Evolution of microstructure in bismuth–indium–tin eutectic alloy

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The bismuth-based eutectic alloy with a composition of 57.2% Bi, 24.8% In, and 18% Sn (all in weight pct.), which melts at 77.5 °C, could be used as thermal-fuse or thermal-cut-off safety devices to prevent overheating of various types of electronic equipment. For this type of application, it is essential that the thermal-fuse alloy forms a uniform microstructure to ensure homogeneous composition and thus consistent performance. Therefore, an investigation of the formation of microstructures under various crystallization conditions for this alloy is of importance. Ruggiero and Rutter [1] studied the microstructure of the alloy after solidifying thin specimens unidirectionally at very slow speeds of 0.74–53 mm/day. It was found that the structures consisted of two coarse two-phase eutectics of BiIn–γSn and Bi–γSn (Fig. 1) instead of solidifying to a three-phase eutectic structure with a repetitive arrangement of three phases, BiIn, Bi and γSn in a lamellar form. The γSn subsequently decomposes upon cooling to BiIn, Bi, and βSn phases resulting in a mottled appearance of the tin phase at room temperature. For brevity, the decomposed Bi–γSn and BiIn–γSn eutectics will be described as Bi–Sn and BiIn–Sn, respectively.

Although, gravity-induced segregation was not mentioned in their investigation, it could be encountered under practical casting conditions depending on the sequence of nucleation events and due to the much higher density of bismuth 9.78 g/cm^3 in comparison with tin and indium both 7.31 g/cm^3. Since the microstructure is strongly influenced by solidification processes and conditions, in this work the ternary eutectic alloy was solidified within the furnace with a cooling rate of approximately 1 °C/min and also solidified by continuous casting. The microstructures were compared in order to obtain an understanding of solidification structure and morphology changes under different solidification conditions. The alloy was prepared from each elemental metal of 99.99% purity melted together in a graphite crucible under an argon atmosphere. The melt was cast into a wire approximately 2 mm in diameter at a speed of 79 mm/min using the Ohno continuous casting (OCC) process, which is described elsewhere [2–4]. At this speed, the process generates a cast microstructure free from segregation as shown in Fig. 2. About 7 g of the cast wire was inserted in a glass tube 3.2 mm i.d., 4.2 mm o.d. and placed in the vertically oriented furnace. After melting, the furnace assembly with the glass tube containing the alloy specimen was positioned horizontally for solidification. Fig. 3 shows a schematic diagram of the furnace and specimen assembly together with the temperature distribution inside the furnace, which consists of a temperature plateau and temperature gradient region. Fig. 4 shows a typical example of the structure solidified within the temperature plateau region of the furnace. Under these conditions the eutectic alloy exhibited a gravity induced, highly non-uniform structure which consisted of primary bismuth blocks (white), mottled tin dendrites (dark), and Bi-Sn eutectic cells with laced patterns (white) in a BiIn-Sn eutectic matrix (gray). Massive gravity induced segregation has also been reported for a Sn-Pb eutectic composition in which lead primary dendrites nucleated in the undercooled melt and segregated to the lower region of the ingot resulting in compositional shifts in the remaining melt with tin rich dendrites nucleating in the upper zone creating an ingot with a compositional gradient and a mixture of two primary phases rather than the eutectic structure [5]. In the 77.5 °C-Bi-In-Sn ternary eutectic, two primary phases are also observed but it is difficult to determine from the microstructure shown in Fig. 4 which primary phase, tin dendrites or bismuth blocks, nucleates first. However, from an anomalous structure observed in the sample continuously cast at 57 mm/min (Fig. 5), bismuth blocks are captured inside the tin dendrites, indicating that the bismuth phase preceded the tin phase. Thus, the nucleation events responsible for the final microstructure in Fig. 4 may take place in the following order: bismuth blocks, tin dendrites, Bi-Sn eutectic, and BiIn-Sn eutectic cells. As shown in Figs 6 and 7, primary tin dendrites do not seem to act as nucleating agent for either BiIn-Sn eutectic nor Bi-Sn eutectic, whereas primary bismuth blocks often nucleate Bi-Sn eutectic and also to a lesser extent, BiIn-Sn eutectic (Fig. 8).

