In-Situ Monitoring of a Bismuth-Tin alloy solidification using MEPHISTO

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Abstract

Experiments were carried out to study the morphological stability of Bi- 1 atomic % Sn alloys using the MEPHISTO directional solidification apparatus aboard Space Shuttle Columbia (STS-87, launched Nov. 19, 1997) and in ground-based studies. The Seebeck signal and temperature measurements indicate that convection was significant for ground-based studies. In the space-based experiments, interface breakdown was observed at growth velocities of 6.7, 27, and 40 μm/sec, but not at 1.8 and 3.3 μm/sec.

Introduction

An investigation of the solidification of Bi- 1 atomic % Sn was performed using both ground- and space-based experiments. The solidification experiments for this faceted alloy used an apparatus developed by Centre National d'Etudes Spatiales (CNES, Toulouse, France) and Commissariat à l'Energie Atomique (CEA, Grenoble, France) called MEPHISTO, which stands for Materiel pour l'Etude des Phenomenes Interessant la Solidification su Terre et en Orbit apparatus. The apparatus was developed for investigating directional solidification of metallic alloys and doped semiconductors. The space-based experiments were performed aboard the Fourth United States Microgravity Payload (USMP-4), and built upon results from the three previous Microgravity Payload missions.

The interface between a crystalline solid and its liquid can be either faceted or non-faceted (which are smooth or rough, respectively, on an atomic scale). The growth of a faceted interface is dominated by the nucleation and lateral growth of new layers, or if the interface contains dislocations, by layers generated by a combination of nucleation and dislocation based growth. For a rough interface, on the other hand, growth can take place at sites throughout the solid-liquid interface. The kinetics of solidification for faceted and rough interfaces are markedly different, such that the undercooling required to maintain a given growth rate on a smooth interface of reasonable size can be orders of magnitude greater than required on a rough interface.[1,2,3,4,5] The morphological stability threshold (plane front to cellular transition) has also been found to depend on crystalline orientation in a faceted material. During the Second United States Microgravity Payload (USMP-2) Mission, the solidification of a bismuth- 0.1 atomic % tin alloy was studied using experiments at different growth velocities and growth distances. As expected, under suitable growth conditions the alloy began solidification with a planar interface, but eventually broke down into a

cellular growth mode. However, dramatic differences in the distance to break down were found in adjacent grains with different orientations. [6] Though differences in breakdown distance for different growth directions are predicted by models of morphological stability, the results for the Bi-Sn alloy are not fully understood.

These observations suggest that kinetics and growth anisotropy have a strong influence on the stability of planar solidification for a faceted material. To extend our understanding of these effects requires experiments in which the growth velocity, interface undercooling, liquid and solid composition, solid orientation and microstructure, thermal profile, segregation coefficient, and liquid diffusion coefficient are known or can be measured. To this end, the space experiments offer a unique opportunity as convective effects are eliminated, thus enabling accurate measurements and/or calculations of the diffusional profiles ahead of the interface

Equipment and Samples

The MEPHISTO apparatus (which has been described previously [7,8]) is capable of simultaneous processing of three rod shaped samples, each of which is approximately 900 mm in length and 6 mm in diameter. The central part of MEPHISTO consists of two furnaces each with a neighboring heat sink. One of the furnace-heat sink structures is stationary, while the other is on a moving platform. Between the heaters special reflectors and insulation are used to maintain a nearly uniform temperature. In the experiments to be described the furnaces were heated to 750° C, while the cold zones were kept near 50° C, resulting in a molten zone in the middle of each sample. When the movable furnace-heat sink structure is translated away from the fixed furnace the extent of the hot zone is lengthened, increasing the extent of the molten zone in the sample. Near the solid-liquid interfaces, which are located between each furnace and its accompanying heat sink, temperature gradients on the order of 200° C/cm are established.

The alloy used for the experiments was Bi with 1 atomic % Sn. Bi and Sn form a simple eutectic, with a maximum solubility of 1.63 atomic % Sn at the eutectic temperature of 140° C. The melting temperature of bismuth is 271.4°C, and the distribution coefficient for Sn in Bi is approximately 0.03. Each of the three samples consisted of a rod of Bi-1 atomic % Sn alloy approximately 900 mm in length and 6 mm in diameter within a quartz tube. A 2 mm ID, 3 mm OD quartz capillary is located on the moving furnace side, which extends about 250 mm into the sample. Thin quartz capillaries (approximately 0.6 mm OD) for the thermocouples were also inserted for the thermocouples in the two of the three samples.

