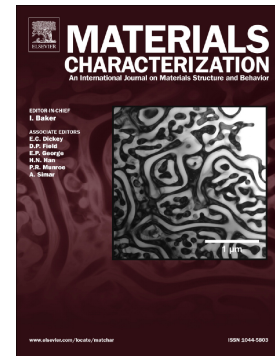


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Microstructure characterization and tensile properties of directionally solidified Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys

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Abstract

Sn-Bi-based Thermal Interface Materials (TIM) are adequate alloys to promote heat dissipation in power electronics. However, despite the necessary thermal connection, mechanical support for different components and substrates are of prime importance in microelectronic devices. In this framework, the effects of Antimony (Sb) additions on the microstructure and tensile properties of the Sn-52wt.% Bi alloy are investigated. Various Sn-Bi(-Sb) samples solidified at different cooling rates and two levels of Sb-containing alloys allow a comprehensive examination of length scales of either dendritic or eutectic microstructures. A number of experimental techniques is used here to permit a sound analyses of the ternary Sn-Bi(-Sb) alloys: transient directional solidification, optical microscopy (OM), triangle and intercept quantification methods, scanning electron microscopy (SEM), x-ray fluorescence (XRF), x-ray diffraction (XRD), tensile tests and fractography. The addition of Sb enhances the nucleation of primary dendritic trunks, which resulted in a decrease in the primary dendritic arm spacing (λ_1) by about 5 times for the Sn-52wt.% Bi-2wt.% Sb alloy as compared to the results for the binary Sn-Bi alloy. The relationships found for tensile properties as a function of the secondary dendritic arm spacing (λ_2) demonstrate that Sb additions increase the alloy strength while preserving the ductility. This is due to very thin SnSb intermetallic particles formed in the Sn-rich dendritic matrix. The influence of λ_2 variation on both the yield and ultimate strengths is roughly insignificant while the ductility varies strongly between 14.4 % and 52 % for samples solidified from 0.05 °C/s to 5.0 °C/s respectively. When 2.0 wt.% Sb is added, there is a maintenance in the levels of ductility as those found for the binary Sn-Bi alloy. This occurs especially for very refined dendritic and eutectic microstructures samples, which also exhibit a ductile fracture mode.

Keywords: Sn-Bi-Sb alloys; thermal interface materials; solidification; microstructure; tensile properties; fracture surface.

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1. Introduction

In order to increase the dissipation of heat from electronics devices, materials of high thermal conductivity, called Thermal Interface Materials (TIMs), are used to reduce the interfacial thermal resistance between jointed solid surfaces such as heat sinks and microprocessors [1]. Normally, TIMs of reasonable bulk thermal conductivity is sandwiched between the two mating surfaces, thus giving rise to a path of improved heat conduction [2]. During thermal cycling, these materials demand high adhesion, suitable ductility, mechanical strength and low thermal resistance. Several of these materials have been extensively investigated, including some Sn-based solder alloys. This type of alloys has attracted many interests in power electronics applications because they have large adhesion strength when joined to metals, and low thermal resistance [3]. For example, Sn-Pb [4], Sn-Sb [5] and Sn-Bi [6] alloys have been used as thermal interface materials.

Due to continued densification and miniaturization of electronic products in the past decades, there is still a need to establish low-temperature packaging processes performing low thermal loads on packaging components as well as their surroundings. Because of that, low-melting-point solder alloys such as Sn-Bi and Sn-Bi-X [7] are considered a priority to be developed. It is also important to note that solder alloys perform important roles in maintaining the necessary mechanical and electrical interrelationship in an electronic assembly. Throughout the electronic packaging industries, Sn-Pb solders were widely used in the past years. Nonetheless, concerns over the toxicity of Pb in these alloys have driven efforts to restrain their use in electronics manufacturing by Japan, European Union and USA, among other countries. As a consequence, more and more worldwide attention is given to the investigation of lead-free solders [8].

As an alternative to Sn-Pb alloys, Sn-Bi lead-free solder alloys are generally used due to their relatively high tensile strengths, low-melting temperatures and good solderability [9]. Sn-Bi and Sn-Bi based solder joints may have suitable properties and characteristics as far as adequate as-soldered microstructures could be formed. A number of studies found that the microstructure of the Bi-Sn eutectic alloy is constituted by Bi-rich and Sn-rich lamellar phases, as well as by Bi precipitates in the Sn-rich phase [10–15]. In order to improve microstructure features and properties of Sn-Bi solders,

researchers have done much research on the effect of addition of dopant elements. According to the existing results, important bases to the understanding of the development of these alloys have been provided. Shen *et al.* [9] investigated the effects of additions of Cu and Zn on microstructures, thermal and mechanical properties of Sn-Bi-based solder alloys. Thermal analysis indicated that the addition of Cu decreased both paste region and melting point while the addition of Zn played an opposite effect. Increase in both ultimate tensile strength and ductility by adding Cu to Sn-Bi-based solders has also been reported. Such improved strength was associated with the uniform distribution and microstructural refinement of the Cu_6Sn_5 intermetallic particles. Improved strength of the Zn-containing alloy was also reported, which was attributed to the presence of both structural refinement and globular CuZn_2 particles. A major decrease in the elongation of a Sn-40Bi-2Zn-0.1Cu solder alloy was noted and associated with the formation of needle-like Zn particles with high aspect ratio at positions around the Bi-rich phase.

Zhang *et al.* [8] studied the effects of the addition of Sb on properties of Sn-Bi solders (in the range 48-58 wt.% Bi). With the increase in the alloy Sb content, the amount of the eutectic mixture also increases. The Sn-Bi-Sb alloys exhibit a higher melting point and a wider melting range at a heating rate of 5 °C/min as compared to the Sn-Bi alloys. According to these authors, Sb also affects the wettability on a Cu substrate. The spreading ratio first increases and then drops, with the increase in the alloy Sb content from 1.0 to 3.0 wt.%, reaching the superior limit when the Sb content was 2.0%. For all the alloys studied, the highest spreading ratio was 78.2%, which is higher than that of the Sn-58%Bi alloy (48%).

Due to the fact that Sb is an effective solid solution strengthener in Sn [16], few studies verified its effects as a third element added to Sn-Bi alloys. Dominguez *et al.* [17], for instance, demonstrated that the compressive strength increased by about 50% by adding Sb to the Sn-58wt.%Bi eutectic alloy. This increase in the compressive strength is supposed to be associated with the presence of the SbSn intermetallics within the microstructure. According to the present authors' knowledge, there are no detailed studies elucidating the effects of Sb both on the microstructure formation and tensile properties of Sn-Bi alloys solidified under a wide range of cooling rates.

Based on the existing literature regarding the Sn-Bi alloys, experimental studies emphasizing interrelations between solidification microstructures and mechanical properties for near-eutectic compositions remain scarce. Moreover, systematic studies devoted to ternary Sn-Bi-X alloys in comparison to the binary Sn-Bi alloys are limited. To increase the capacity of these alloys to resist loads delaying fracture, the addition of third elements can collaborate positively. Sb appears to be a good candidate due to its proved efficiency as a strengthener element. With the aim to better comprehend the potential for applications of a near-eutectic Sn-Bi alloy doped with Sb, a deeper microstructure investigation is required. For this purpose, this research focuses on the microstructure characterization of samples of Sn-52wt.% Bi-1 and 2 wt.% Sb alloys directionally solidified (DS) under transient heat flow conditions. Determination of thermal solidification parameters and characterization of the interactions of Sb with the Sn-Bi microstructure are performed. It is aimed establishing experimental dependences of microstructural features, such as dendrite arm spacing and eutectic spacing, on the cooling rate and growth rate. Moreover, tensile properties are interrelated with the length scales of the eutectic and the dendritic microstructures.

2. Experimental procedure

The Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys were prepared by melting weighed quantities of high purity (99.9%) Sn, Bi and Sb in a silicon carbide crucible inserted into an induction furnace. After allowing time for melt homogenization, the molten alloy was poured into the mold located inside a vertical directional solidification system while the electric heaters were disabled. When the molten alloy achieved the desired overheating temperature, the controlled bottom water flow was opened to initiate the directional growth from the bottom to the top. Continuous temperature measurements were performed by using type J thermocouples, placed at several positions along the casting length. The schematic diagram of the experimental setup used in the present research work is shown in Fig. 1. The employed system can produce various solidification velocities and cooling rates along the length of DS castings. A low carbon steel bottom (SAE 1020) was used to separate the

bottom of the casting from the cooling water. To avoid radial heat losses, the lateral inner mold surface was covered with an insulating ceramic layer.

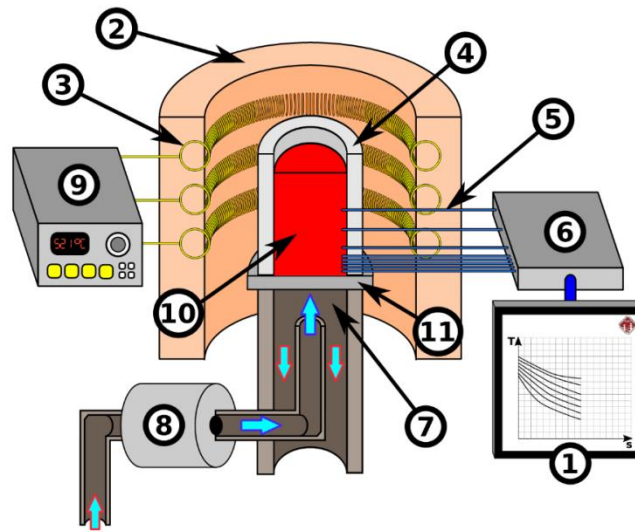


Fig. 1 - Representation of the upward directional solidification furnace: 1 - acquired cooling curves; 2 - ceramic insulation; 3 - electric resistances; 4 - stainless-steel mold; 5 - type J thermocouples; 6 - data logger; 7 - water flow circulation; 8 - flowmeter; 9 - temperature controller; 10 - molten alloy and 11 - water-cooled bottom part.

In order to represent the expected formation of phases in equilibrium conditions for the alloys of interest, diagrams of properties were computed by using Thermo-Calc software as can be seen in Fig. 2. One of the possibilities to express phase equilibria is plotting the results as property diagrams as performed here. Although the TCSD3 database in the Thermo-Calc software has determined the eutectic composition around 53 wt.% Co, the literature [10,13,14] has demonstrated 58 wt.% Co content as being the eutectic composition. Despite this inaccuracy, it is still possible to observe the comparative developments between the Sn-Bi alloys. It is worth mentioning that these simulated results will not necessarily represent the real microstructures in conditions far from the thermodynamic equilibrium.