In the present investigation, although the growth rate under furnace cooled conditions (∼2 mm /min. in the temperature gradient region) is significantly faster than those employed by Ruggiero and Rutter [1], the alloy also formed a double binary structure. A distinctive difference in this case, however, is that BiIn-Sn binary eutectic cells tended to grow in a dendrite form in which the BiIn dendrite stems and arms can be clearly seen (Fig. 9) and the Bi-Sn binary eutectic grew in the form of a complex-regular structure that segregated between the BiIn-Sn eutectic grains to constitute a double binary eutectic structure. The quenched interface in the micrograph (Fig. 1) reported by Ruggiero and Rutter revealed that the Bi-Sn eutectic (indicated by A in Fig. 1) grows ahead of the BiIn-Sn eutectic (indicated by B in Fig. 1). This suggests that in a specimen from the temperature gradient region (Fig. 9a), Bi-Sn cells could form just ahead of the BiIn-Sn cell and, as a result, Bi-Sn cells

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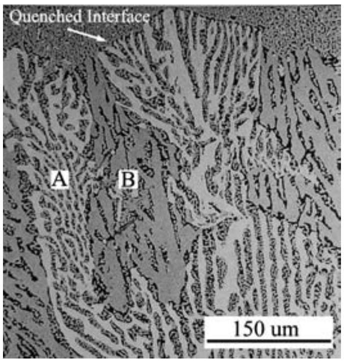


Figure 1 Back scattered SEM image (longitudinal section) of the 77.5 °C-Bi-In-Sn eutectic unidirectionally solidified at the growth rate of 53 mm/day, showing two two-phase eutectic structures of (A) Bi-γSn and (B) BiIn-γSn (after Ruggiero and Rutter [1]).

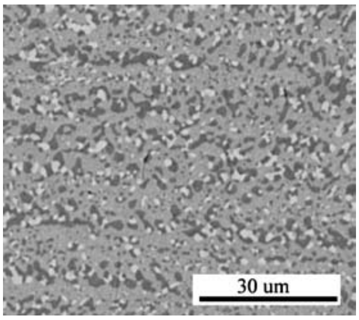


Figure 2 Microstructure (longitudinal section) of the 77.5 °C-Bi-In-Sn eutectic wire produced by the OCC process with a casting speed of 79 mm/min.

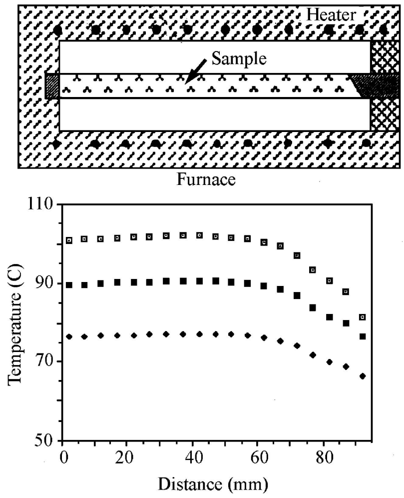


Figure 3 Furnace and specimen assembly used for solidification showing the temperature distribution within the furnace at three different settings [4].

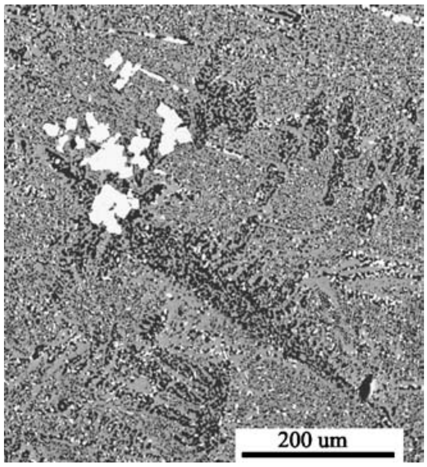


Figure 5 Bismuth blocks captured within tin dendrites indicating the bismuth nucleated elsewhere before the tin.

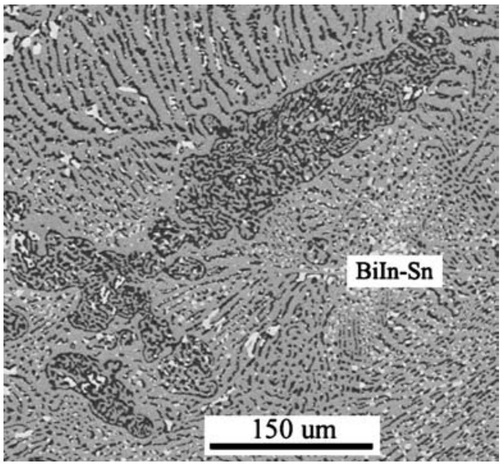


Figure 6 Tin dendrite (decomposed) engulfed by BiIn-Sn eutectic showing that the tin dendrite does not act as a nucleating agent for BiIn-Sn eutectic.

are pushed into the boundaries without being engulfed by growing BiIn-Sn cells. It also appears that in a specimen from the temperature plateau region, Bi-Sn cells were pushed into more localized areas contributing to macro-segregation (Fig. 9b).

