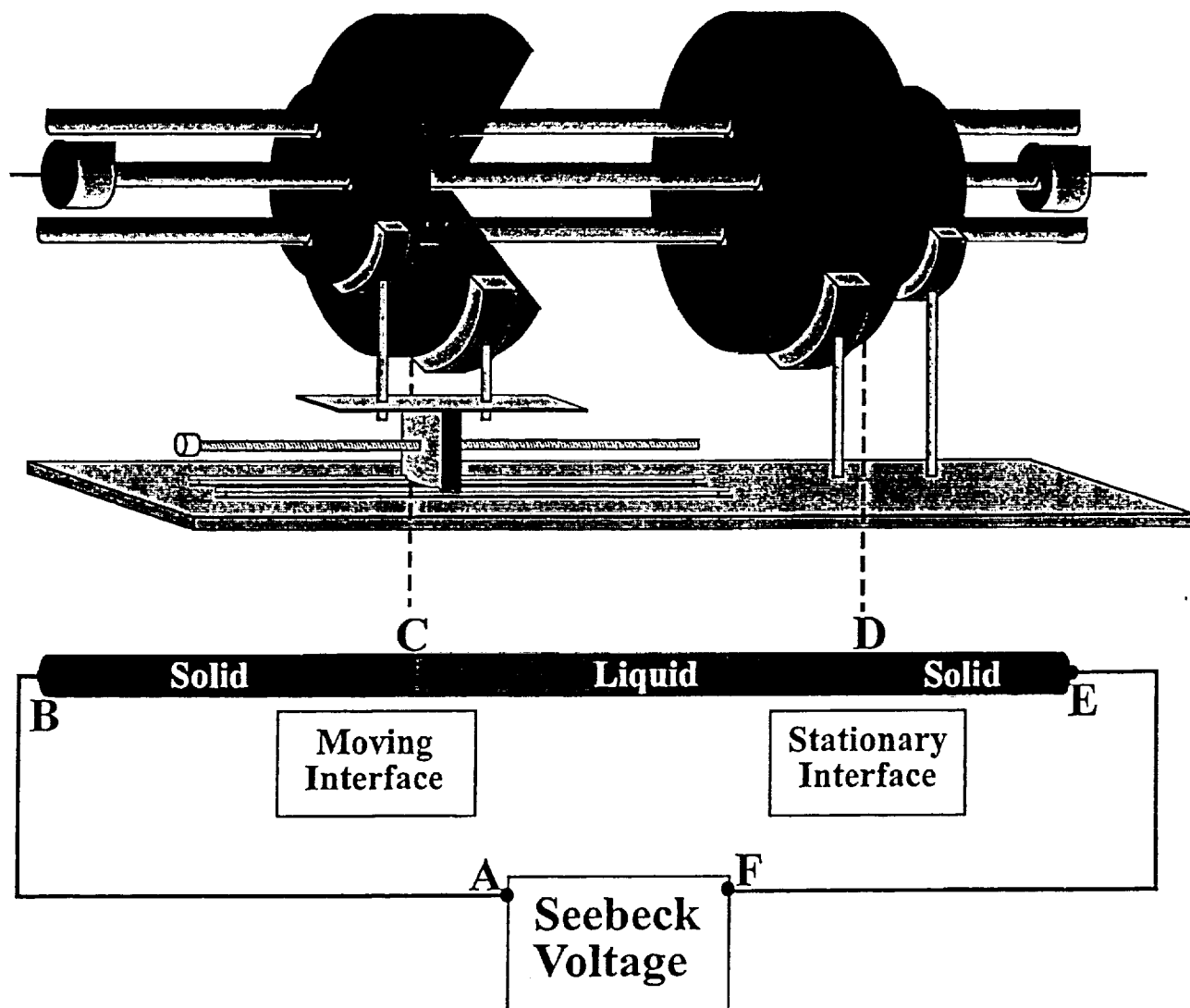
Figure 1. MEPHISTO Apparatus is shown with two furnace/heat sink structures. The three long cylinders going through the two furnace/heat sink structures are the Quenching, Peltier, and Seebeck Samples. The three samples are subjected to the same temperature field, except the Seebeck sample has additional temperature regulation to match the temperature