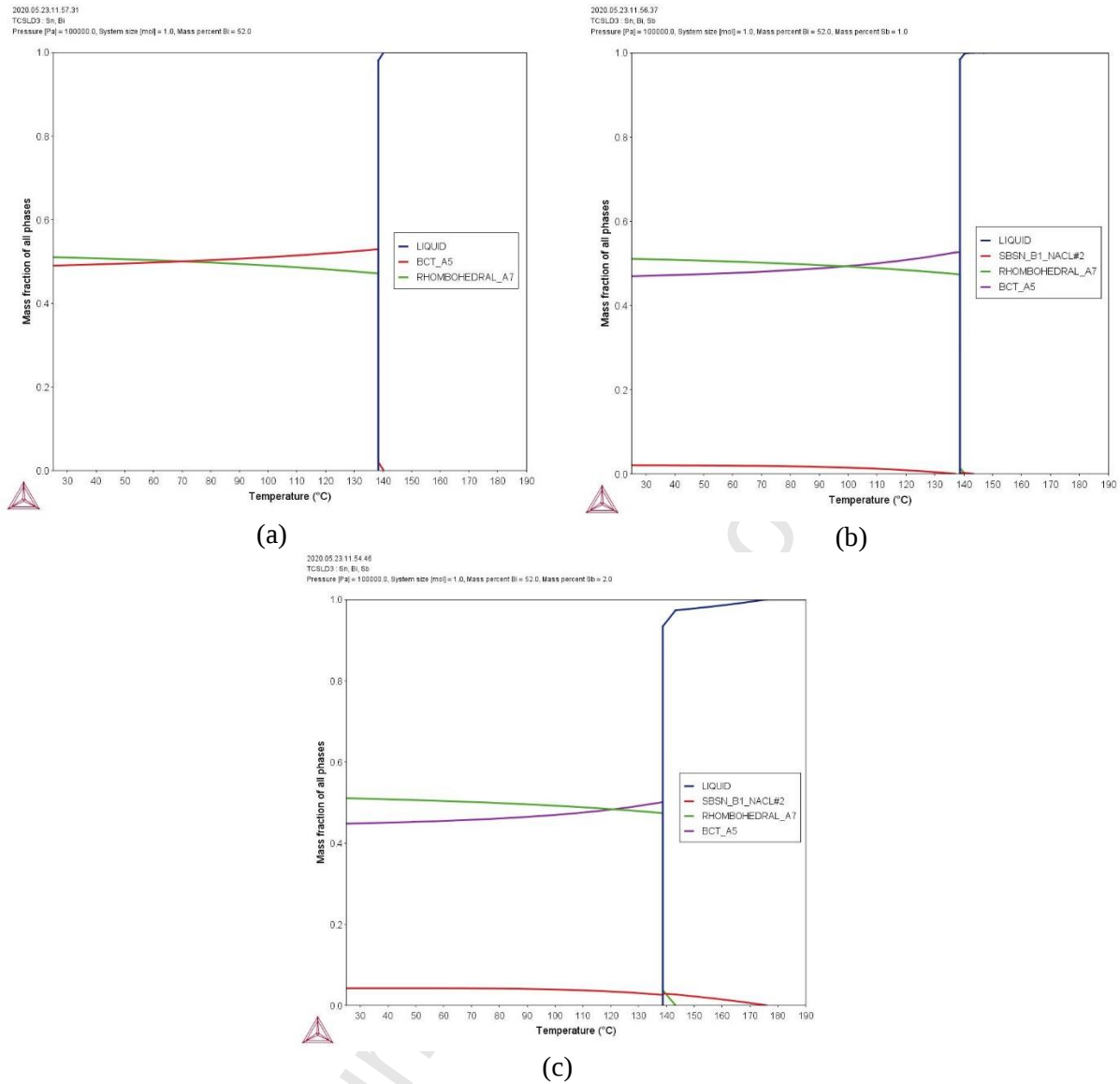


Fig. 2. Stable mass phase fraction as a function of temperature of the (a) Sn-52wt.% Bi, (b) Sn-52wt.% Bi-1wt.% Sb and (c) Sn-52wt.% Bi-2wt.% Sb alloys computed using TCSLD3 database of the Thermo-Calc software. SBSN_B1_NACL#2: SnSb, RHOMBOHEDRAL_A7: Bi-rich and BCT_A5: Sn-rich phases.

To reveal the macrostructure, the DS castings were sectioned along its vertical axis by using a precision saw, with the surface sanded successively by #150, #240, #320, #400 and #600 mesh sandpaper and etched with the following reagent: 100 mL of distilled H₂O, 2.5 mL of HCl and 10 g of FeCl₃. Eight (8) pieces of longitudinal and cross-section samples were examined at different positions from the cooled surface of the casting, which are: at 5 mm, 10 mm, 15 mm, 20 mm, 30 mm, 50 mm, 70 mm and 90 mm. The samples were sanded successively by #150, #240, #320, #400, #600, #1200 and #2000 mesh sandpapers. After sanding, the samples were manually polished with a metallographic

suspension of alumina (1 μm particle size) and water. Each sample was etched during at least 10 seconds by immersion with a solution containing 100 mL distilled of H_2O , 2.5 mL of HCl and 10 g of FeCl_3 , and then subjected to optical microscopy analyzes in a Nikon instrument (Eclipse MA2000 model).

The alloys' microstructures were examined by an image processing system [18]. The triangle method (see Fig. 3(a)), proposed by Gündüz and Çadirli [19], was employed to determine the primary dendrite arm spacing (λ_1), with measurements performed on the transverse sections of the samples. Whereas, the intercept method was adopted on longitudinal samples in order to determine the secondary dendrite arm spacing (λ_2), see Fig. 3(b), and on transverse sections for both the tertiary dendrite arm spacing (λ_3) and the eutectic spacings (λ_{CE} and λ_{FE}), as shown in Fig. 3(c). At least 40 measurements were performed for each selected position and for each type of microstructural spacing.

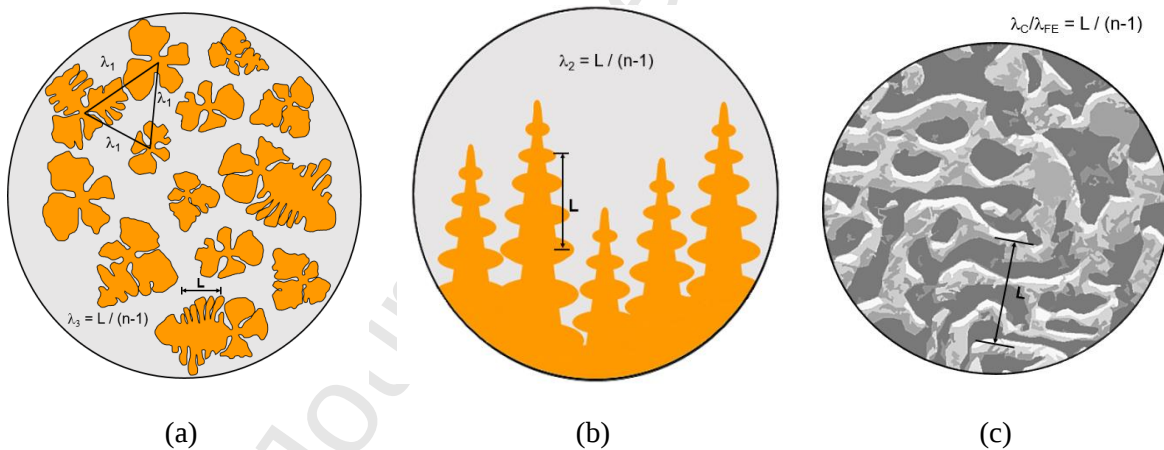


Fig. 3 - Schematic drawing of (a,c) transverse and (b) longitudinal sections as used for measurement procedures related to dendritic and eutectic spacings, that is, intercept method for λ_{FE} , λ_{CE} , λ_2 and λ_3 and triangle method for λ_1 . 'L' is the length of the line while 'n' is the number of intercepted phases.

The X-Ray Fluorescence technique (XRF) was used for long-term chemical analyses of the Sn-52%Bi-1%Sb and Sn-52%Bi-2%Sb alloys castings. This technique allows the quantitative identification of the elements present in each alloy examined in different regions of analysis. The equipment used was a Shimadzu EDX-720. In order to determine the phases present in the microstructures obtained along the length of the castings, X-Ray Diffraction (XRD) tests were

performed for different positions in the DS castings. XRD spectra of both tested alloys were obtained using a Shimadzu XDR-700 diffractometer.

Microstructural characterization was supplemented using a scanning electron microscope Zeiss (Auriga 40 model). These analyzes were performed to the overall set of phases existing in the Sn-52wt.%Bi-1wt.%Sb and Sn-52wt.%Bi-2wt.%Sb alloys castings.

According to specifications of the ASTM Standard E 8M/04, transverse specimens were extracted along the length of the DS castings and machined for tensile tests, as shown in Fig. 4. These specimens were tested in an Instron 5500 machine at a strain rate of about $3 \times 10^{-3} \text{ s}^{-1}$. To ensure reproducibility, four specimens of each selected position were examined for each examined alloy.

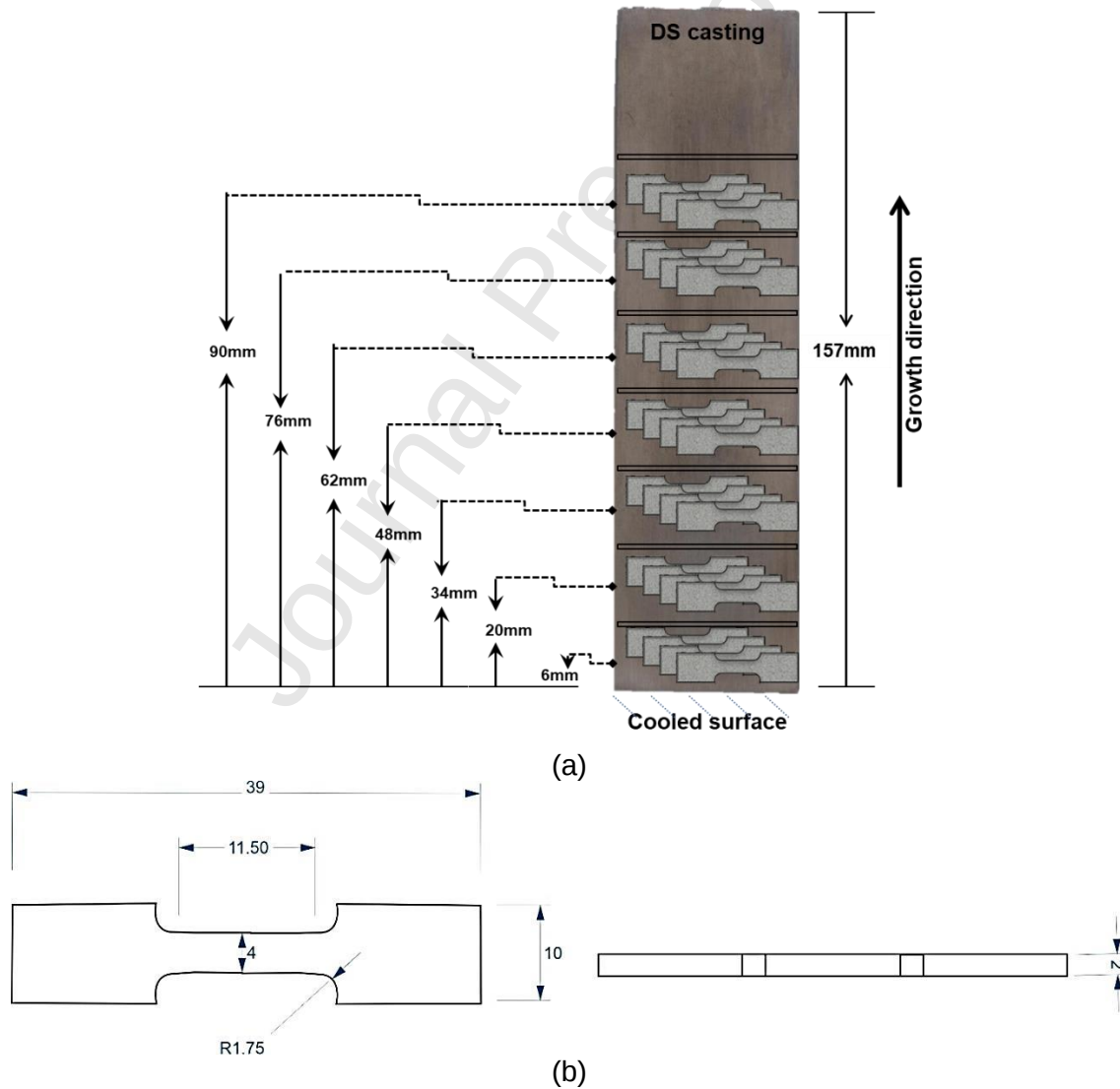


Fig. 4 - (a) Relative positions across the Sn-Bi-Sb alloys castings from where the samples for tensile tests were extracted having as reference the cooled surface; and (b) specimen geometry and dimensions for tensile tests (values in mm).