A significant difference exists between the alloy structure produced at the extremely low rate of 54 mm/day (Fig. 1) [1] and the microstructure of the alloy solidified at 79 mm/min which contains an undefined mixture of discrete bismuth and tin phases in a BiIn matrix (Fig. 2). For specimens cooled in the temperature gradient region of the furnace at a growth rate

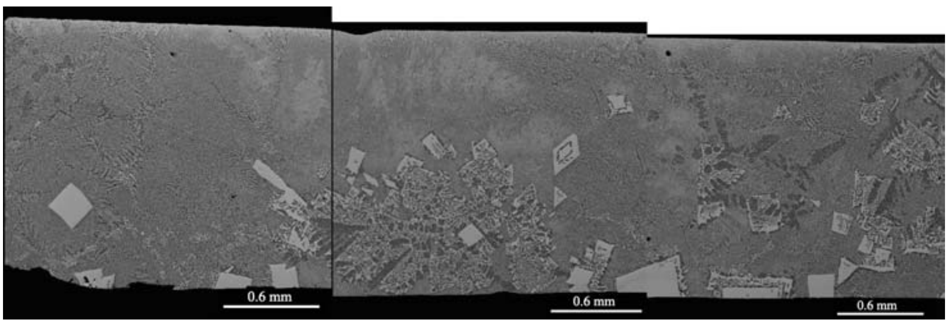


Figure 4 77.5 °C-Bi-In-Sn ternary eutectic alloy solidified within the temperature plateau region of the furnace, exhibiting gravity-induced segregation. The cooling rate was 1 °C/min.

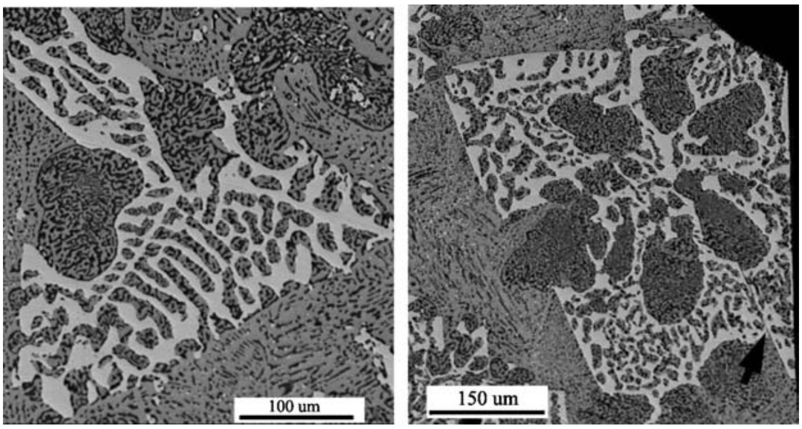
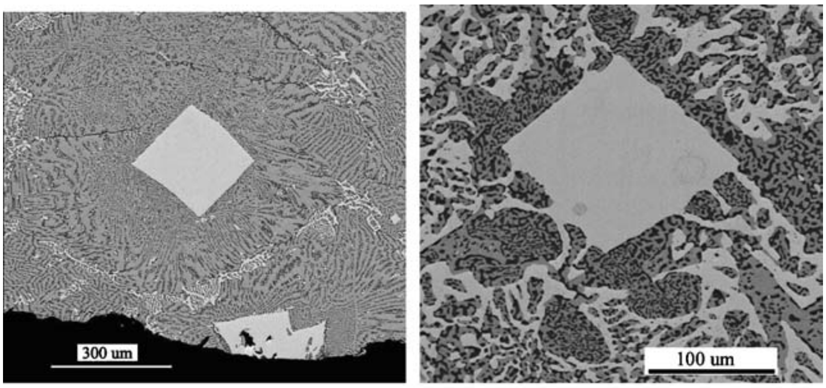
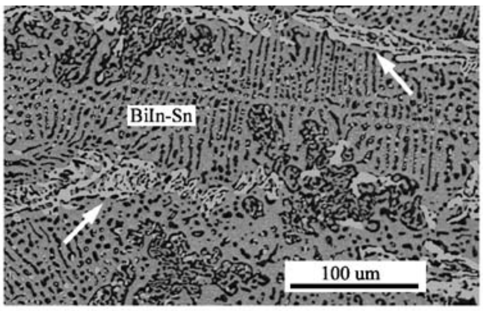


Figure 7 Tin dendrite being engulfed by Bi-Sn eutectic rather than Bi-Sn eutectic radiating from tin dendrite showing no evidence of nucleation of Bi-Sn eutectic on tin. Note two Bi-Sn solidification fronts meeting at one location creating demarcation (indicated by a dark arrow).