at its ends. The furnace/heat sink structure on the left can move, causing melting or solidification at the moving solid-liquid interface. In the schematic of the Seebeck sample the ends marked B and E while the sold-liquid interfaces are marked C and D. When solidifying/melting at the moving interface, the temperatures at C and D will not be the same due to compositional and kinetic undercooling/superheating.
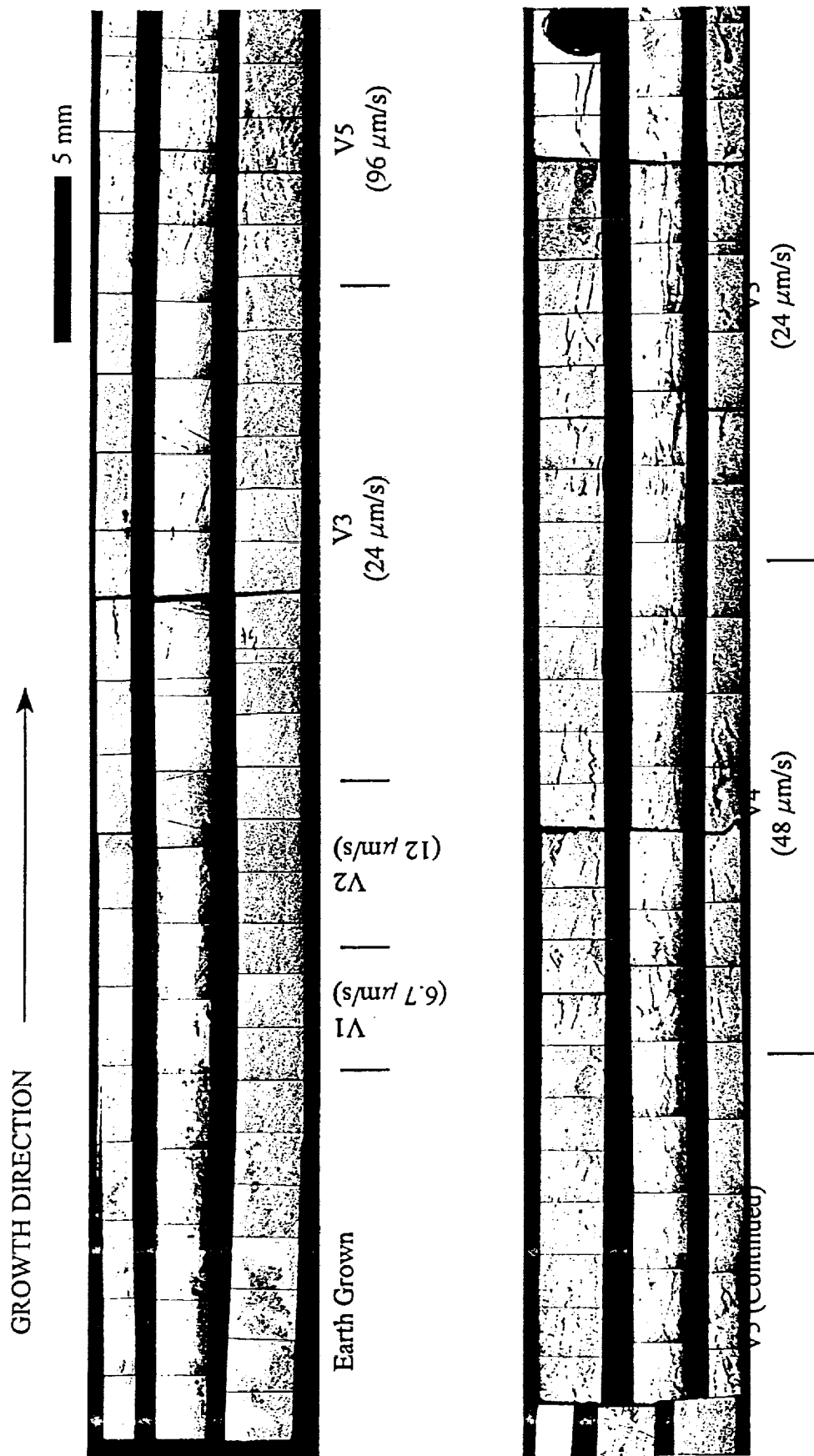
Figure 2a. - Microstructural evolution of the Seebeck sample from the earth grown material to growth in the capillary section.
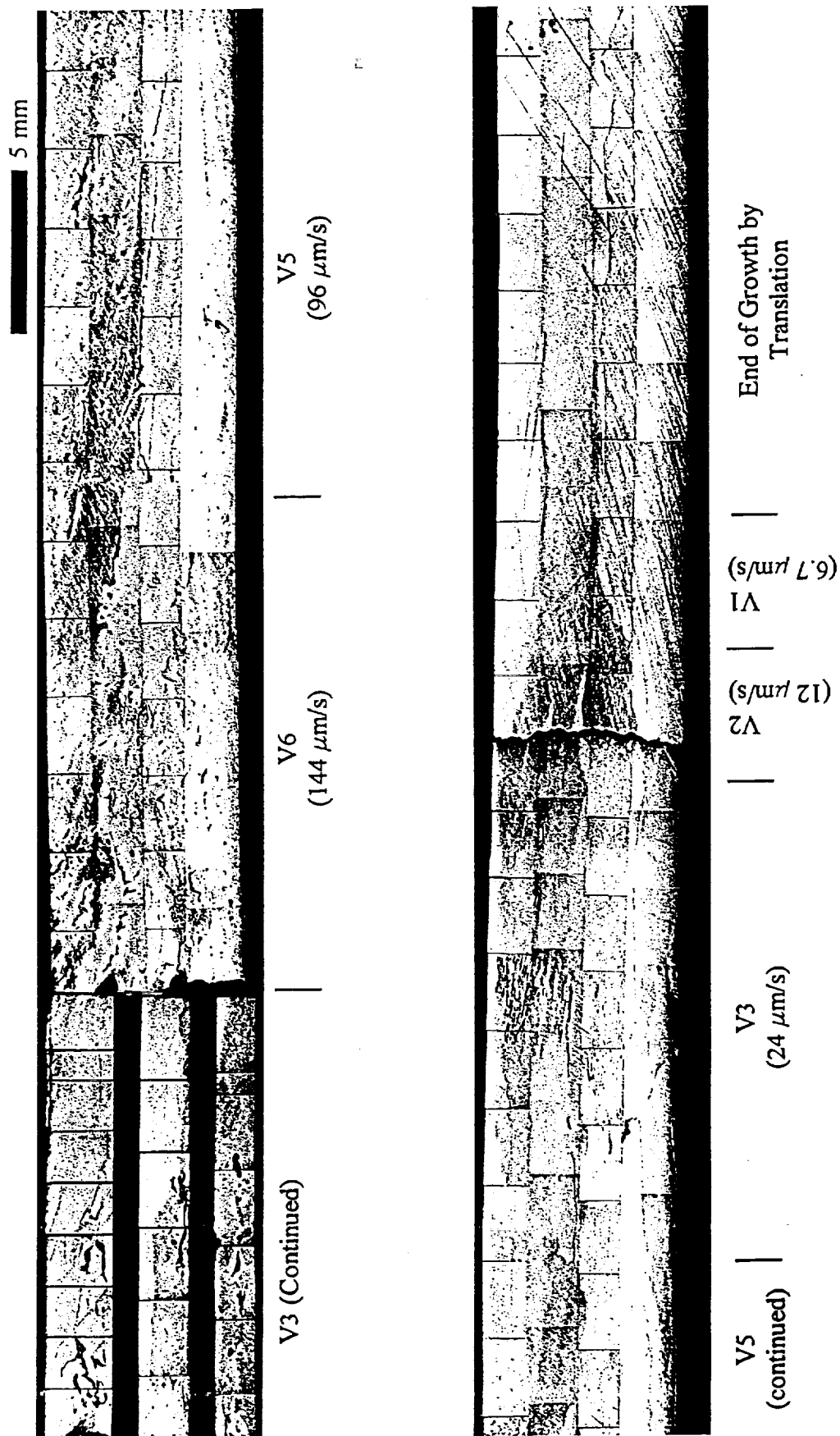
Figure 2b. Continued microstructure of the Seebeck sample extending into the section outside the capillary and finishing in the region where translation finished.

