THE INFLUENCE OF GRAVITY ON EUTECTIC PbSn ALLOY GROWN BY THE VERTICAL BRIDGMAN METHOD

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ABSTRACT

Composition profiles of eutectic alloy $Pb_{25.9}Sn_{74.1}$ atomic % grown by the normal and inverted Bridgman methods are presented and the study of the solute alloy redistribution is made. The inverted vertical Bridgman method, where the solidification occurs from the top to the bottom of the melt under a destabilizing thermal gradient, allows the growth of crystals with buoyancy-driven convection different from that with the usual vertical Bridgman configuration. The scope of this work is to study the influence of the gravity acceleration in the convection process.

Keywords: Bridgman method, eutectic alloy, solidification, convective flows.

INTRODUCTION

Solidification behavior of eutectic alloys in many systems arouses the interest because of their influence on the properties and performance of materials containing eutectic constituents. Eutectic alloys are important to materials engineering, causing extensive theoretical and experimental study of the relationship between microstructure and solidification conditions. In the process of solidification of eutectic alloys, thermal convection plays a very important role by affecting heat and mass transfer and therefore the solute distribution. Instabilities of the flow in the melt can cause the appearance of temperature oscillations and influence the interface velocity. This in turn can lead to morphological instabilities of the plane front during directional solidification. In addition, asymmetric flow patterns can lead to an inhomogeneous structure of the sample (1-7).

The vertical Bridgman method is one of the commonly used methods for the directional solidification the alloys. This method offers simultaneously an industrially efficient process and an interesting configuration for fundamental studies (3, 4).

The classical vertical Bridgman method (VB), where the sample is heated from the top, is more stable. The flow is weak and is mainly due to the two-dimensional temperature field that results in a cold (more dense) stream of fluid descending towards the center of the solid interface. Thus for this classical case, the two contra-rotating cells accumulate solute near the interface and this species accumulation can leads to morphological instabilities [(4-6)].

For the inverted vertical Bridgman method (IVB), where the higher temperature is on the bottom, flow results not only from the two dimensional temperature fields but also due to the classical Rayleigh-Bénard configuration. The flow obtained for the same controlling parameters is much stronger and results in better species mixing as can be seen in the thinner boundary layer. The flow intensity and direction on the solid-liquid interface induces a more homogeneous species [(4-6)].

Tin-lead solder for metal interconnects were widely used until the early 2000s when policies restricting the use of toxic materials in electrical and electronic equipment began [(8)]. In this work we chose to use the eutectic alloy Pb-Sn because of the wide literature available.

The objective of this work is aimed to confirm the theoretical results that An et al [(5)], Bennacer et al [(6)] and Verhoeven et al [(7)] found that the IVB method reduces the micro-segregation as compared to the VB method, producing samples more homogeneous, and the influence of convective flows in the formation of dendrites in eutectic alloys.

EXPERIMENTAL

The experimental system consists of a resistive furnace, temperature controller, speed controller and stepping motor. The solidification experiments were performed with the vertical furnace in accordance with the scheme and the furnace temperature gradient shown in Fig. 1.

The alloy was prepared from pure lead (99.998 %) and tin (99.9999 %). A mass of 20.0 g of the alloy was put into a quartz tube with an 8 mm diameter and 15 mm length. The quartz tube was sealed in an evacuate ampoule (10^{-6} Torr) and the final growth ampoules are shown in Fig. 2. The furnace was heated to 250 °C, yielding a temperature gradient of 1.4 °C/mm for VB and 0.55 °C/mm for IVB along the sample at the estimated position of solid-liquid interface. Growth was caused by moving the ampoule with a stepping motor through the furnace at 0.75 mm/h.