3. Results and discussions

3.1 Thermal Analysis

Thermal profiles of the Sn-Bi(-Sb) alloys castings were assessed by using thermocouples during directional growth under transient heat flow conditions. Fig. 5(a) and Fig. 5(b) present quantitative Temperature (T) – Time (t) data obtained at a number of positions across each examined casting, that is, from regions solidified closer to the water-cooled bottom ($P = 4$ mm, 9 mm and 14 mm) until farther regions associated with slower cooling conditions ($P = 44$ mm, 69 mm and 89 mm). Quite similar slopes are related to equivalent cooling curves when the temperature profiles of both Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys are compared.

The *liquidus* temperatures of the tested alloys were those indicated in Fig. 5(c) and Fig. 5(d). These cooling tests were conducted inside a furnace so that a very low cooling rate of about 0.01 °C/s could be attained. Based on the resulting *liquidus* temperatures, it was possible to follow the path of the *liquidus* isotherm across each casting from the bottom to the top. This is executed by determining the related times (t_L) of each of the *liquidus* isotherms passing by each thermocouple position (P). Consequently, functions $P = f(t_L)$ are generated. Time-derivatives of these functions enable the growth velocities (V_L) to be determined. The cooling rates ($\dot{T}_L$) are determined through the T-t derivative of each cooling curve at the level of the passage of the *liquidus* front by each thermocouple.

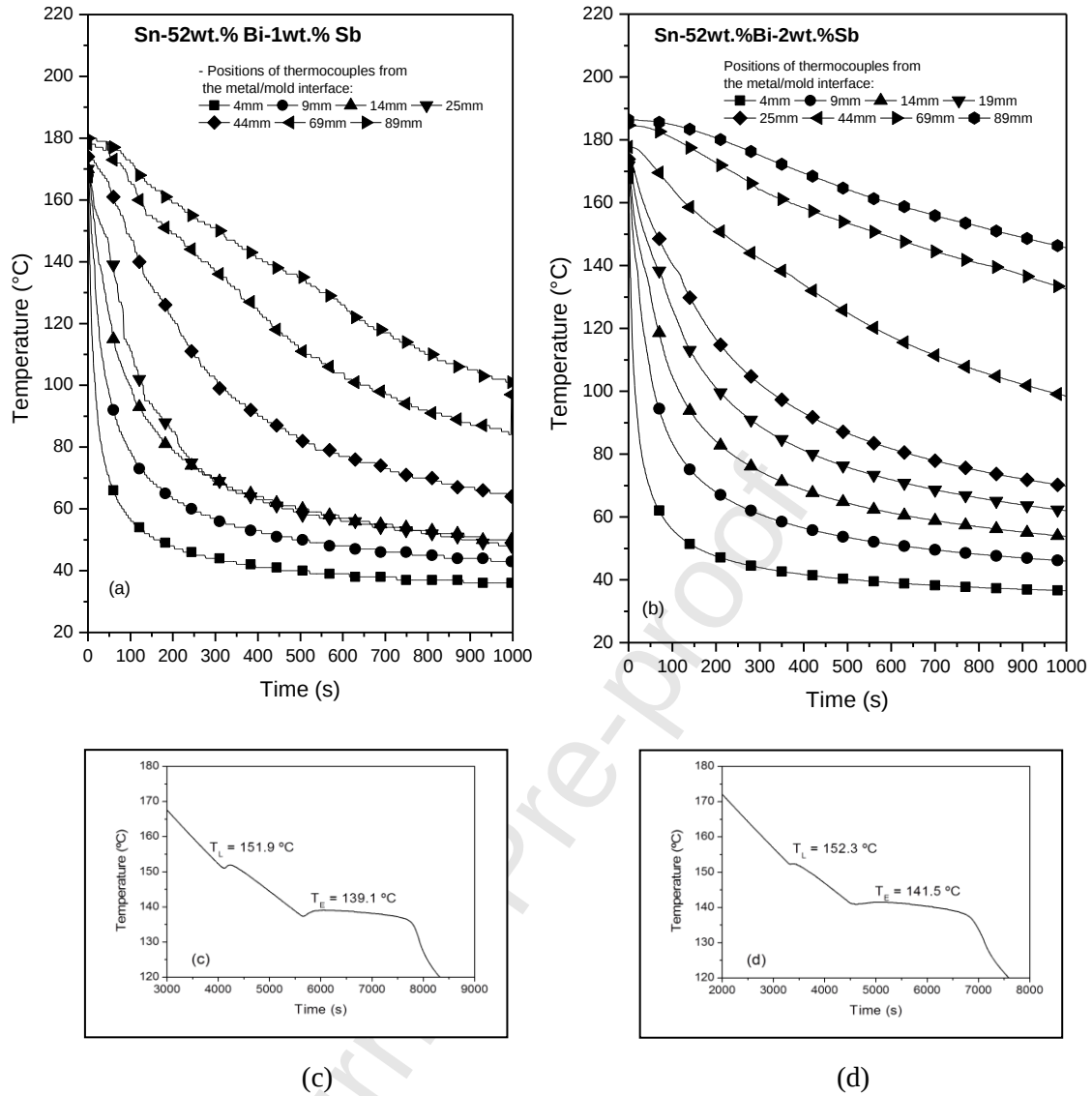
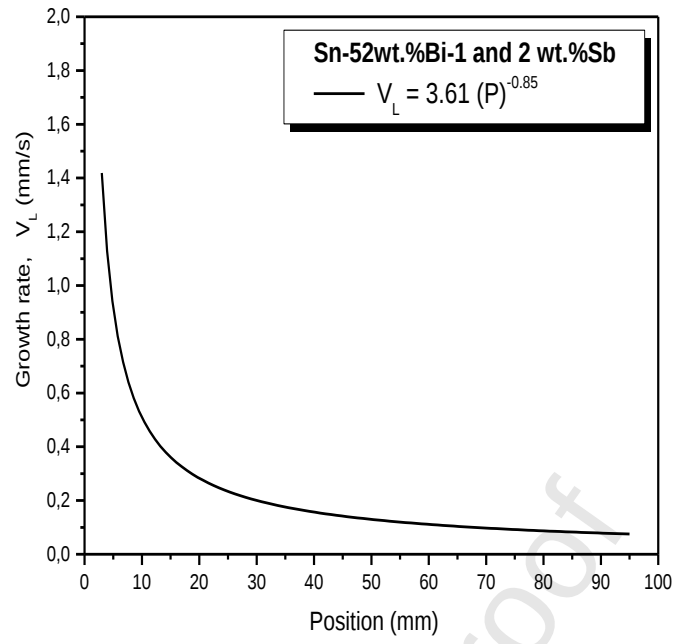
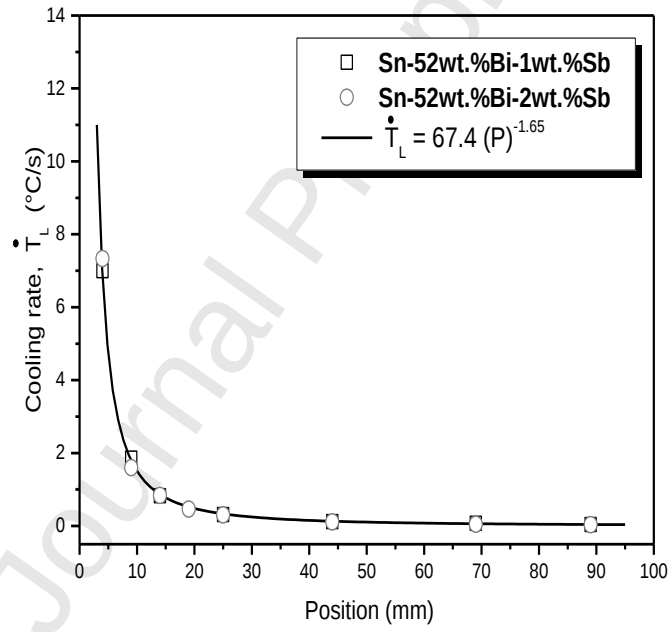


Fig. 5 - Cooling curves acquired either during unsteady-state directional solidification (a,b) or during near-equilibrium solidification (c,d) for the Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys.

Fig. 6 shows effective variations in cooling rate, $\dot{T}_L$, growth velocity, V_L , and thermal gradient, G_L , for different positions along the length of the DS castings. Decrease of all these solidification thermal parameters is associated with increasing solid + mushy zone thermal resistances with the progress of solidification. Single power functions for each solidification thermal parameter represent the experimental variations observed along the length of both Sn-52wt% Bi-1wt% Sb and Sn-52wt% Bi-2wt% Sb alloys castings. Consequently, it is worth noting that the two-fold increase in Sb-alloying was not enough to change the solidification kinetics related to the tested alloys.



(a)



(b)

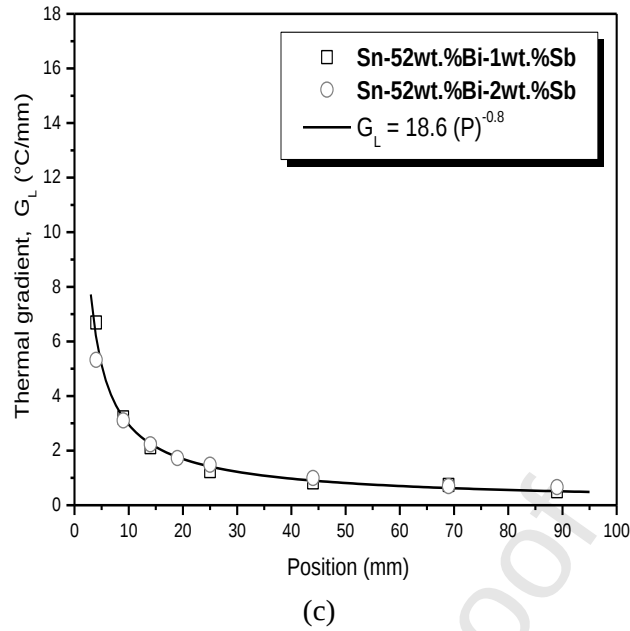


Fig. 6 – Solidification thermal parameters variations for the Sn-Bi(-Sb) solder alloys: (a) growth rate- V_L , (b) cooling rate- $\dot{T}_L$ and (c) thermal gradient- G_L along the length of the DS castings (i.e., with a function of position).

3.2 Microstructural characterization

Fully dendritic microstructural arrangements can be noted for both Sn-Bi(-Sb) solder alloys as observed in Fig. 7 and Fig. 8. Some longitudinal and transverse dendritic arrays across the upward solidification direction are shown in Fig. 7 and Fig. 8, related to some selected positions in the casting marked in the center of the revealed macrostructures.

In spite of changes in the dendritic length scale owing to the very distinct cooling rates along the length of the castings, the microstructure is constituted by Sn-rich dendrites (darker phases) with Bi and SnSb precipitates in their own core, surrounded by a complex eutectic mixture (lighter areas). The eutectic is formed by Bi-rich and Sn-rich phases. Considering that the eutectic composition of the Sn-Bi system is 58 wt.% Bi, great fractions of eutectic structure enveloping the Sn-rich dendrites can be seen in the images of Fig. 7 and Fig. 8.

