A comparative analysis of microstructural features, tensile properties and wettability of hypoperitectic and peritectic Sn-Sb solder alloys

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ABSTRACT

Sn-Sb alloys are among the current alternatives for the development of alloys for high-temperature lead-free solders. The Sn-Sb alloys having 5.5 wt.% Sb or less are known to have good mechanical properties, and despite the quite low liquidus temperature have been considered adequate in the development of solder joints. The increase in the Sb content up to the limit of solubility in Sn at about 10 wt.% is supposed to be detrimental to the mechanical properties due to the extensive formation of an intermetallic compound. Investigations on the interrelation of microstructure of this alloy and the corresponding mechanical properties are fundamental to an appropriate evaluation of its application in solder joints. The present investigation analyses the relationship between microstructural features of the peritectic Sn-10 wt.% Sb alloy, solidified under a wide range of cooling rates, and the resulting mechanical properties. A cellular β-Sn matrix, typified by cellular spacings that decrease with the increase in the solidification cooling rate, and Sn3Sb2 particles are shown to characterize the alloy microstructure. The ultimate tensile strength is higher as compared with the corresponding values of the hypoperitectic Sn-5.5 wt.% Sb solder alloy, however the elongation is shown to decrease. A comparison with Bi-Ag alloys, considered good high temperature soldering alternatives, has shown that the tensile properties of the Sn-10 wt.% Sb alloy, including elongation, are significantly higher. Wettability tests have been carried out and the experimental results, according to reports from the literature, are associated with good wettability.

1. Introduction

In the light of pressures to remove lead from electronics around the world, the lead-free manufacturing has demanded studies on new solder alloys to replace the traditional tin-lead alloys, which were the mainstay of the electronics industry in the last century. Not only yield production but also field reliability has been the challenging issues faced by various candidate alloys that hardly compete with lead-based alloys in terms of cost and technical benefits, such as low processing temperatures associated with appropriate mechanical properties. Each lead-free alloy has advantages and disadvantages i.e., none alloy is recognized to fit all demands, and in this sense each different alloy composition is suitable for niche applications [1–5]. A particular process, known as step soldering, involves solder alloys related to high temperature electronic devices (from 270 °C to 350 °C), in which multiple solders of successively lower melting points are used in consecutive joints, in order to preserve the integrity of earlier soldered joints [6–8]. This kind of technique employs mostly alloys far from eutectic compositions, but with higher melting temperatures, and aggregating as consequence, more complex transformations such as the peritectic one. The literature is scarce on information related to solder alloys comprising a peritectic reaction, denoting a gap to be explored in terms of characterization of microstructure and determination of properties.

The peritectic reaction is an invariant transformation in which a liquid phase (L) reacts with a solid phase (α) on cooling, giving rise to a second solid phase (β), i.e., L + α → β. The solid (α) separate out from (L) at the peritectic temperature and must dissolve in L, and β must freeze out of L. Because the high cooling rates used in industrial processing, the completion of the equilibrium peritectic reaction is rarely observed, since β surrounds α and the peritectic reaction is stifled since L cannot reach α [9]. The literature reports works on peritectic alloys under fast cooling rates such as: ferrous [10–12] and non-ferrous alloys [13–16]. Regarding the soldering process, high cooling rates are
inherent during solidification inducing the formation of metastable phases. The Sn-Cu [17] and Sn-Sb [18] alloys systems are practically the only binary tin-based alloy systems used in high temperature soldering that undergo peritectic reactions. There exists a broad literature related to alloys of the Sn-Cu system, although more concentrated in low temperature applications, because of its importance as base of ternary alloys such as Sn-Cu-Ni [19,20] and Sn-Ag-Cu alloys [21,22]. On the other hand, the same does not occur in similar extent to alloys of the Sn-Sb system, which deserve to be investigated in greater depth.