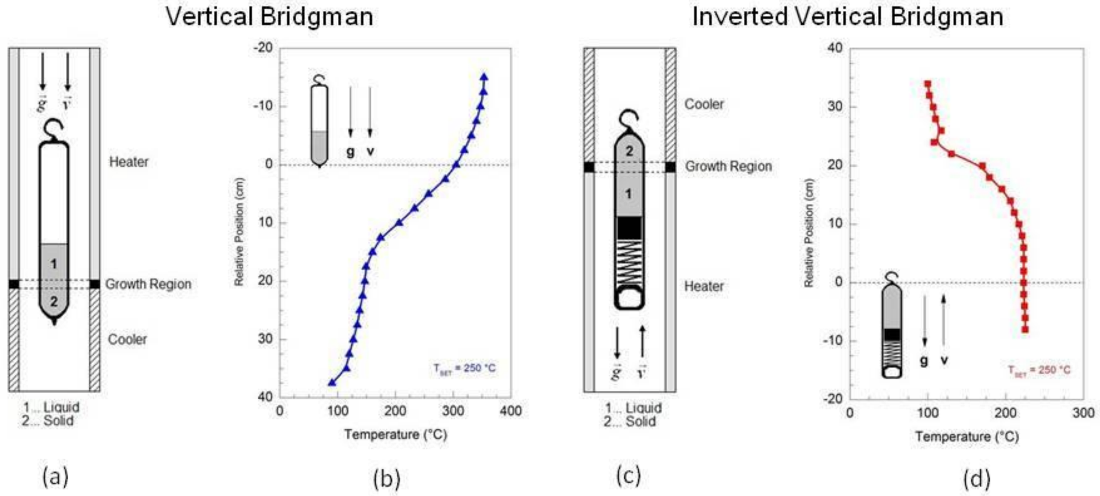

Fig. 1. (a) Schematic diagram of vertical Bridgman; (b) Temperature gradient of the solidification furnace of vertical Bridgman; (c) schematic diagram of inverted vertical Bridgman; (d) Temperature gradient of the solidification furnace of inverted vertical Bridgman.

Fig. 2. (a) Growth ampoule for the vertical Bridgman (VB); (b) growth ampoule for the inverted vertical Bridgman (IVB) with an internal spring and a plug to hold the melt in the upside down position.

Two samples were made in each growth method and, after solidification, were cut into several discs and its density was determined by Archimedes method to calculate the solute distribution versus the solidified fraction (fs). The other sample was cut in the longitudinal direction. After polishing and etching, the structure morphologies of the samples were examined using an electronic microscope JEOL/SEM model 5310.

Results and discussion

In the Pb-Sn system, an aligned lamellar structure was obtained by using directional solidification. The directionally solidified Pb-Sn eutectic alloy produces parallel alternating the Pb-rich solid solution and the Sn-rich solid solution, respectively [9, 10].

Fig. 3a shows the graphics of the density versus solidified fraction obtained by the method VB and IVB, determined by the Archimedes method in this work and the density value found in the literature. A general expression (Eq. (A)), where ρ, m and A are respectively the density, mass and atomic weight, can be used to determine the composition x ($0 \le x \le 1$) of eutectic alloys $M_{1-x}N_x$, in function of the density. The formula is based on the rule of mixture, which considered the additivity of masses and volumes of the constituent elements, such as used by An et al in the deduction of the general equation for the density of isomorphic binary alloys [11, 12]. Based on this equation, Fig. 3b shows the graphics of the solute distribution versus the solidified fraction (fs).

$$x = \frac{(\rho_M - \rho)}{\left(1 - \frac{A_N}{A_M}\right)\rho_M - \left(1 - \frac{A_N \rho_M}{A_M \rho_N}\right)\rho}, \qquad (0 \le x \le 1) \qquad \text{(A)}$$

The graphics shows that the density profile and distribution of the solute are closer to the nominal values, confirming the reduction in convection and consequently the micro-segregation of the solute in the IVB method when compared to the VB method, as predicted by An et al [5] and Bennacer et al [6].