The as-cast microstructure of the Sn-52wt.%Bi solder alloy is formed by a complex regular eutectic mixture, Bi-rich and Sn-rich, surrounded by Sn-rich dendrites with Bi precipitates in their inside. In this case, the phases formed during the non-equilibrium solidification are: (1) L (liquid phase); (2) L + (primary Sn-rich dendrites); (3) L + (Sn-rich dendrites + Bi precipitates) and (4) (Sn-rich dendrites + Bi precipitates) + (Bi-rich+Sn-rich, from liquid phase) [23]. The ternary Sn-

52wt.%Bi-1wt.%Sb and Sn-52wt.%Bi-2wt.%Sb solders show a similar solidification path as compared to the binary Sn-Bi alloy. The difference remains in the precipitation stage. It has to the combined presence of Sb in solid solution within the Sn-rich matrix, which provides the precipitation of SnSb particles as well. As such, the sequence slightly changes for: (1) L (liquid phase); (2) L + (primary Sn-rich dendrites); (3) L + (Sn-rich dendrites + Bi precipitates + Sn-Sb precipitates) and (4) (Sn-rich dendrites + Bi precipitates + SnSb precipitates) + (Bi-rich+Sn-rich, from liquid phase)

The solidification cooling rates associated with the microstructures in Fig. 7 and Fig. 8 are representative of those usually adopted in the soldering practice during assembly processes [20].

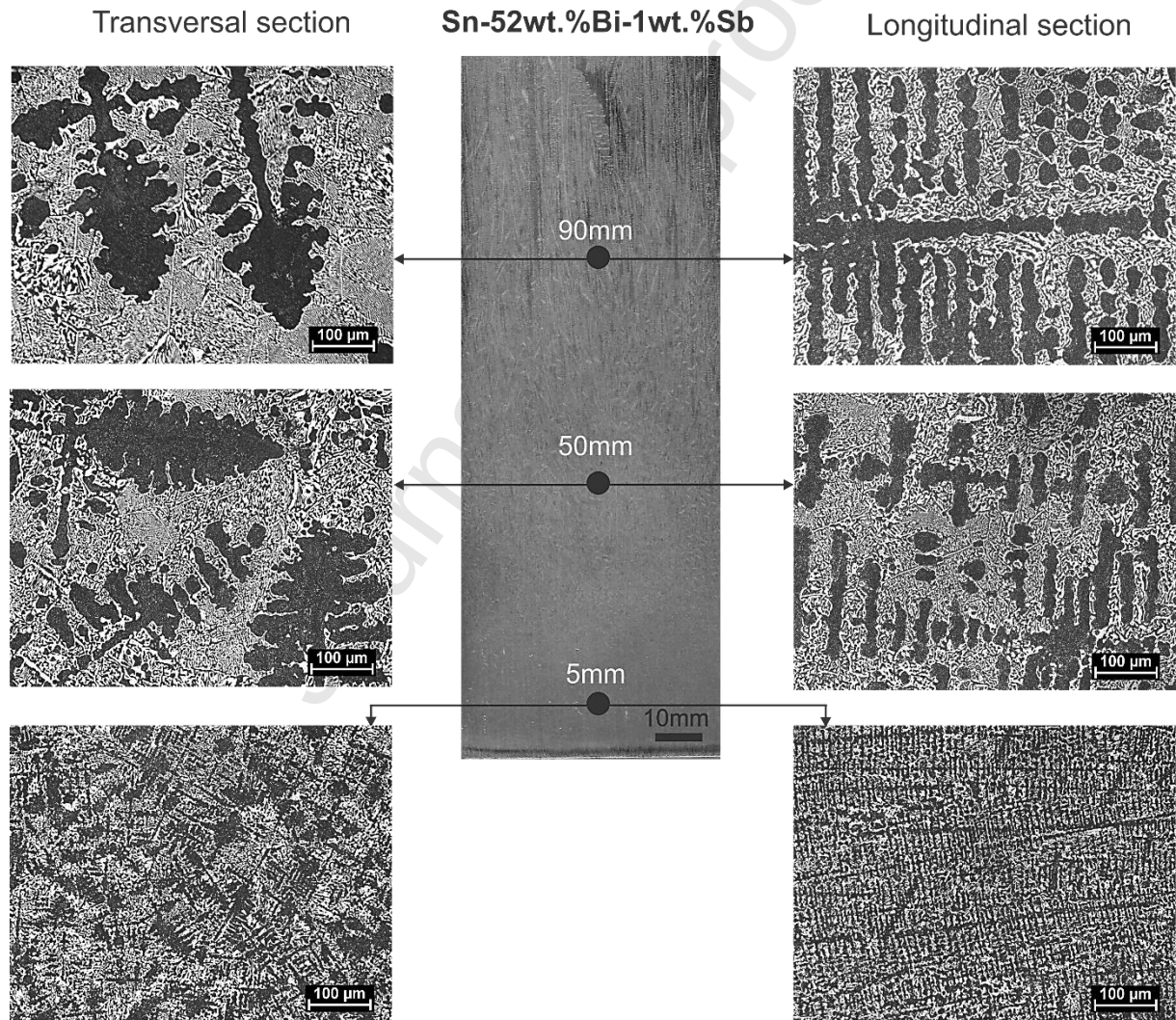


Fig. 7 - Macrostructure and some representative microstructures revealed along the length of the DS Sn-52wt% Bi-1wt% Sb alloy casting. Samples at 5 mm, 50 mm and 90 mm are associated with $\dot{T}_L = 6.0$ °C/s, $\dot{T}_L = 0.15$ °C/s and $\dot{T}_L = 0.05$ °C/s, respectively.

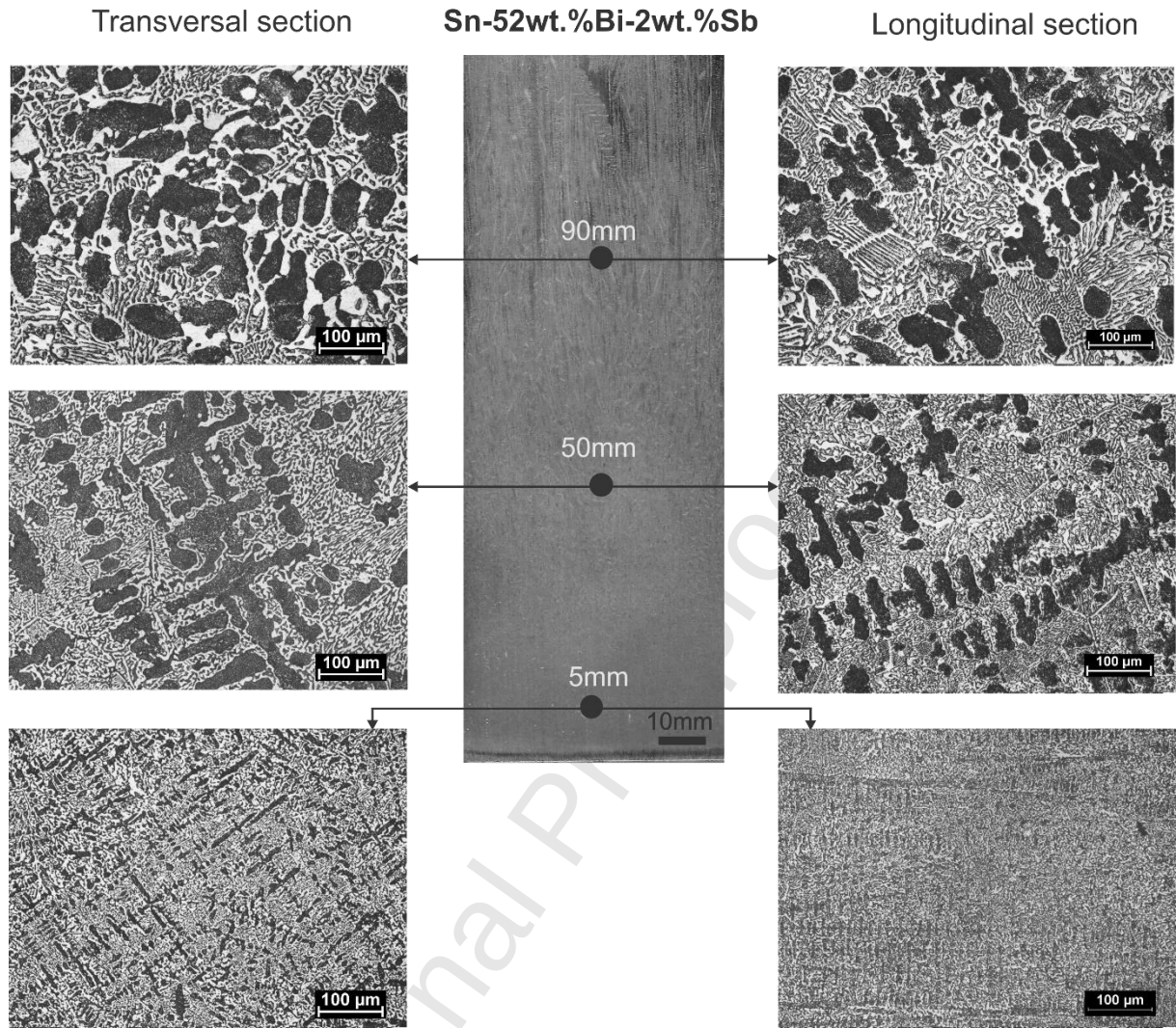


Fig. 8 - Macrostructure and some representative microstructures revealed along the length of the DS Sn-52wt% Bi-2wt% Sb alloy casting. Samples at 5 mm, 50 mm and 90 mm are associated with $\dot{T}_L = 6.0$ °C/s, $\dot{T}_L = 0.15$ °C/s and $\dot{T}_L = 0.05$ °C/s, respectively.

More detailed optical images in Fig. 9 reveal that the eutectic microstructure is characterized by a complex regular morphology. The formation of two typical regions - zones with repeating regular pattern and zones showing random orientation - occurred regardless of both the magnitude of the local cooling rate and the alloy Sb-containing. On the whole, the features revealing the complexity of the eutectic mixture is the same as those reported in previous studies for binary Sn-Bi alloys solidified in a variety of conditions ^[21,22].

This non-conventional microstructure in binary Sn-Bi alloys has demonstrated some other isolated features, which can be correspondingly observed in Fig. 9 for the Sn-Bi(-Sb) alloys. Some

examples are the angular structures and fishbone-like eutectics. Moreover, the eutectic is shown to be formed by two scales of lamellar structure. These two sizes were defined as being ‘finer’ and ‘coarser’ lamellar eutectic. They must be associated with thermal instabilities at the solidification interface during the growth of the eutectic under non-equilibrium solidification conditions.