microstructure. The plane front microstructure was characterized by a complete absence of the Sn-rich second phase indicating plane-front solidification. In contrast, the microgravity-processed sections of samples grown at V3 through V6 velocities exhibited a morphological transition to a cellular growth mode. A much narrower planar to cellular transition zone was seen at higher growth velocity (V5, V6) than that at lower growth velocity (V3).
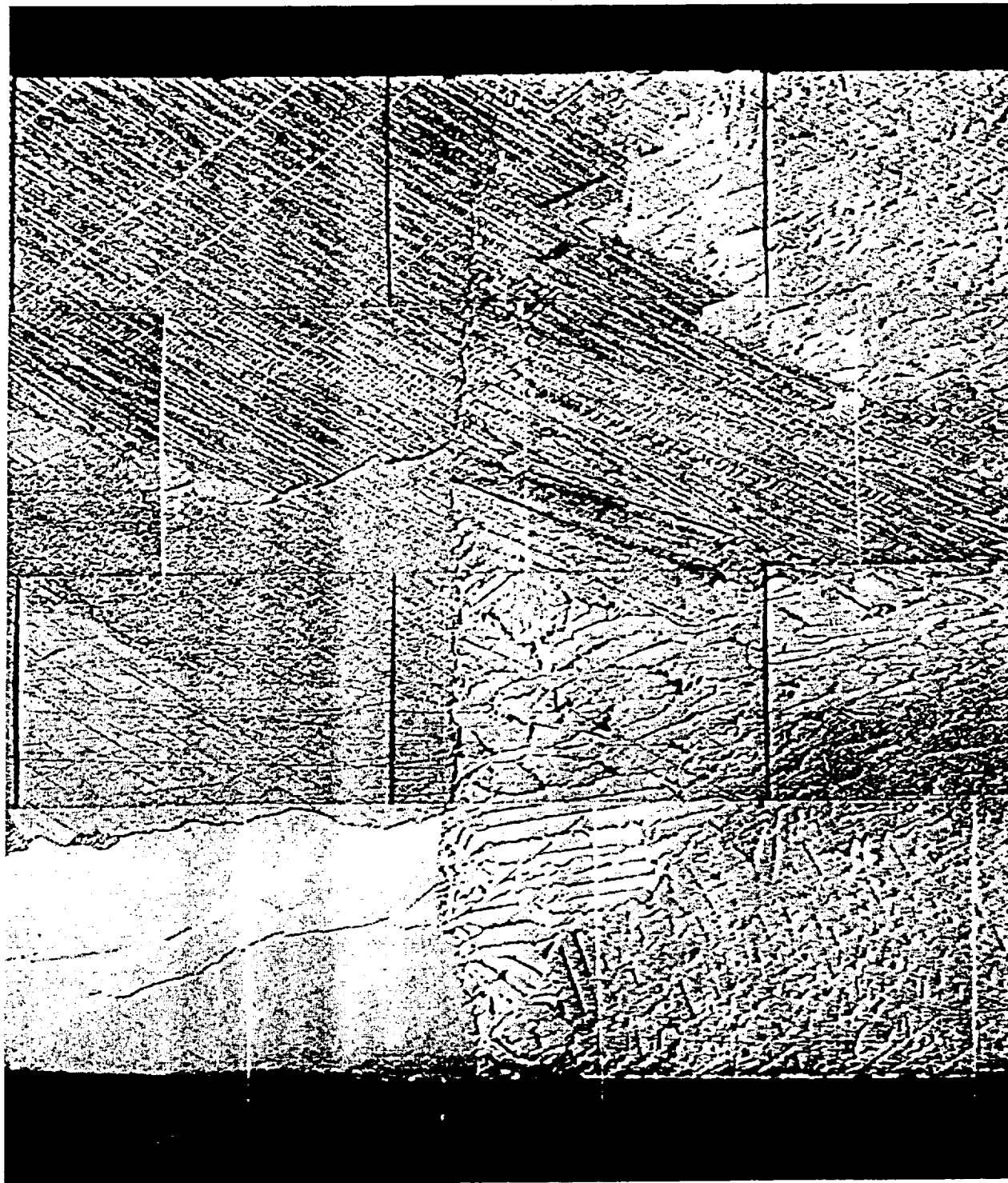
When an interface was revealed, for example during the interface breakdown, it was found that the interface was nearly flat, with a slight curvature near the s/l/crucible triple junction. Upon closer examination, the boundary across each grain appears to be fairly flat, but the small angles between different grains gives the appearance of an overall slight curvature of the interface, as shown in Figure 3 by the micrograph of the interface where the sample was quenched.