Figures 3a and 3b show the variation in density and the variation of the solute (lead) in the eutectic PbSn alloy solidified by VB and IVB methods. It is observed in Fig. 3a a decreasing profile of the density values in the range 0 < fs < 0.30 due to accumulation of lead (show Fig. 3b) caused by natural convection and sedimentation; the interval 0.30 < fs < 1 presents a constant profile of the density values. The profile of the density values presented in IVB solidification was opposed to VB, with an increase of density values in the range 0 < fs < 0.30 with a tendency to stabilize afterwards.

Fig. 4, 5 and 6 shows the images, obtained by electron backscattering, of the samples solidified by VB. It is observed the presence of two eutectic phases: an α phase rich in Pb (light gray color) and a β phase rich in Sn (dark gray color). In Fig. 4, was observed the formation of dendrites in the α phase at the beginning of the sample (fs < 0.50).

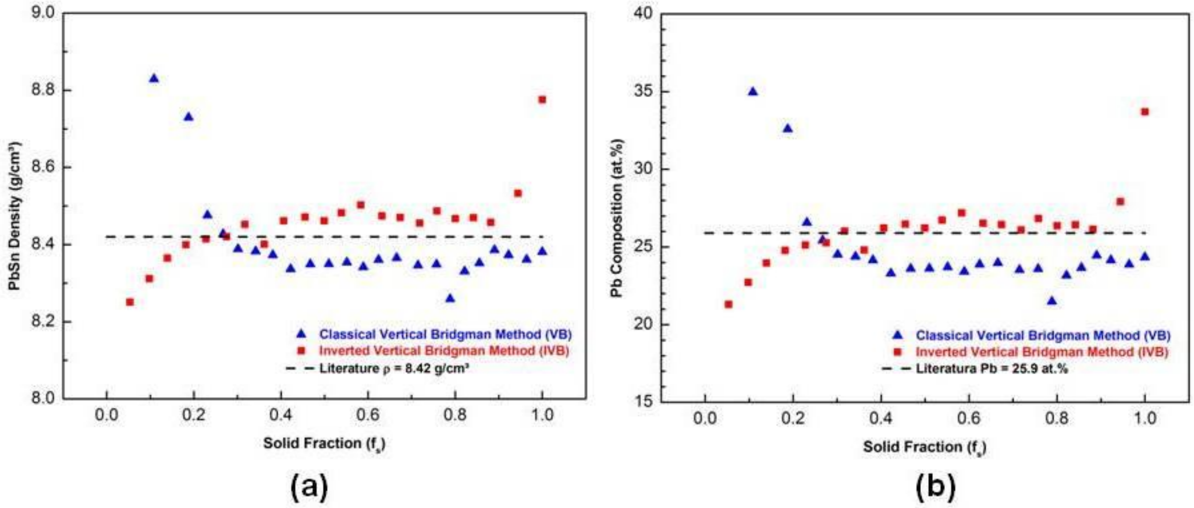

Fig. 3. (a) Average density of PbSn eutectic alloys as function of the solidified fraction; (b) Lead composition profile for VB and IVB PbSn eutectic alloy analyzed by densimetric technique.

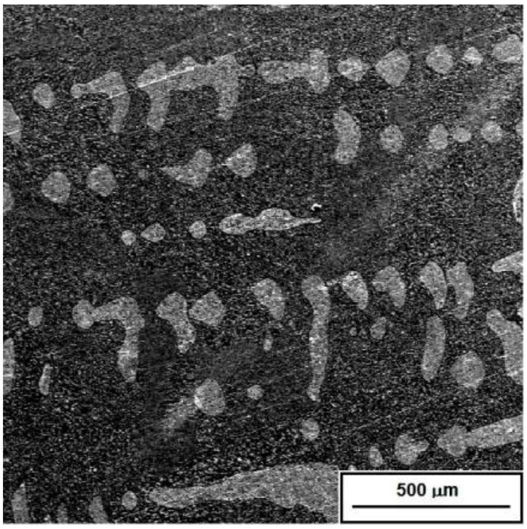

Fig. 4. SEM image of the longitudinal direction analysis (with fs < 0.50) the eutectic PbSn obtained by VB.