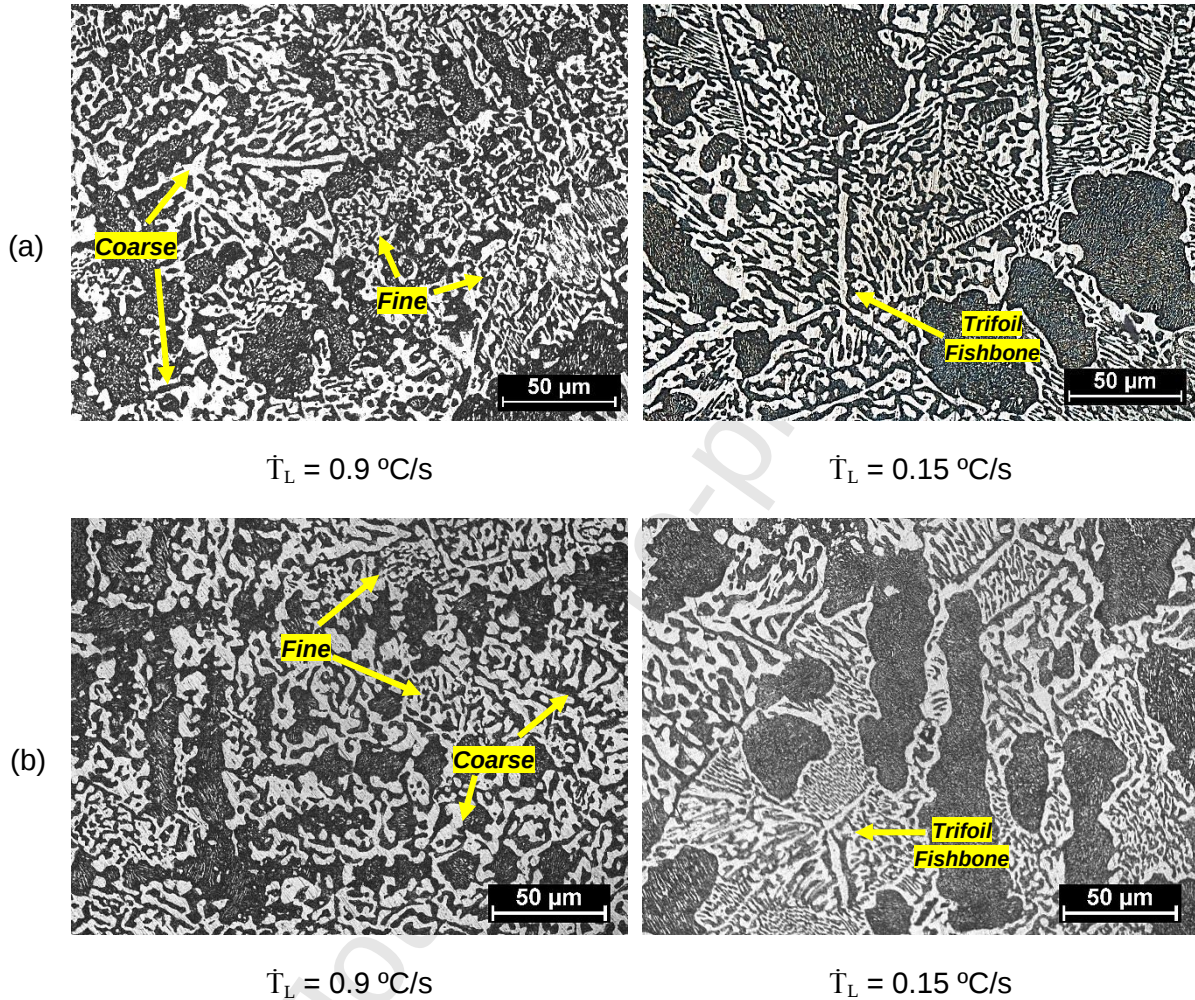


Fig. 9 - Microstructures showing features of the eutectic mixture associated with samples solidified at distinct cooling rates ($\dot{T}_L$) for the (a) Sn-52wt.% Bi-1wt.% Sb and (b) Sn-52wt.% Bi-2wt.% Sb alloys.

Experimental relationships relating the primary (λ_1) and secondary (λ_2) dendrite arm spacings to the cooling rate and the growth rate are shown in Fig. 10, where average λ_1 and λ_2 values and the corresponding standard deviations are presented based on measurements performed in various positions along the length of both alloys castings.

The fitted lines in Fig. 10 are power functions representing the experimental scatters. Despite the higher slope for the λ_1 plot associated with the Sn-52wt.% Bi-1wt.% Sb alloy, $-1/4$ and $-1/2$ exponents represented well the other fits to the experimental λ_1 and λ_2 results with cooling rate and growth rate, respectively. These same exponents performed well for the binary Sn-52wt.% Bi alloy, whose lines (dashed) were inserted into the graphs in Fig. 10 for comparison purposes [23]. The results related to the Sn-52wt.% Bi alloy are derived from our previous work [23] demonstrating microstructural evolution and mechanical properties of this binary alloy. While λ_2 decreases about 30% with the addition of Sb, when a direct comparison is made with the results for the non-modified alloy a reduction of about 80% is shown to occur for λ_1 values in the range of cooling rates between 0.05 °C/s and 6.0 °C/s.

Such increase in emergence of primary trunks also induced the formation of tertiary dendrite arms in the Sn-Bi(-Sb) alloys samples, whose occurrence can be observed in Fig. 7 and Fig. 8. While values of cooling rate lower than 1.5 °C/s were shown to be associated with the onset of tertiary dendritic branches for the binary Sn-52wt.% Bi alloy, λ_3 varied between 7 μm and 34 μm for corresponding cooling rates of 6 °C/s and 0.05 °C/s, respectively, when the Sn-Bi-Sb alloys are examined. The addition of Sb induced the growth of this high-order structure also for samples solidified at faster cooling conditions.

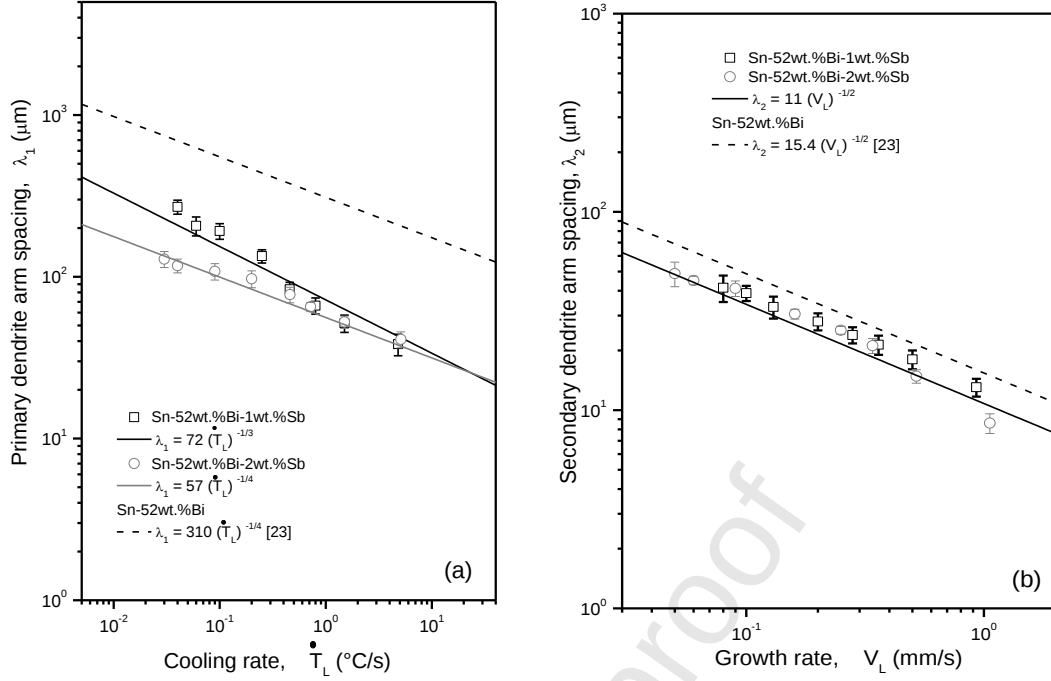


Fig. 10 - (a) Primary and (b) secondary dendritic arm spacing as a function of cooling rate ($\dot{T}_L$) and growth rate (V_L), respectively, for the DS Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys castings.

The high eutectic proportions as well as the presence of Sb seem to impose a particular character of the eutectic growth when correlating eutectic spacing with growth rate as shown in Fig. 11. In both scales of eutectic structure evaluated (fine and coarse), the aforementioned conditions lead to a much lower exponent than that described by the growth law for eutectics proposed by Jackson and Hunt, i.e., $-1/2$ [24]. It appears that the addition of Sb decreases the sensitivity of the eutectic spacing in relation to the growth rate, resulting in the $-1/5$ exponent, despite sustaining all microstructure features as those of the eutectic formed in the binary Sn-52wt.% Bi alloy.

Single growth laws given to each eutectic spacing scale can be seen in Fig. 11: coarse - $\lambda_{CE} = 4.0 \times (V_L)^{-1/5}$ and fine - $\lambda_{FE} = 0.9 \times (V_L)^{-1/5}$. The ranges of eutectic spacing varied between $0.7 \mu\text{m}$ and $2.1 \mu\text{m}$ for the fine scale and between $4.4 \mu\text{m}$ and $6.6 \mu\text{m}$ for the coarse scale.

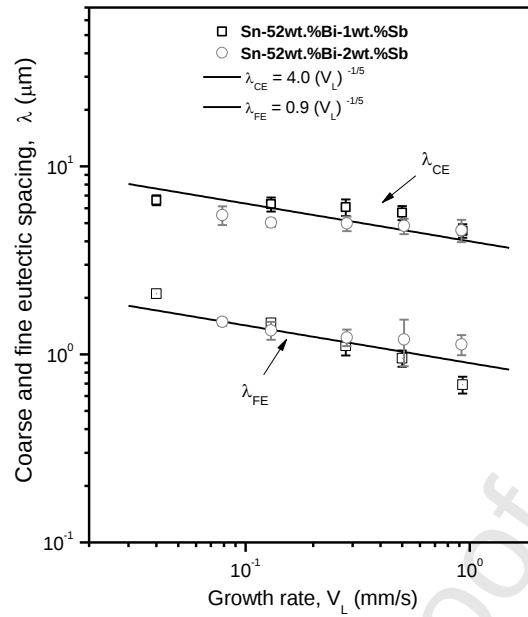


Fig. 11 – Coarse (λ_{CE}) and fine (λ_{FE}) eutectic spacing variations with the growth rate (V_L) for the Sn-Bi(-Sb) solder alloys.

3.3 Chemical analysis of phases

The SEM-EDS separated area maps of the elements forming the Sn-Bi(-Sb) alloys in Fig. 12 show the presence of Bi precipitates within the Sn-rich dendritic cores. The samples subjected to this SEM analysis were those solidified at low cooling rates of 0.05 °C/s. Moreover, an ellipsoidal morphology predominates for these precipitates across the entire length of the DS castings. It is also possible to see a Bi-rich lamella constituting the eutectic mixture at the right in the images.

While the Bi precipitates received blue contrast, Sb in green contributed mainly to solid solution formation and also to a lesser extent to the nucleation and growth of SnSb precipitates in solid state. Very thin SnSb precipitates are pointed with white arrows in Fig. 12.

Based on the Bi-Sn; Sb-Sn and Bi-Sb binary phase diagrams: (i) the solid solubility of Bi in Sn is about 21 wt.% Bi at the eutectic temperature (139 °C) [25]; (ii) a previous research demonstrated that the solid solubility of Sb in Sn is limited to about 10 wt.% Sb at 243 °C, decreasing to 1.2 wt.% Sb at 127 °C and to almost zero at room temperature [26]; and (iii) the Bi-Sb system, in its turn, is able to form a continuous series of solid solutions when freezing from the liquid [17]. Still on the Bi-Sb system it is worth reporting that this phase diagram predicts the existence of a miscibility gap in the (Bi,Sb) phase when approaching room temperature [27].

The presence of these phases in the core of the dendrites is due to the precipitation in the solid state after the solidification stage. The decrease in the solid solubility of Bi in Sn during cooling is more severe than that of Sb in Sn. Moreover, at the temperatures at which the samples were subjected ($< 140\text{ }^{\circ}\text{C}$), the solid solubility of Bi in Sn is much higher than that of Sb in Sn. This explains the higher rate of precipitation related to the Bi particles while Sb is easier kept in solid solution.