The thermal profile during the experiments was monitored and controlled using nine thermocouples located in each of the furnace diffusers and heat sinks. Four thermocouples were also placed inside the Quenching and Peltier samples. A typical thermal measurement by three of the sample thermocouples is shown in Figure 4. Also shown in the figure are the corresponding furnace position. The temperature gradients in the solid and liquid near the interface were measured as 260 and 204 K/cm for growth within the 6mm silica tube.

Figure 5 gives the temperature profile for ground- and space-based experiments within the Peltier sample. Note the temperature gradients for the space-based experiments are both about 260° C/cm. The thermal profile in the solid (below about 270° C) for the ground-based experiments is very similar to the space-based measurements. However, the average temperature gradient in the liquid for the ground-based mission is only about 100 °C/cm. The measured thermal profiles agreed well with those calculated from a mathematical model developed for heat, momentum and solute transfer during the directional solidification experiments. For the modeling, a Bridgman furnace is considered in which a moving temperature profile, consisting of a cold zone, a nominally adiabatic zone (which is simulated by a linear temperature profile) and a hot zone is imposed on the boundary of the ampoule. This boundary temperature profile is translated with a constant pulling velocity as a result of the furnace movement, causing the s/l interface to move along the ampoule. More detailed results can be found elsewhere [14-17].