Each of the three samples, which will be referred to as the "Quenching", "Peltier", and "Seebeck" samples, have a special purpose in the study of alloy solidification. The Quenching sample is used to measure the rate of solidification using the resistance change across the sample during processing and to produce a short section of quenched sample. The quench is achieved using a mechanism that pulls the sample about 2 cm towards the cold zone in approxiamtely 0.5 seconds. The Peltier sample has connections to allow marking the sample with short electrical pulses which cause heating or cooling at the solid-liquid interface according to the equation:

$$Q_P = -(\pi_S - \pi_L) J \Delta t.$$

Q_P is the heat generated at the solid-liquid interface, π_S and π_L are the Peltier coefficients of the solid and liquid alloy respectively, J is the current (positive for flow from solid to liquid), and Δt is the pulse duration. If the current direction results in cooling at the interface, the rate of solidification will momentarily increase and there will be a build up of solute at the interface. The accompanying

change in the composition of the solid can be revealed with etching and optical microscopy. Details of Peltier interface demarcation for a Bi-1 wt % Sb alloy is discussed in reference. [9] The Seebeck sample is used to measure the difference between the temperature of the stationary and moving solid-liquid interfaces. If the structural and compositional dependence of the Seebeck coefficient of the solid are neglected, the relation of the temperature of the two interfaces and the Seebeck signal, E_S, is

$$T_{MI} = T_{SI} + \frac{Es}{\eta S - \eta L},$$

where T_{MI} and T_{SI} is the temperature of the moving and stationary interfaces repsectively. [8,10] η_S and η_L are the Seebeck coefficient of the solid and liquid near the melting temperature.

Experiments and Growth Conditions

The flight experiments were performed with the help of Société Européene de Propulsion (SEP) by telecommanding. The experiments were initiated by heating the movable and stationary furnaces to 750°C. This established a liquid zone approximately 340 mm long. Melting and solidification experiments were performed by commanding the apparatus to move the mobile furnace/heat sink structure. The fully open position was referenced as 0 mm and the fully closed 150mm. Increasing the furnace position corresponded to freezing, and decreasing the furnace position to melting. Figure 1 is a plot of the MEPHISTO movable furnace position during the USMP-4 mission. Many of the experiments consisted of a freezing period where the furnace position was increased, a hold period where the furnace was kept stationary, and a melt period where the furnace was moved back to the original position for the cycle with the opposite velocity of the freezing period. Figure 2 is an example with a start position of 115 mm, freezing for 15 mm at 13.5 μm/s, and a hold period of ½ hour, and then melting back to the 115 mm position at 13.5 μm/s. The detailed analysis of the Seebeck, resistance and thermocouple measurements will benefit from the large number of experiments performed aboard USMP-4. As shown in figure 1 the experiments included thirty-five freeze-hold-melt cycles during the mission and eleven periods of final solidification. The experiments were over a range of solidification rates from 0.74 to 40 μm/s.

Preliminary Results

The thermal profile in the MEPHISTO apparatus was monitored using several thermocouples located in each of the furnace diffusers and heat sinks. The thermocouples in the heater and heat sink diffusers were used to control the overall thermal conditions of the furnace. Since the thermal profile is not fully determined by the temperatures imposed at the diffusers, but also on the properties of sample being processed, four additional thermocouples were placed inside small quartz capillaries located in the Quench and Peltier samples. Based on the thermocouples located within the Quartz and Peltier samples, the temperature gradient in the liquid, G_L, for the ground-based mission was approximately 90 °C/cm, while the temperature gradient in the liquid for the space-based experiments was approximately 200 °C/ cm. The significant small significantly smaller than G_L for the ground-based experiments is evidence of hydrodynamic mixing on the ground-based experiments, (as well as the differences in the heat transfer coefficient between the metals, the quartz tube, and the surrounding graphite diffuser).