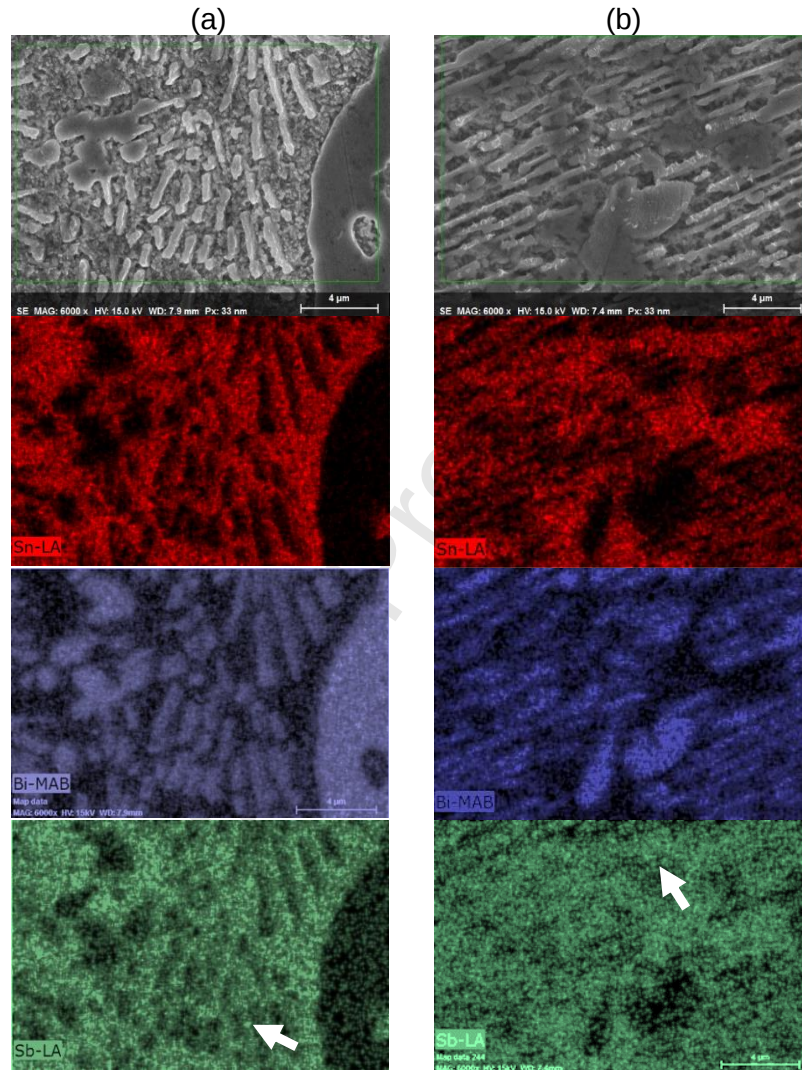


Fig. 12 - Elemental SEM-EDS mappings associated with transverse specimens solidified at $0.05\text{ }^{\circ}\text{C/s}$ for: (a) Sn-52wt.% Bi-1wt.% Sb and (b) Sn-52wt.% Bi-2wt.% Sb alloys (magnification: $6,000\times$).

Fig. 13 depicts SEM-EDS images of the samples solidified at higher cooling rates ($6.0\text{ }^{\circ}\text{C/s}$) with spots as highlighted in the images. These spots and corresponding tables depict the compositions characterizing the phases constituting both tested alloys. The EDS analyses confirmed that high atomic percentages of Sb are part of the precipitates associated with the points #2. These precipitates also

appear in blue contrasted islands pointed with white arrows in the images at the right side of Fig. 13. However, the majority of light gray precipitates (spot #5) refer to the Bi phases while the pro-eutectic Sn-rich phase remains with small contents of Bi and Sb in solution (spots #3).

From these EDS results for fast cooled Sn-Bi(-Sb) alloys samples, one can infer that Sb reaches supersaturation beyond the solid solubility limit of the SnSb compound. Under such local condition, SnSb precipitates in the Sn-rich matrix. Higher cooling rates lead to a larger content of Sb dissolved in the Sn-rich matrix owing to the solidification stage. As such, the occurrence of SnSb precipitates is greater in samples solidified more quickly.

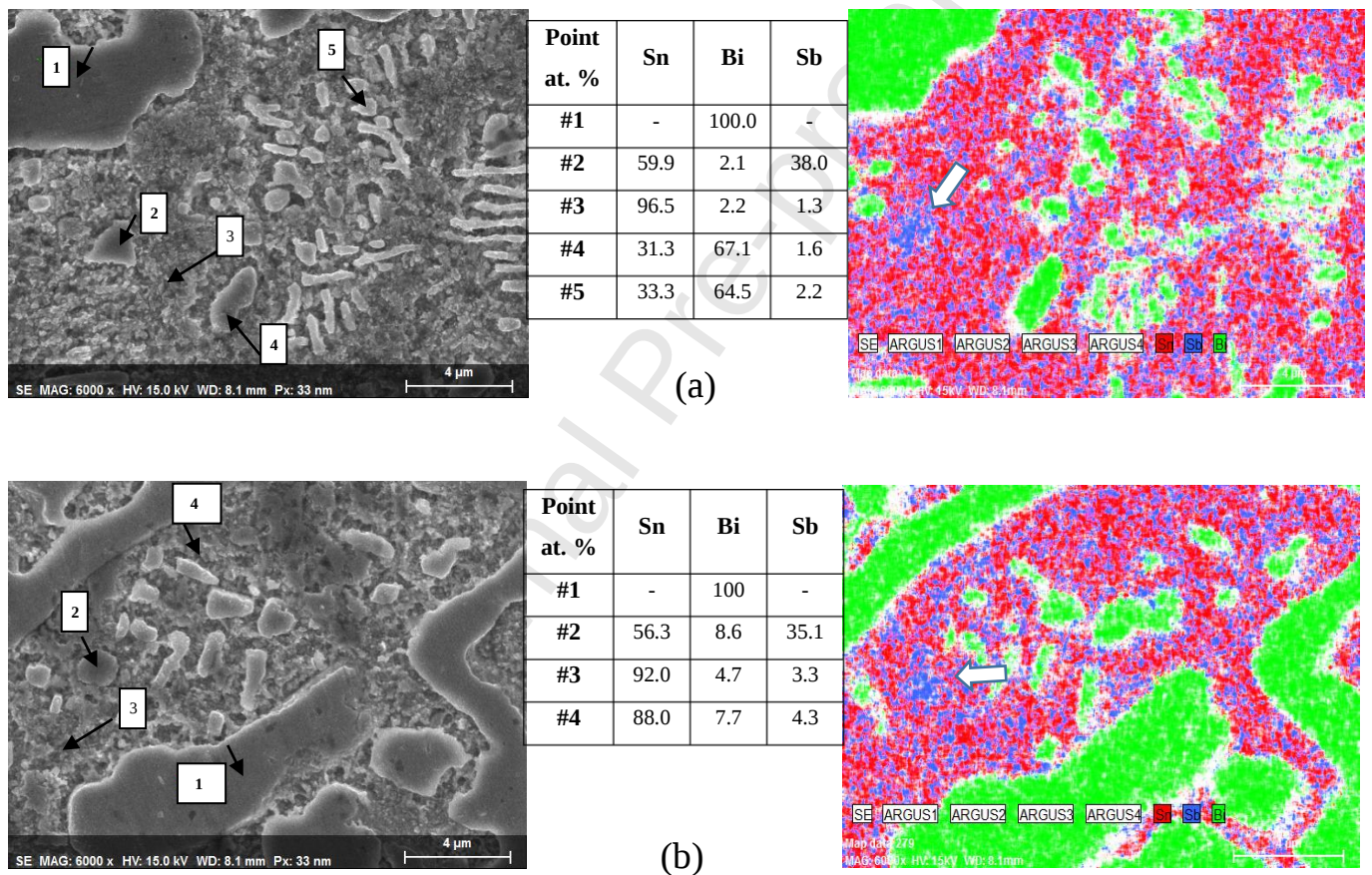


Fig. 13 - SE SEM images at left containing point results of EDS probes of the phases compositions (at. %) as well as three superimposed elemental maps (Sn, Bi and Sb) at right associated with the transverse specimens solidified at 6.0 °C/s for: (a) Sn-52wt.% Bi-1wt.% Sb and (b) Sn-52wt.% Bi-2wt.% Sb alloys.

Through decoding the XRD patterns in Fig. 14, the reflections related to Sn, Bi and SnSb phases were identified. The less intense 2θ peaks of the SnSb precipitates were 42.1° , 44.2° , 76.5° and

87.4°. More intense peaks of this phase are related to the Sn-52wt.%Bi-2wt.%Sb alloy, possibly caused by the higher Sb-alloying, which promoted higher supersaturation.

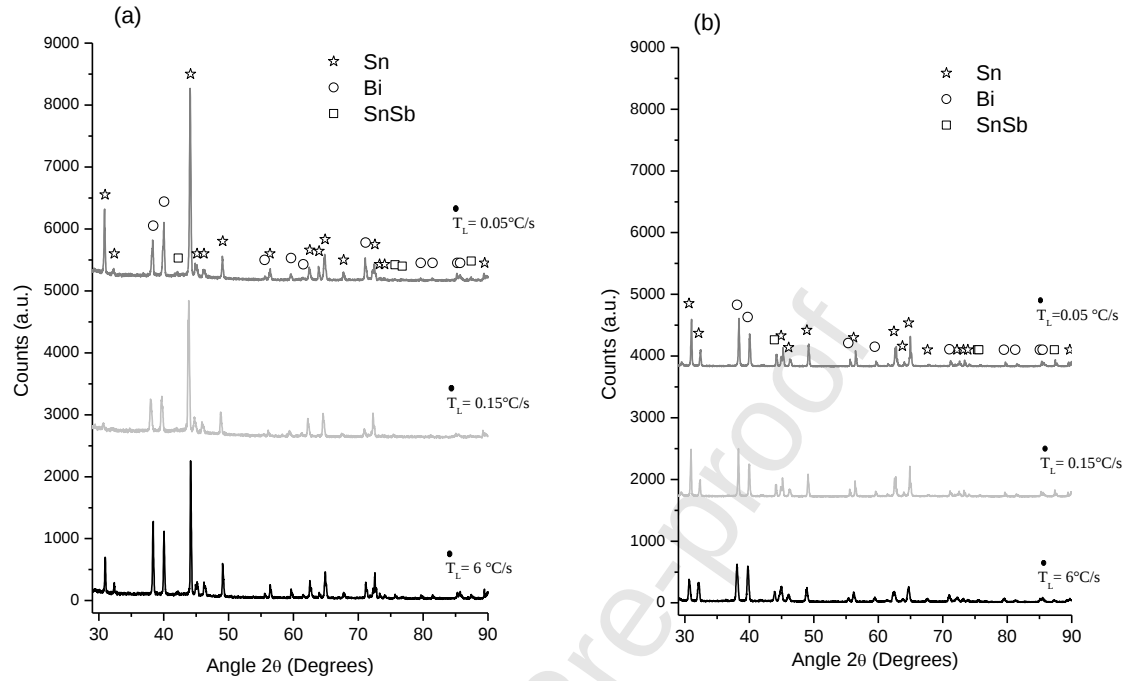


Fig. 14 - X-ray diffraction (XRD) patterns of: (a) Sn-52wt.%Bi-1wt.%Sb and (b) Sn-52wt.%Bi-2wt.%Sb alloys samples.

The experimental Bi and Sb long-range content variations across the DS castings are displayed in Fig. 15. Despite some small enrichment with Bi in the first positions of the castings, overall, the profiles can be considered rather constants, since the deviations from the nominal compositions are quite small. This unchanging of Bi and Sb's compositions guarantees microstructural and mechanical analysis disregarding possible effects arising from compositional variations along the length of both tested alloys castings.

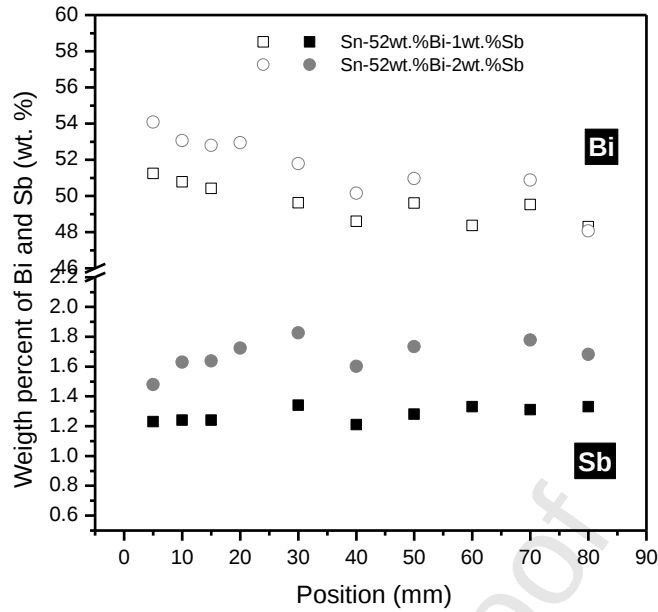


Fig. 15 - Experimental Sb and Bi macrosegregation profiles along the length of the Sn-52wt.% Bi-1wt.% Sb and Sn-52wt.% Bi-2wt.% Sb alloys castings.