Two complementary techniques were used to determine the solidification rate during the experiments. The first was to use the translation rate of the moving furnace. Since the temperature gradient near the s/l interface is fairly steep, it is expected that the moving interface would follow the furnace translation closely. However, this may not be the case at the beginning because of the thermal lag between the temperature imposed on the exterior of the ampoule and the temperature within the sample. The decrease in the melting temperature of the s/l interface caused by the build-up of solute would also cause the interface to lag the furnace. In addition to this chemical undercooling, there is also a kinetic undercooling associated with growth of faceted interfaces[18-20]. A more accurate determination of the interface migration was made from the change in resistance of the Quenching sample. While the two data sets correlated nicely, more detailed analysis showed that there is a slight lag in the resistance change at the beginning of solidification.

The moving interface temperature was measured using the Seebeck signal generated by a solid-liquid-solid structure. Figure 8 gives the Seebeck signals acquired for a ground- and a space-based

1 mm

Figure 3. Composite micrograph of quenched section of the Quench sample showing the S/L interface shape.
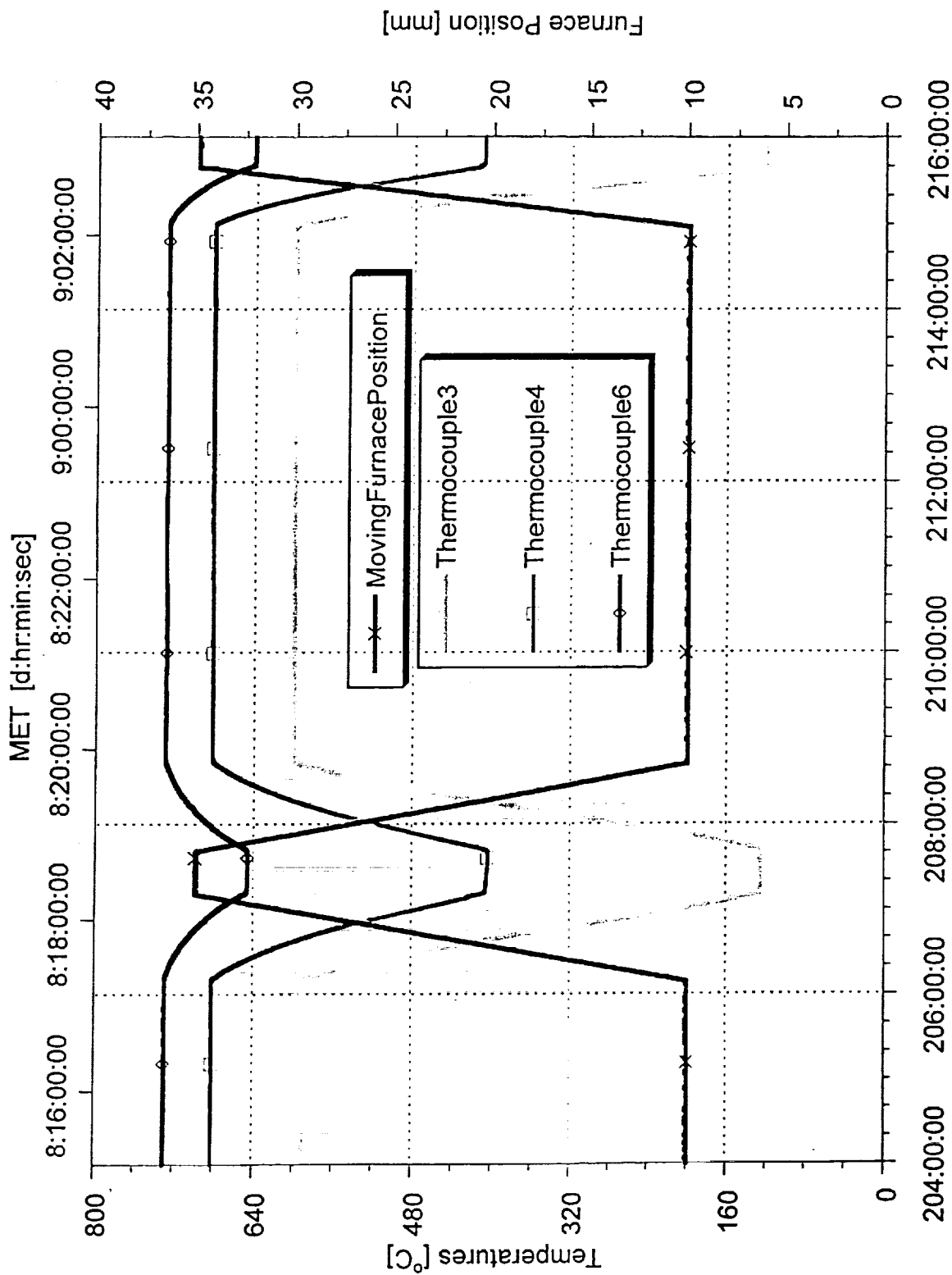
Figure4. Thermal profiles and furnace position in the Peltier and Quench samples.
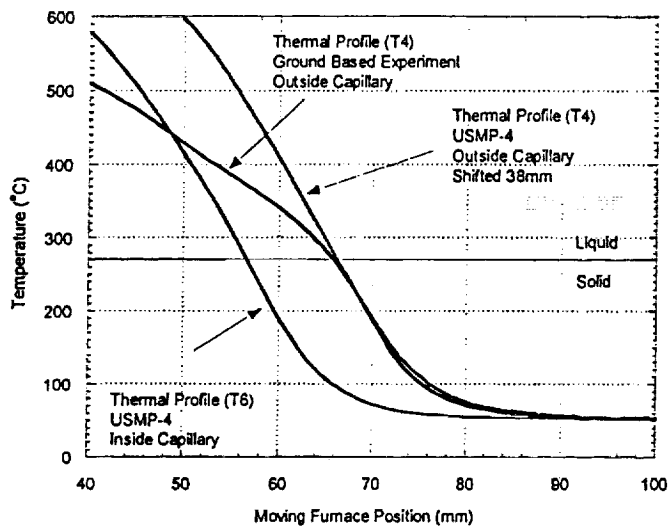
Figure 5: Thermal profile for ground- and space-based samples. Above the melting point of the liquid, the temperature gradient for the ground-based experiments is significantly lower. The profile is very similar inside and outside capillary on space-based experiments.
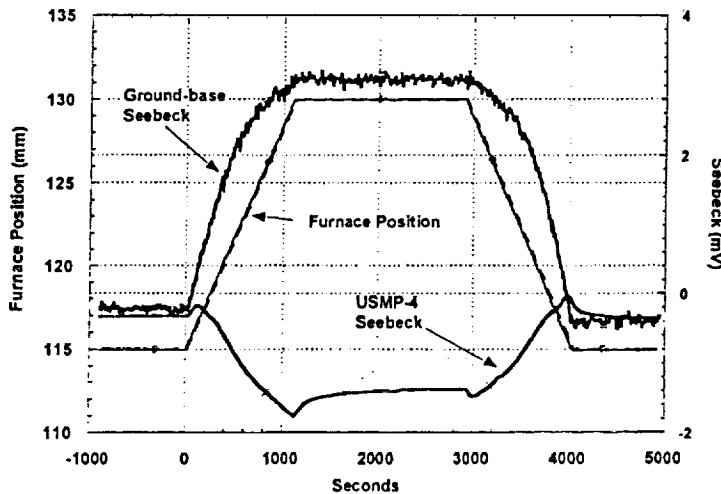