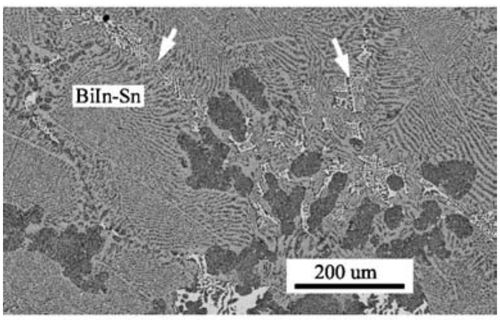


(a) (b)

Figure 8 The growth of (a) BiIn-Sn eutectic and (b) Bi-Sn eutectic from bismuth block (white).



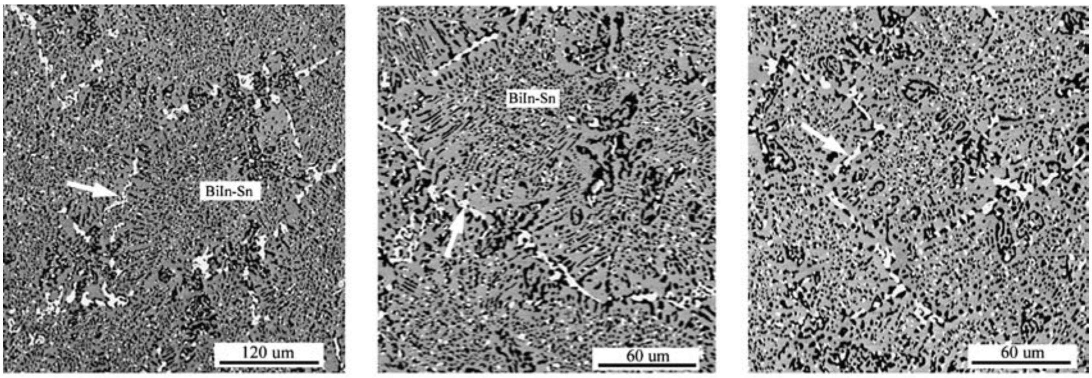
(a)



(b)

Figure 9 BiIn-Sn eutectic growing in the form of dendrite cells and Bi-Sn eutectic cells (indicated by arrows) being segregated along the BiIn-Sn dendrite cell boundaries as observed in specimens (a) from the temperature gradient region (the growth rate was ∼2 mm/min) and (b) from the temperature plateau region.

of approximately 2 mm/min (Fig. 9a), the two, two-phase eutectic structures still clearly exist although the morphology of the BiIn-Sn eutectic structure differs from the structure reported by Ruggiero and Rutter. Fig. 10a through c shows the transverse cross section of specimens produced by the OCC process in order of increasing casting speed. These depict sequential changes in the morphologies, which bridge between the structures of Figs 1 and 2. The Bi-Sn binary eutectic cells, with complex morphologies segregated along the boundaries of the BiIn-Sn cells (Fig. 9a), no longer exist in the microstructures shown in Fig. 10. Instead, they remain only as short bands of bismuth phases delineating the grain boundaries while BiIn-Sn eutectic cells still retain the morphology of the lamellar type eutectic structure in some locations of the specimens cast at the speeds of 14 and 34 mm/min. However, they no longer exist in the microstructures obtained at a speed of 57 mm/min. The elongated tin phase has changed to discrete particles in the BiIn matrix. The evolution of a double binary eutectic microstructure into a more uniform mixture of phases may be related to the decrease in phase spacing with growth rate within individual eutectic cells. When the inter-phase region becomes narrower with an increase in growth rate, the phases within are either squeezed out of the region or remain as particulates. It is noted that the phase spacing λ and growth rate R of the alloy, followed the relation $\lambda^2 R =$



(a) (b) (c)

Figure 10 Transverse cross section of wire specimens cast at (a) 14, (b) 34 and (c) 57 mm/min showing the progressive degeneration of eutectic cells. The remnants of Bi-Sn eutectic (white bands indicated by white arrows) are still visible along the BiIn-Sn cell boundaries.

constant and the Bi–Sn phase spacing was always smaller than the BiIn–Sn phase spacing [1]. This is perhaps why the Bi-Sn eutectic cells were reduced to bands of bismuth along the boundaries of the BiIn-Sn cells before the latter degenerated.

In summary, with a cooling rate of approximately 1 °C/min. the ternary eutectic alloy exhibited extensive gravity induced segregation. The microstructure of the alloy also exhibited two, two-phase eutectic structures of BiIn-Sn and Bi-Sn, which is in accord with the findings reported by Ruggiero and Rutter. However, the BiIn-Sn binary eutectic tended to grow in a dendritic form, causing the Bi-Sn eutectic to segregate into the grain boundaries thus contributing to macrosegregation. At high cooling rates the degeneration of the two distinctive binary eutectic structures to produce a more uniform mixture of phases, has been attributed to a decrease in the phase spacing.

Acknowledgments
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