A peritectic reaction, \( \text{L} + \text{Sn}_3\text{Sb}_2 \rightarrow \text{Sn} (\beta) \), occurs at the tin-rich part of the Sn-Sb binary phase diagram (243 °C), and from the peritectic composition the liquidus temperature \( T_L \) increases with increasing Sb content [7,23]. It is worth noting the existence of conflicting interpretation in the literature concerning the composition of the first solid phase to separate out from the liquid at the liquidus temperature (i.e. the intermetallic compound - IMC). The occurrence of either \( \text{Sn}_3\text{Sb}_2 \) or \( \text{SnSb} \) IMCs is reported in the literature. Some works affirm that \( \text{Sn}_3\text{Sb}_2 \) decomposes into SnSb and \( \beta \) below 242 °C [24,25]. The most promising Sn-Sb alloys for soldering are the Sn-5wt.%Sb, which has a near peritectic composition, and the Sn-10 wt.% Sb alloy, the peritectic composition. Kim and collaborators [6] have obtained samples of Sn-5 wt.% Sb and Sn-10 wt.% Sb alloys solidified in air and performed characterization of the resulting phases using X-ray diffraction and energy-dispersive X-ray analyses. For both alloys, a \( \beta \)-Sn matrix and \( \beta \)-SbSn were shown to constitute the microstructure. Recently, Yilmaz and collaborators using the same characterization techniques, found the same phases in a Sn-10.2 wt.% Sb alloy directionally solidified under steady-state conditions [26]. The Sn-5.5wt.%Sb alloy was reported to have both good mechanical strength and creep properties, which are fundamental to pin-attachment reliability. Dias et al. [18] established

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### Table 1
Chemical composition (wt.%) of metals used to prepare the Sn-10 wt.% Sb alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pb</th>
<th>Fe</th>
<th>Sb</th>
<th>Sn</th>
<th>Cd</th>
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<th>Cu</th>
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<td>0.0047</td>
<td>0.0046</td>
<td>0.0001</td>
<td>–</td>
</tr>
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<td>0.075</td>
<td>Balance</td>
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<td>–</td>
<td>0.034</td>
<td>0.034</td>
<td>–</td>
<td>–</td>
<td>0.009</td>
</tr>
</tbody>
</table>

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Fig. 1. Schematic representation of the solidification experimental setup.
correlations between the length scale of the microstructure of monophase Sn-2 wt.% Sb and Sn-5.5 wt.% Sb alloys and the corresponding tensile properties, and demonstrated that the size of the cellular matrix has a significant effect on the tensile properties of the Sn-5.5 wt.% Sb alloy. With the increase in the alloy Sb content, the extensive formation of the intermetallic phase has been considered to have possible deleterious effect on the mechanical properties, mainly when the maximum solubility of Sb in Sn is reached, i.e. about 10 wt.% Sb [1,27,28].
2. Experimental procedure

2.1. Solidification experiment

A water-cooled directional solidification setup was used, in which transient solidification takes place vertically upwards from a water-cooled bottom made of low carbon steel, as shown schematically in Fig. 1. Some of the present authors and collaborators have described the casting assembly, mold details and the thermocouples arrangement along the length of the casting in previous studies [15,29]. The alloy was melted in situ and the lateral electric heaters had their power controlled in order to achieve a desired melt superheat. In the case of the present experiments when a superheat of 10% above the liquidus temperature was reached, the electric heaters were disconnected and at the same time the water flow was initiated, thus permitting the onset of solidification. The compositions of metals used to prepare the Sn-10 wt. % Sb alloy are shown in Table 1. The amount of Pb in Sn, is in accordance with ASTM B339 “Standard specification for pig tin”, for Tin Grade “A”, which prescribes a lead content < 0.05 wt.%. The dashed line in the phase diagram of Fig. 2 indicates the Sn-10 wt.% Sb alloy. The liquidus temperature (Tl = 268 °C) has been determined by slowly cooling the molten alloy in a refractory crucible having a thermocouple placed in its center. Such arrangement permitted the cooling curve under conditions close to equilibrium, and consequently the change in slope corresponding to the liquidus temperature to be determined.

The solidification setup imposes a wide range of different cooling rates permitting, as a result, a significant variation in microstructure features in a single casting experiment. The cooling curves, recorded by each thermocouple positioned along the length of the directionally solidified (DS) castings, have been used to determine the solidification cooling rates.

2.2. Microstructural characterization

Selected transverse (perpendicular to the growth direction) and longitudinal samples extracted at different locations along the length of the DS casting were polished and etched (with a solution 2% HCl, 3% NH4NO3 and 95% alcohol) for metallography. The same solution was used for checking local alloy composition, were extracted along different positions from the cooled surface of the DS casting. The etching process was performed by carefully immersing the samples in the etchant for only a few seconds, followed by cleaning the samples surface with running water and ethanol. Optical microscopy was performed using an Olympus Inverted Metallurgical Microscope (model 41GX) and the Inca and Nordlys softwares were used, respectively, for the analyses. In order to characterize the intermetallic compounds (IMCs) through Wavelength-Dispersive Spectroscopy (WDS) and Electron Backscatter Diffraction (EBSD) techniques, the surface of the samples was carefully polished with colloidal silica using an automatic polishing machine (Vibromet 2). A Scanning Electron Microscope (SEM) ZEISS-EVO-MA15 equipped with WDS and EBSD, both from Oxford Instrumental, and the Inca and Nordlys softwares were used, respectively, for the analyses.