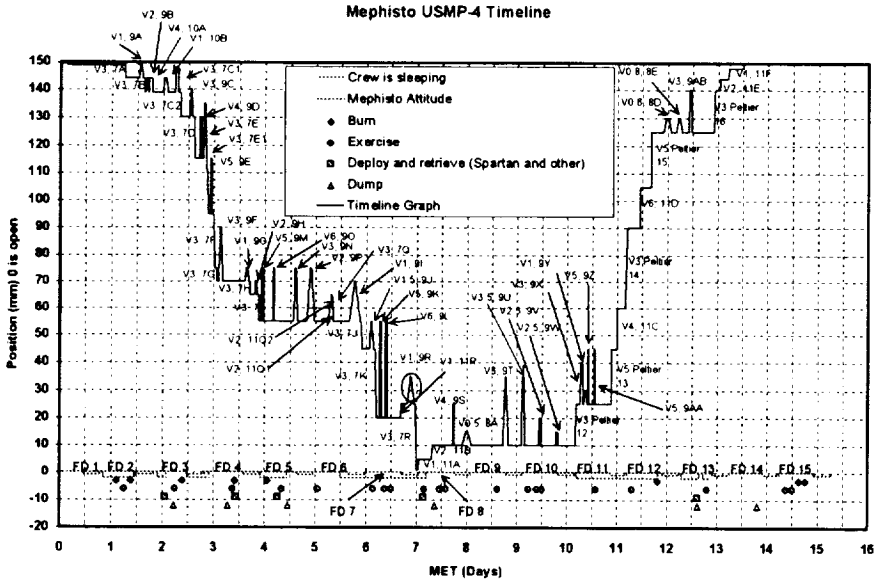

Figure 1: The MEPHISTO moving furnace position as a function of days into USMP-4 mission. The velocities for V0.5, V0.6, V0.8, V1, V1.5, V2, V2.5, V3, V3.5, V4, V5, V6 are 0.74, 1.11, 1.48, 1.85, 2.59, 3.7, 5.2, 6.7, 10, 13.3, 26.7 and 40 μm/s respectively.

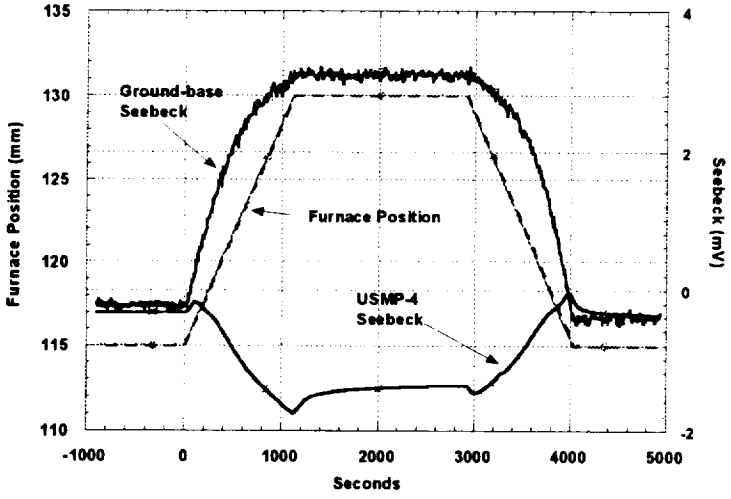

Figure 2: Seebeck signal and position for ground- and space-based experiments for solidification at 13.5 μm/s. The moving furnace position as a function of time into the experiment is very similar for the two experiments. The ground-based experiments have noticeable fluctuations in the Seebeck signal, presumably from hydrodynamic mixing in the melt.