In Fig. 5 dendritic structures (in the α phase) over irregular eutectic structures were observed at the beginning of the samples (fs < 0.50) and lamellar eutectic structure in the remainder of the sample. However, in Fig. 6, were observed dendritic structures (in the α phase) over irregular eutectic structures at the beginning of the samples (fs < 0.20), eutectic structures irregular in the range of 0.20 < fs < 0.30 and lamellar eutectic structure in the remainder of the sample.

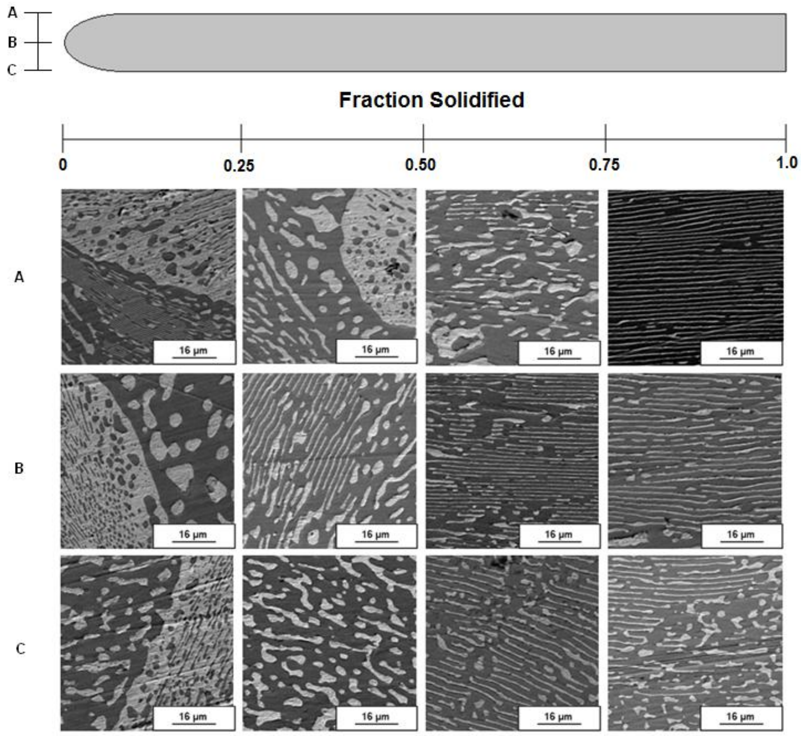

Fig. 5. SEM images of the longitudinal direction analysis the eutectic PbSn obtained by VB.

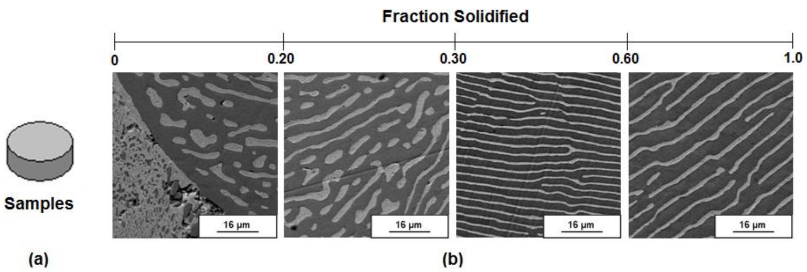

Fig. 6. (a) Samples cut in multiple disks, (b) SEM images of the radial direction analysis the eutectic PbSn obtained by VB.