2.3. Tensile tests

Transverse specimens were extracted from different positions along...
the length of the DS casting, as shown schematically in Fig. 3, and prepared for tensile testing according to specifications of the ASTM Standard E 8M and tested in a MTS 810 machine at a strain rate of about $3 \times 10^{-3} \text{s}^{-1}$. Since the solidification cooling rate is high at regions close to the bottom of the DS casting, decreasing progressively toward the top of the casting, the scale of the microstructure is affected accordingly, i.e., smaller values are associated with regions close to the cooled bottom increasing toward the top of the casting. With a view to examining the effect of the scale of the microstructure on the tensile properties, the tensile specimens were extracted from transverse sections, as shown in Fig. 3. The approach is similar to the representation of a smooth continuous curve (e.g., represented by the trend of experimentally measured cellular spacings along the length of the castings) by a discrete variation in steps. That is, each step is related to a mean $\lambda_c$ value that is the same all along each tensile specimen.

In order to ensure the reproducibility of results, three specimens were tested for each selected position, so that average tensile properties were determined: yield tensile strength ($\sigma_y$), ultimate tensile strength ($\sigma_u$) and elongation ($\delta$).

2.4. Wettability tests

For the wetting tests, specimens consisting of 4.0 mm-height × 4.0 mm-diameter cylindrical bars were extracted from the central part of the DS castings. The samples were dried properly and finally coated by adequate flux (RMA – Rosin Mildly Activated) for testing. The specimens were individually placed on the tester, heated at a rate of 10 °C/min up to temperatures of 20% above the corresponding liquidus temperature of the alloy. The contact angles ($\theta$) were measured in a Goniometer Krüss DSHAT HTM Reetz GmbH model from the average of $\theta_R$ and $\theta_L$ (R—right and L—left) values provided by a computational method (tangent-2) and three tests were carried out for each couple solder alloy/carbon steel substrate. The contact angles have been measured continuously as far as the form of the molten droplet changed.

3. Results and discussion

3.1. Solidification cooling rate, growth rate and microstructure features

The cooling curves acquired during directional solidification of the Sn-10 wt.% Sb alloy are shown in Fig. 4a. They represent the thermal evolution at five different positions along the length of the DS casting measured by thermocouples placed along the centerline of the casting.
shown in Fig. 7. For comparison purposes the corresponding growth [18], has also been included in Fig. 7. It can be seen that the increase in each of the thermocouples, as shown in Fig. 4b as a function of position (P) along the length of the casting.

These temperature-time data allowed the solidification cooling rate (T) to be determined. T has been computed by the time-derivative of the cooling curve (dT/dt) right after the passage of the liquidus isotherm by each of the thermocouples, as shown in Fig. 4b as a function of position (P) along the length of the casting.

It can be seen in Fig. 5 that the DS casting has a typical columnar macrostructure, with the grains aligned along the heat flow path, up to about 25 mm from the cooled bottom. The corresponding optical microstructures shows a cellular β-Sn matrix, characterized by cellular spacings (λc), which increase with the increase in T, as shown in Fig. 5 for P = 4 and P = 10 mm.

With a view to permitting the occurrence of eventual macrosegregation profiles along the length of the DS castings to be analyzed, the experimental Sn and Sb concentrations have been determined, as shown in Fig. 6. The experimental points are quite close to the alloy nominal composition, thus demonstrating that the vertical directional solidification has not induced macrosegregation profiles.

The evolution of λc as a function of T, during the directional solidification of the Sn-10 wt.% Sb alloy, has been experimentally determined and is plotted in Fig. 7. An experimental growth law in the form of a power function relating λc to T has been derived and is also shown in Fig. 7. For comparison purposes the corresponding growth law determined for the Sn-5.5 wt.% Sb solder alloy in a previous study [18], has also been included in Fig. 7. It can be seen that the increase in the alloy solute content gives rise to increase in the cellular spacing (the multiplier of the experimental equation increases with the increase in the alloy Sb content), while preserving a same exponent for both experimental equations.

Since there is some controversy in the literature about the composition of the primary intermetallic phase (IMC), with reports of occurrence of either Sn-Sb [6,32] or SnSb2 [7] IMCs, a deeper microstructural analysis has been carried out by using different characterization techniques such as: X-ray diffractometry (XRD), electron microscopy (SEM)/Wavelength-dispersive spectroscopy (WDS) and Electron backscatter diffraction (EBSD).