3.4 Tensile properties

After evaluating the stress-strain diagrams, it was possible plotting the experimental average and standard deviation values of ultimate tensile strength - σ_u , yield tensile strength - σ_y and strain-to-failure - δ as a function of the corresponding average λ_2 values along the length of the DS castings, as can be seen in Fig. 16.

The joint organization of Sb in solid solution within the Sn-rich matrix and the precipitation of highly hard SnSb particles, promoted strengthening effects in the Sn-Bi(-Sb) alloys. Consequently, excellent tensile strength properties could be achieved. Besides that, Morozumi *et al.* [27] drew attention to the high interface strength between these particles and the Sn-rich matrix. A manner to assess the effects of Sb on the tensile strength is by comparing the present results with those for the binary Sn-Bi alloy [23]. The Sb-modified alloys samples enhanced yield and ultimate tensile strengths by about 20% as compared to those of the binary Sn-Bi alloy.

Even though the tensile strength properties were plotted against the inverse of the square root of λ_2 , which varied from 0.10 to 0.30, independences of these properties from this microstructural parameter could be observed in Fig. 16(a). It appears that the better distribution of the phases forming

the (Sn+Bi) eutectic with the decrease in λ_2 is not a predominant factor affecting the mechanical strength, which is overcome by the strengthening mechanisms provided by either Sb in solid solution or SnSb particles. Furthermore, the strengths are not affected with the increase in the alloy Sb content for all range of λ_2 samples.

Differently from what happened with the tensile strengths, the ductility varied significantly with λ_2 . Hence, a Hall-Petch type curve for strain-to-failure, δ , was fitted to the λ_2 experimental scatter. A single line is able to represent the experimental scatters of both examined alloys castings. If this plot is compared to that obtained by Silva and co-authors [23] for the non-modified Sn-Bi alloy, very close behavior is established. Thus, Sb additions did not impair this property.

Kobayashi *et al.* [28] demonstrated that the crack progress is delayed owing to the formation of SnSb compounds in Sn-Sb alloys. Since SbSn compounds in the Sn-Sb alloy are hard to break, the crack progress must turn around these compounds, which delay the propagation, resulting in higher ductility. In the present results, samples solidified at high cooling rates and with smaller dendritic spacing induce greater Sb supersaturation. Thus, a higher proportion of Sb-bearing compounds are formed, preventing crack progress along the Sn-rich matrix. These samples also present very thin tertiary arms in a more complex dendritic arrangement. The refinement of the dendritic arrangement increases the progress path of the cracks before reaching Bi fragile particles, increasing its coalescence. This explains why improved and balanced tensile properties such as ultimate tensile strength of 71 MPa and ductility of 52% could be attained for $\lambda_2^{-1/2}$ of 0.30 in the case of the Sn-52wt% Bi-2wt.% Sb alloy solidified at approximately 5.0 ° C/s.

In order to have a comparison of the improvements achieved here, Shen *et al.* [9] considered enhanced properties in their research obtained for the Sn-40%Bi-2%Zn-0.1%Cu alloy. This alloy solidified against a massive steel mold achieved 88 MPa of strength and 13.3 % of elongation as its best tensile properties. Despite having higher tensile strength, the plastic region is too short as compared to the present results of the Sn-52wt% Bi (-Sb) alloys.

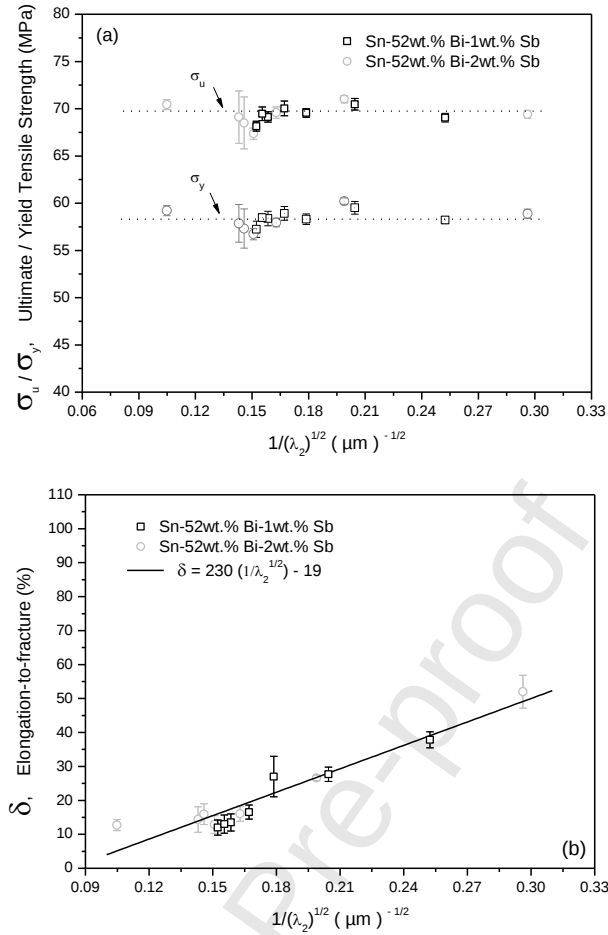


Fig. 16 - (a) Ultimate/yield tensile strengths and (b) elongation-to-fracture as a function of λ_2 for the DS Sn-Bi(-Sb) alloys castings.

3.5 Fracture surface analysis

Considering that the fracture surface characteristics of the two examined Sn-Bi(-Sb) alloys after tensile tests are very similar, it was chosen to present the details found for the Sn-52wt% Bi-2wt.% Sb alloy, as can be observed in Fig. 17. As all fracture surfaces refer to the same alloy composition, the size, morphology and distribution of the phases have a fundamental role, since the ductility varied from 14.4 % to 52 %.

The fracture surface associated with the sample solidified at 5 °C/s demonstrated a particular behavior as compared to the other positions examined. In this case, a typical ductile fracture mode has been noted with formation of dimples all across the area. The prevalence of such fracture mode did not avoid the observation of tongues related to the Sn-Bi eutectic. In the case of the samples associated with slow cooling during solidification, the surface results after tensile tests displayed a pattern with cleavage appearance. The fracture in this case occurred in a more brittle manner due to the coarse Bi-

rich and Sn-rich phases. Overall, the observed patterns are consistent with the elongation results of the tensile tests of the Sn-Bi(-Sb) alloys.

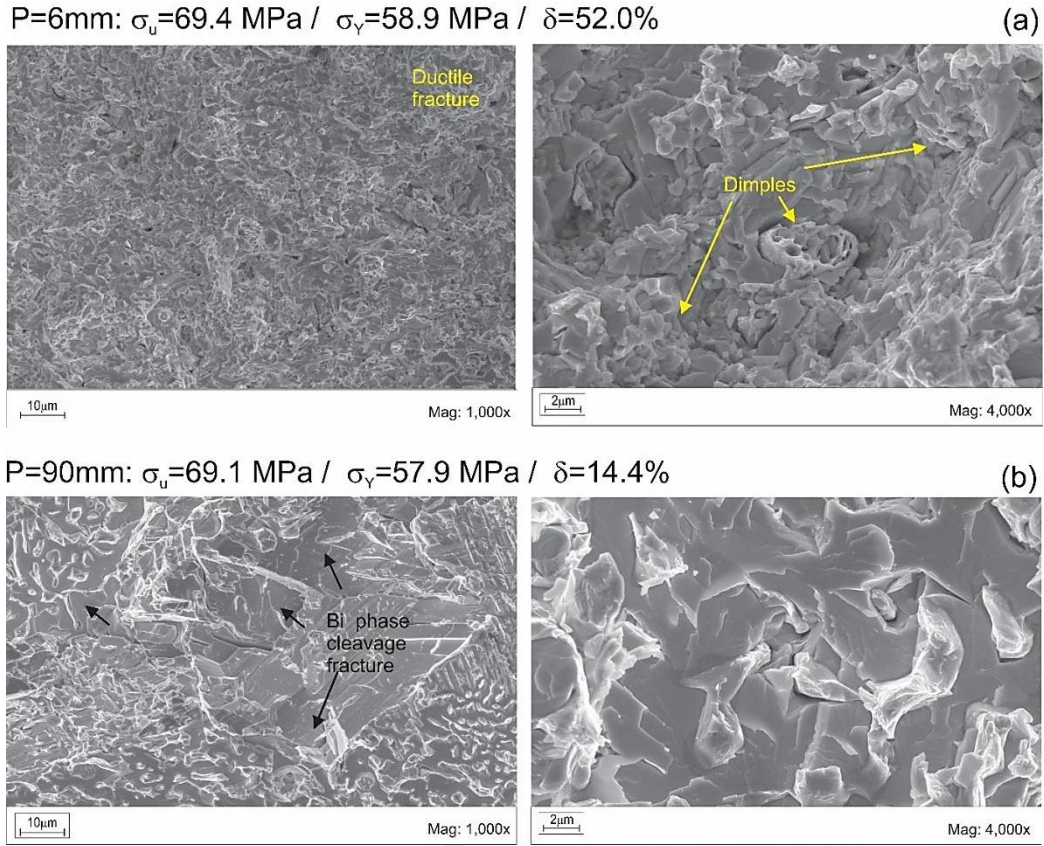


Fig. 17 – Typical SEM fracture surfaces of the Sn-52wt% Bi-2wt.% Sb solder alloy considering two different positions from the cooled surface of the DS casting: (a) 6mm and (b) 90mm, that is, (a) 5.0 °C/s and (b) 0.05 °C/s.

4. Conclusions

- The microstructure along the length of both DS Sn-52wt% Bi-1wt% Sb and Sn-52wt% Bi-2wt% Sb alloys castings was shown to be constituted by Sn-rich dendrites with Bi and SnSb precipitates in their own core, surrounded by a complex regular eutectic morphology, formed by Bi-rich and Sn-rich phases. Moreover, the eutectic was shown to be formed by two scales of lamellar structure, which were defined as being ‘fine’ and ‘coarse’ lamellar eutectic.

- Experimental power function relationships relating the primary (λ_1) and secondary (λ_2) dendrite arm spacings to the cooling rate ($\dot{T}_L$) and the growth rate (V_L) have been determined for both examined Sn-Bi-Sb alloys: $\lambda_1 = 72 (\dot{T}_L)^{-1/3}$; $\lambda_1 = 57 (\dot{T}_L)^{-1/4}$ for the Sn-52Bi-1Sb and Sn-52Bi-2Sb alloys, respectively, and $\lambda_2 = 11 (V_L)^{-1/2}$ for both alloys. As compared to the binary Sn-52wt.% Bi alloy, λ_2 decreased about 30% with the addition of Sb and λ_1 decreased up to about 80%. Moreover, single growth laws have also been derived for each eutectic spacing scale: coarse (λ_{CE}) and fine (λ_{FE}) as a function of V_L : $\lambda_{CE} = 4.0 (V_L)^{-1/5}$ and $\lambda_{FE} = 0.9 (V_L)^{-1/5}$, where $\lambda_{1,2; CE; FE}$ [μm]; $\dot{T}_L$ [K/s] and V_L [mm/s].
- The tensile properties: ultimate (σ_u) and yield (σ_y) strengths and strain to failure (δ) were experimentally related to λ_2 for both examined alloys and compared to results of the binary Sn-52wt.% Bi alloy, indicating that: (i) the Sb additions increased the alloy strength while preserving the ductility; (ii) the tensile strengths were shown not to be affected by either the Sb content of the examined ternary alloys nor by the magnitude of λ_2 along the length of the castings, and (iii) in contrast, despite having the same evolution for both ternary alloys, the ductility varied significantly with λ_2 , i.e. from 14.4 % to 52 % according to an experimental equation given by $\delta = 230 (1/\lambda_2^{1/2}) - 19$.