Figure 6. Seebeck signal and position for ground- and space-based experiments for solidification at 13.5 μm/s. The ground-based experiments have noticeable fluctuations in the Seebeck signal, presumably from hydrodynamic mixing in the melt.

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experiment. Each consisted of a solidification, hold, and melt period. The Seebeck signal for the ground-based experiment rose during freezing, fluctuated around an average value during the hold, then decreased during melting. The fluctuations in the signal are due to hydrodynamic mixing in the liquid. The signal for the space-based experiment had an initial increase, then decreased during freezing. After furnace movement stopped, the signal increased due to the interface temperature increase caused by the exponential decay of solute at the interface. During melting the signal decreased, then increased back to near its initial value before the freeze-hold-melt cycle. The differing behavior of the ground- and space-based Seebeck results is due to the differences in the amount of solute build-up at the interfaces (caused by convection) as well as structural changes in the solid.

Summary

Many of the parameters important for studying morphological instabilities were successfully measured during directional solidification of Bi 1 at% Sn. The Seebeck signals and calculated temperature gradient in the liquid for the ground- and space-based sets of experiments were significantly different. The differences are consistent with strong hydrodynamic mixing in the liquid during the ground-based experiments. The analysis of the Seebeck measurements indicated that for bismuth-based alloys, the structure and composition of the solid alloy have strong influences on the Seebeck signal generated. The microstructural examination of the directionally solidified samples also revealed strong influences of interfacial kinetics and anisotropy on the morphological instability of the solid-liquid interface.

Acknowledgments

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