Fig. 8 shows the XRD diffraction patterns (CuKα radiation i.e., λ = 1.5418 Å), of samples extracted from positions along the DS casting associated with quite different solidification cooling rates (T = 7.3; 14 and 23.5 K/s). The XRD patterns were compared with crystallographic data from the Inorganic Crystal Structure Database–ICSD [33] and the JCPDS - Joint Committee on Powder Diffraction Standards file number 04-16-8009. It can be seen that despite the significant differences in T, the SnSb2 IMC has been identified in any alloy sample examined. Furthermore, selected SEM microstructures and WDS analyses have also been employed to determine the phase composition of the IMC particles disseminated throughout the microstructure, as shown by the SEM image of Fig. 9a. Table 2 shows the elemental SEM-WDS results of the IMC particles: 43.3 wt.% Sb and 56.7 wt.% Sn. Chen et al. [7] reported that the SnSb2 IMC was found to have 43.2 wt.% Sb and 56.2 wt.% Sn, which are values quite close to those experimentally determined in the present study.

According to Okamoto [30] the crystal structure of the SnSb2 IMC is still unknown. Lidin et al. [34] emphasize the enigmatic nature of such compound and report that some evidences indicate a possible cubic structure, however, they pointed out that even one of the elements forming such compound, i.e. Sb, has in fact a rhombohedral distorted cubic lattice. The EBSD micrograph of Fig. 9b, and Backscatter Kikuchi patterns (Fig. 9c) obtained through this technique, have shown the presence of the SnSb2 IMC that, associated with the X-ray diffraction data of Fig. 8 (with high intensity angles of 2θ = 28.9° and 41.6°), give evidences that the Sn3Sb2 IMC has a rhombohedral crystal phase: Fm-3m Wycko space group and lattice parameters: a = 0.434 nm, b = 0.434 nm, c = 0.523 nm [33]. The β-Sn phase has been identified by XRD patterns in Fig. 8, with high intensity angles of 2θ = 30.5°, 31.9° and 44.7°. Also, the detection of this crystalline phase allows establishing a correspondence of these results with those observed in the EBSD patterns of Fig. 9b, since the β-Sn phase has a tetragonal crystal phase, R-3m Wycko space group and lattice parameters: a = 0.583 nm, b = 0.583 nm, c = 0.318 nm [34–36].

3.2. Tensile properties and wettability

The length scale of the cellular microstructure was shown to affect hardness and tensile properties of a number of solder alloys. Refined microstructures having lower cellular spacings, which are associated with higher cooling rates during solidification, have been related to higher hardness for Zn-(10–40 wt.%Sn) alloys [37] and higher tensile strength for Sn-0.7wt.%Cu-xNi (0–0.1wt.%Ni) [38]; Sn-2.0 and 5.5 wt. % Sb alloys [18]. This is generally attributed to the more homogeneous distribution of the reinforcing phase throughout the microstructure typified by cells that are more refined. The morphology and the representative length scale of the microstructure of a Sn-based solder was also shown to affect other final properties, such as the electrochemical corrosion resistance [39].

In the present study, along the range of experimental cellular spacings examined, the tensile properties, that is, the ultimate tensile stress (σu), the yield stress (σy: 0.2% proof stress) and the elongation (δ) were shown not to be affected by the size of the cells. The reinforcing phase, that is, the SnSb2 IMC particles (shown in Fig. 9) seem to be more effective in the blockage of dislocations making the role of the scale of
the cellular $\beta$-Sn matrix not significant. This is reflected by the constant values of ultimate and yield strengths and elongation vs. the cellular spacing, shown in Fig. 10. However, a previous study with the monophasic Sn-5.5wt.%Sb alloy [18] has shown that the increase in the cellular spacing provokes decrease in tensile strength and increase in elongation, and these results have been inserted in Fig. 10 for comparison purposes. These results refer to cooling rates higher than 1.2 K/s, i.e., despite having a monophasic alloy composition, the non-equilibrium solidification conditions induced the presence of lower Sn$_3$Sb$_2$ volume fraction. Under these microstructural conditions associated with the Sn-5.5wt.%Sb matrix, the more refined cells have played a reinforcement role, that is, with a more complex cellular network, the cell boundaries contributed to block more efficiently the motion of dislocations, thus increasing the tensile properties with the decrease in the cellular spacing, as shown in Fig. 10a and b. Such increase in strength is associated with the way the refined microstructure makes the dislocation pile-up more efficient during deformation. Smaller cellular spacings are related to better distribution of the harder Sn$_3$Sb$_2$ phase throughout the alloy microstructure.