The results obtained by both densitometry and microstructural analysis are consistent with the theory of Verhoeven et al. (7). In the VB, for alloys with solute heavier than the solvent (PbSn eutectic alloy case), the solid-liquid interface is unstable (due to solutal convection and sedimentation), occurring an accumulation of solute (lead) ahead of the solid-liquid interface causing a constitutional undercooling which alters the growth rate of the lead rich phase which, in turn, causes the appearance of dendrites and a profile of variable composition throughout the sample. Moreover, in the solidification by IVB, the solid-liquid interface is stable (solutal and thermal convection vanish), which inhibits the development of dendrites and results in a stable composition profile along the sample.

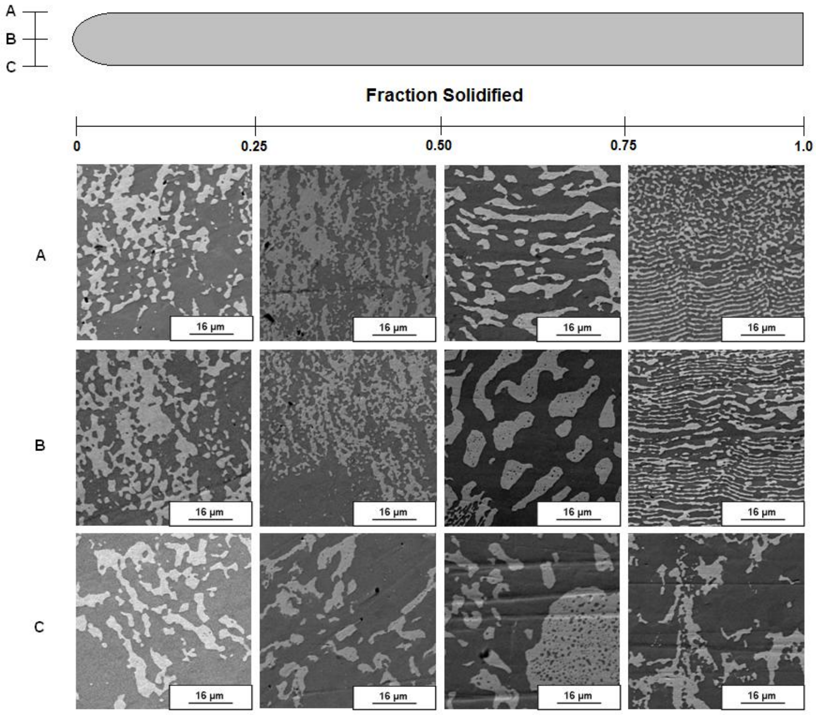

Fig. 7. SEM images of the longitudinal direction analysis the eutectic PbSn obtained by IVB.

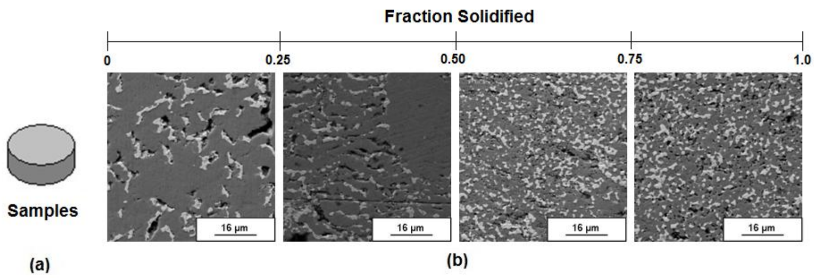

Fig. 8. (a) Samples cut in multiple disks, (b) SEM images of the radial direction analysis the eutectic PbSn obtained by IVB.

CONCLUSION

PbSn eutectic alloys were solidified by the Bridgman method in a vertical furnace. The convection is lower in samples solidified by IVB, having density and solute distribution profiles more stable. The samples solidified by VB have dendritic structure plus irregular eutectic structure at the beginning of the solidification and lamellar eutectic structure almost in all its extension, while samples solidified by IVB have irregular eutectic structure along its entire length.

Acknowledgements

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