Acknowledgements

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References

- [1] N. K. Kesarkar, T.M.; Sardana, “How TIM impacts thermal performance of electronics: A thermal point of view study to understand impact of Thermal Interface Materials (TIM),” in *International Conference on Electronics Packaging -ICEP*, 2019, pp. 200–206.
- [2] J. Due and A. J. Robinson, “Reliability of thermal interface materials: A review,” *Appl. Therm. Eng.*, vol. 50, no. 1, pp. 455–463, Jan. 2013, doi: 10.1016/j.applthermaleng.2012.06.013.

- [3] R. Zhang *et al.*, “Thermal Resistance Analysis of Sn-Bi Solder Paste Used as Thermal Interface Material for Power Electronics Applications,” *J. Electron. Packag.*, vol. 136, no. 1, Mar. 2014, doi: 10.1115/1.4026616.
- [4] J. G. Bai, Z. Z. Zhang, G.-Q. Lu, and D. P. H. Hasselman, “Measurement of Solder/Copper Interfacial Thermal Resistance by the Flash Technique,” *Int. J. Thermophys.*, vol. 26, no. 5, pp. 1607–1615, Sep. 2005, doi: 10.1007/s10765-005-8107-4.
- [5] K. Stinson-Bagby, D. Huff, D. Katsis, D. Van Wyk, and G. Q. Lu, “Thermal performance and microstructure of lead versus lead-free solder die attach interface in power device packages,” in *IEEE International Symposium on Electronics and the Environment, 2004. Conference Record. 2004*, pp. 27–32, doi: 10.1109/ISEE.2004.1299683.
- [6] C.-P. Chiu, J. G. Maveety, and Q. A. Tran, “Characterization of solder interfaces using laser flash metrology,” *Microelectron. Reliab.*, vol. 42, no. 1, pp. 93–100, Jan. 2002, doi: 10.1016/S0026-2714(01)00129-9.
- [7] S. Sakuyama, T. Akamatsu, K. Uenishi, and T. Sato, “Effects of a Third Element on Microstructure and Mechanical Properties of Eutectic Sn-Bi Solder,” *Trans. Japan Inst. Electron. Packag.*, vol. 2, no. 1, pp. 98–103, 2009, doi: 10.5104/jiepeng.2.98.
- [8] C. ZHANG, S. LIU, G. QIAN, J. ZHOU, and F. XUE, “Effect of Sb content on properties of Sn—Bi solders,” *Trans. Nonferrous Met. Soc. China*, vol. 24, no. 1, pp. 184–191, Jan. 2014, doi: 10.1016/S1003-6326(14)63046-6.
- [9] J. Shen, Y. Pu, H. Yin, D. Luo, and J. Chen, “Effects of minor Cu and Zn additions on the thermal, microstructure and tensile properties of Sn-Bi-based solder alloys,” *J. Alloys Compd.*, vol. 614, pp. 63–70, Nov. 2014, doi: 10.1016/j.jallcom.2014.06.015.
- [10] Z. Mei and J. W. Morris, “Characterization of eutectic Sn-Bi solder joints,” *J. Electron. Mater.*, vol. 21, no. 6, pp. 599–607, Jun. 1992, doi: 10.1007/BF02655427.
- [11] L. Mostofizadeh, M.; Pippola, J.; Frisk, “Reliability and microstructural evolution of Sn- Bi-Ag solder paste during salt spray test,” in *Carts International*, pp. 2163–2170.
- [12] T.-H. Chuang and H.-F. Wu, “Effects of Ce Addition on the Microstructure and Mechanical Properties of Sn-58Bi Solder Joints,” *J. Electron. Mater.*, vol. 40, no. 1, pp. 71–77, Jan. 2011, doi: 10.1007/s11664-010-1385-z.
- [13] A. Xiaowu, H.; Ke, L.; Fanrong, “Research on lamellar structure and micro-hardness of directionally solidified Sn-58Bi eutectic alloy,” *China Foundry*, vol. 9, pp. 360–365, 2012.
- [14] F. Hua, Zequn Mei, and J. Glazer, “Eutectic Sn-Bi as an alternative to Pb-free solders,” in *1998 Proceedings. 48th Electronic Components and Technology Conference (Cat. No.98CH36206)*, pp. 277–283, doi: 10.1109/ECTC.1998.678706.
- [15] E. P. Wood and K. L. Nimmo, “In search of new lead-free electronic solders,” *J. Electron. Mater.*, vol. 23, no. 8, pp. 709–713, Aug. 1994, doi: 10.1007/BF02651363.
- [16] M. M. EL-Bahay, M. E. EL Mossalamy, M. Mahdy, and A. A. Bahgat, “Study of the mechanical and thermal properties of Sn-5 wt% Sb solder alloy at two annealing temperatures,” *Phys. status solidi*, vol. 198, no. 1, pp. 76–90, Jul. 2003, doi: 10.1002/pssa.200306592.
- [17] A. Torres, L. Hernández, and O. Domínguez, “Effect of Antimony Additions on Corrosion and Mechanical Properties of Sn-Bi Eutectic Lead-Free Solder Alloy,” *Mater. Sci. Appl.*, vol. 03, no. 06, pp. 355–362, 2012, doi: 10.4236/msa.2012.36051.

- [18] M. D. Abràmoff, P. J. Magalhães, and S. J. Ram, “Image Processing with ImageJ Second Edition,” *Biophotonics Int.*, vol. 11, no. 7, pp. 36–42, 2004, doi: 10.1017/CBO9781107415324.004.
- [19] M. Gündüz and E. Çadırlı, “Directional solidification of aluminium–copper alloys,” *Mater. Sci. Eng. A*, vol. 327, no. 2, pp. 167–185, Apr. 2002, doi: 10.1016/S0921-5093(01)01649-5.
- [20] D. W. Henderson *et al.*, “Ag 3 Sn plate formation in the solidification of near ternary eutectic Sn–Ag–Cu alloys,” *J. Mater. Res.*, vol. 17, no. 11, pp. 2775–2778, Nov. 2002, doi: 10.1557/JMR.2002.0402.
- [21] L. Shen, P. Septiwerdani, and Z. Chen, “Elastic modulus, hardness and creep performance of SnBi alloys using nanoindentation,” *Mater. Sci. Eng. A*, vol. 558, pp. 253–258, Dec. 2012, doi: 10.1016/j.msea.2012.07.120.
- [22] W. R. Osório, L. C. Peixoto, L. R. Garcia, N. Mangelinck-Noël, and A. Garcia, “Microstructure and mechanical properties of Sn–Bi, Sn–Ag and Sn–Zn lead-free solder alloys,” *J. Alloys Compd.*, vol. 572, pp. 97–106, Sep. 2013, doi: 10.1016/j.jallcom.2013.03.234.
- [23] B. L. Silva, G. Reinhart, H. Nguyen-Thi, N. Mangelinck-Noël, A. Garcia, and J. E. Spinelli, “Microstructural development and mechanical properties of a near-eutectic directionally solidified Sn–Bi solder alloy,” *Mater. Charact.*, vol. 107, pp. 43–53, 2015, doi: 10.1016/j.matchar.2015.06.026.
- [24] J. D. Jackson, K.A.; Hunt, “Lamellar and rod eutectic growth,” *Trans. Met. Soc. AIME*, vol. 236, pp. 1129–1142, 1966.
- [25] F. A. . Hansen, M.; Elliott, R.P.; Shunk, *Constitution of binary alloys*. New York: McGraw-Hill, 1958.
- [26] V. P. Vasil’ev, “A complex study of the phase diagram of the SnSb system,” *J. Phys. Chem.*, vol. 79, no. 1, pp. 20–28, 2003.
- [27] H. Okamoto, “Bi-Sb (Bismuth-Antimony),” *J Phase Equilib Diff*, vol. 33, pp. 493-494, 2012.
- [28] A. Morozumi, H. Hokazono, Y. Nishimura, E. Mochizuki, and Y. Takahashi, “Influence of Antimony on Reliability of Solder Joints Using Sn-Sb Binary Alloy for Power Semiconductor Modules,” *Trans. Japan Inst. Electron. Packag.*, vol. 8, no. 1, pp. 8–17, 2015, doi: 10.5104/jiepeng.8.8.
- [28] T. Kobayashi, K. Kobayashi, K. Mitsui, and I. Shohji, “Comparison of Sn-5Sb and Sn-10Sb Alloys in Tensile and Fatigue Properties Using Miniature Size Specimens,” *Adv. Mater. Sci. Eng.*, vol. 2018, pp. 1–9, Jun. 2018, doi: 10.1155/2018/1416942.

List of figure captions

Fig. 1 - Representation of the upward directional solidification furnace: 1 - acquired cooling curves; 2 - ceramic insulation; 3 - electric resistances; 4 - stainless-steel mold; 5 - type J thermocouples; 6 - data logger; 7 - water flow circulation; 8 - flowmeter; 9 - temperature controller; 10 - molten alloy and 11 - water-cooled bottom part.

Fig. 2 - Stable mass phase fraction as a function of temperature of the (a) Sn-52wt.% Bi, (b) Sn-52wt.% Bi-1wt.% Sb and (c) Sn-52wt.% Bi-2wt.% Sb alloys computed using TCSLD3 database of the Thermo-Calc software. SBSN_B1_NACL#2: SnSb, RHOMBOHEDRAL_A7: Bi-rich and BCT_A5: Sn-rich phases.

Fig. 3 - Schematic drawing of (a,c) transverse and (b) longitudinal sections as used for measurement procedures related to dendritic and eutectic spacings, that is, intercept method for λ_{FE} , λ_{CE} , λ_2 and λ_3 and triangle method for λ_1 . 'L' is the length of the line while 'n' is the number of intercepted phases.

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Fig. 7 - Macrostructure and some representative microstructures revealed along the length of the DS Sn-52wt% Bi-1wt% Sb alloy casting. Samples at 5 mm, 50 mm and 90 mm are associated with $\dot{T}_L = 6.0$ °C/s, $\dot{T}_L = 0.15$ °C/s and $\dot{T}_L = 0.05$ °C/s, respectively.

Fig. 8 - Macrostructure and some representative microstructures revealed along the length of the DS Sn-52wt% Bi-2wt% Sb alloy casting. Samples at 5 mm, 50 mm and 90 mm are associated with $\dot{T}_L = 6.0$ °C/s, $\dot{T}_L = 0.15$ °C/s and $\dot{T}_L = 0.05$ °C/s, respectively.

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Fig. 11 - Coarse (λ_{CE}) and fine (λ_{FE}) eutectic spacing variations with the growth rate (V_L) for the Sn-Bi(-Sb) solder alloys.

Fig. 12 - Elemental SEM-EDS mappings associated with transverse specimens solidified at 0.05 °C/s for the (a) Sn-52wt.% Bi-1wt.% Sb and (b) Sn-52wt.% Bi-2wt.% Sb alloys (magnification: 6,000x).

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RESEARCH HIGHLIGHTS

- The growth of complex regular Sn+Bi eutectic prevailed for the ternary Sn-Bi(-Sb) alloys.
- Bi showed a higher rate of precipitation while Sb was more kept in solid solution.
- Sb additions increased the alloy strength while preserving the ductility.
- Enhanced tensile properties could be attained for the Sn-Bi(-Sb) samples having $\lambda_2^{-1/2}$ of 0.30.

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