It can be seen in Fig. 10 that both $\sigma_u$ and $\sigma_y$ values of the Sn-10wt.%Sb alloy are quite higher when compared with the corresponding values of the Sn-5.5wt.%Sb alloy (from 18% up to 51% and 10% up to 47% for

![Fig. 9. (a) SEM image highlighting the distribution of IMCs throughout the Sn-10 wt.% Sb alloy microstructure; (b) EBSD micrograph: Sn$_3$Sb$_2$ (black) and $\beta$-Sn (gray); (c) Typical Backscatter Kikuchi Pattern of the Sn$_3$Sb$_2$ IMC.](image)

<table>
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<tr>
<th>Element</th>
<th>wt.%</th>
<th>Sigma</th>
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<td>Sb</td>
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</tr>
<tr>
<td>Sn</td>
<td>56.678</td>
<td>0.162</td>
</tr>
<tr>
<td>Total</td>
<td>100.000</td>
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</table>

Table 2 Composition of the IMCs analyzed by WDS.
σ_u and σ_y, respectively). This is explained by the higher volume fraction of the hard Sn_sSb_2 particles that are present in the microstructure of the Sn-10 wt.% Sb alloy. In contrast, the elongation decreased from 0.4 up to 2.5 times. The mean experimental values of tensile properties obtained for the Sn-10 wt.% Sb alloy are: σ_u = 53 MPa, σ_y = 44 MPa and δ = 16%. Suganuma et al. [2] evaluated various characteristics of high-temperature lead-free alternative solders and concluded that Zn-Sn and Bi-Ag alloys are among the best choices. Comparing the present results with those reported in the study of Suganuma et al. [2], it can be seen that σ_u and δ of the Sn-10wt.%Sb alloy are lower than the corresponding values of the Zn-Sn alloys, while σ_y values are similar. However, when compared with the values reported by the Bi-Ag alloys, the tensile properties of the Sn-10 wt.% Sb alloy are significantly higher.

Fig. 11 depicts the progression of contact angles along the wetting ability tests of Sn-5.5 wt.% Sb and Sn-10 wt.% Sb alloys on a carbon steel substrate. The inset images refer to the initial contact angles.
The initial contact angles of both alloys tested are quite close, that is, 45.1° and 43.7° for the Sn-5.5 wt.% Sb and Sn-10wt.%Sb alloys, respectively. The present results are in agreement with some studies reported in the literature. Mahidhara et al. [40] reported a contact angle of 43 ± 4° for the Sn-Swt.%Sb alloy, which has been considered adequate for solder joints in microelectronics packaging. Plevachuk et al. [41] carried out an experimental study of density, surface tension and contact angle of Sn-Sb based alloys and concluded that a contact angle of 40° is associated with good wettability. Kim et al. [6] investigated the wettability of Sn-5 wt.% Sb and Sn-10wt.%Sb alloys on Cu and Ni substrates and reported contact angles of 13° (Cu); 14° (Ni) and 46° (Cu); 28° (Ni), respectively.

4. Conclusions

The following conclusions can be drawn from the present experimental investigation:

- Under the range of experimental cooling rates examined (2.5 to 25 K/s) the optical microstructures of the Sn-10 wt.% Sb alloy were shown to be characterized by a cellular β-Sn matrix, with the cellular spacing, \( \lambda_c \), increasing with the decrease in the solidification cooling rate, \( T_c \). An experimental growth law relating \( \lambda_c \) to \( T_c \) has been proposed.
- SEM images have shown IMC particles disseminated throughout the microstructure. The composition of such IMC has been identified as Sn$_2$Sb$_2$ by SEM-WDS, XRD and EBSD analyses.
- The ultimate tensile stress (\( \sigma_u \)), the yield stress (\( \sigma_y \)) and the elongation (\( \delta \)) of the Sn-10wt.%Sb alloy were shown not to be affected by the size of the cells. The mean experimental values were shown to be: \( \sigma_u = 53 \text{ MPa}, \sigma_y = 44 \text{ MPa} \) and \( \delta = 16\% \). These tensile strength values, are quite higher when compared with the corresponding values of the Sn-5.5 wt.% Sb solder alloy, however, the elongation decreased. As compared to values reported in the literature for high-temperature Bi-Ag solder alloys, the tensile properties of the Sn-10 wt.% Sb alloy are significantly higher.
- The results of wettability tests of Sn-5.5 wt.% Sb and Sn-10 wt.% Sb alloy samples indicated contact angles of 45.1° and 43.7° for the Sn-5.5 wt.% Sb and Sn-10 wt.% Sb alloys, respectively, that, according to reports in the literature, are associated with good wettability.
- The melting point of 268° C associated with the good mechanical properties and wettability determined in the present study, give indications that the peritectic Sn-10 wt.% Sb alloy can also be a competitive high-temperature lead-free solder alternative.

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