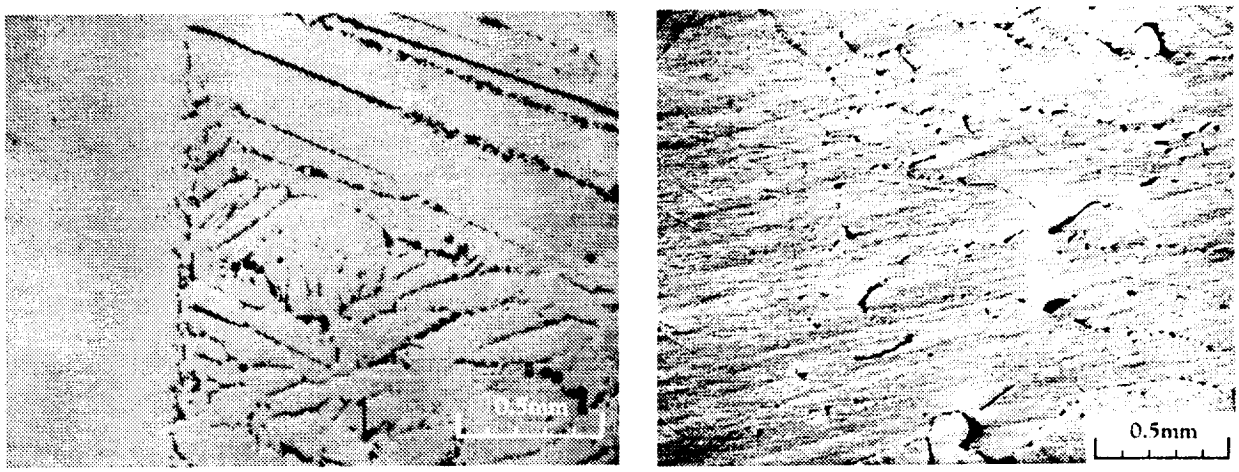

Figure 3, on the left, shows the transition from growth at 1.85 μm/sec to a quench. Figure 4, on the right, is another picture of the quench sample. The region pictured in figure 4 resulted from translation the moving furnace at 6.7 μm/sec, a period of no translation, and then translation at 40 μm/sec. The scale bar in each is 0.5mm long, and the growth direction was to the right.

Figure 2 gives the Seebeck signals acquired for a ground- and a space-based experiment. Each consisted of solidification, hold, and melt. The Seebeck signal for the ground-based experiment rose during freezing, fluctuated around an average value for the hold, then decreased during melting. The fluctuations in the signal are due to hydrodynamic mixing in the liquid. It was observed that the magnitude of the fluctuations strongly depended on the temperature of the melt. The signal for the space-based experiment had an initial increase, then decreased during freezing. After the furnace stopped, the signal increased at a decaying rate. During melting the signal decreased, then increased back to near its initial value before the freeze-hold-melt cycle was begun. The simplified equation relating the Seebeck signal and the stationary and moving interface temperature does not explain these results. Instead a more general relationship which includes, for example, the structure of the solid must be used to determine the moving interface temperature.

The quench sample from the USMP-4 mission was sectioned and polished to reveal the microstructure. The section of the sample from the end of the growth capillary (approximately 90 mm furnace position) to the end of the quench zone included growth velocities of 1.85, 3.7, 6.7, 26.7 and 40 μm/sec. Evidence of interfacial breakdown was not found at the regions grown at 1.85 and 3.7 μm/sec. However, evidence of breakdown was found in the regions grown at 6.7, 26.7, and 40 μm/sec and the quenched region. Figure 3 shows the transition from growth at 1.85 μm/sec to the quench. Figure 4 is a picture of the microstructure resulting from a transition from holding the furnace at a stationary position to translation of the furnace at 40 μm/sec. Preliminary findings are the distance to interfacial breakdown was about 2.0 cm for the 6.7 μm/sec growth region and less than 0.3 mm for the growth at 26.7 and 40.0 μm/sec. Accurate analysis will be based on additional results from the Peltier and Seebeck samples including interface position during solidification.

Summary

Over 45 cm of directionally solidified Bi- 1 at % Sn alloy was recovered from the USMP-4 mission. The Seebeck signal and resistance were measured during the entire solidification process, and Peltier pulses were successfully administered. Seebeck signals and temperature gradient in the liquid for the space and ground-based experiments are markedly different. These results indicate a strong influence of convection on ground-based solidification experiments. Breakdown of the solid-liquid interface is observable for growth rates of 6.7, 26.7, and 40 μm /sec., but not at 1.85 and 3.7 μm /sec (over the distances observed). Analysis of results from Seebeck and Peltier samples including interface shape and position, and Seebeck signals will enable accurate tests of theories of morphological instabilities

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