Correlation between microstructure and hardness of a Bi-1.5wt%Ag lead-free solder alloy

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Abstract. In the present study a hypoeutectic Bi-1.5wt%Ag alloy was directionally solidified under transient heat flow conditions and the microstructure was analysed. Bi-Ag alloys are considered as potential alternatives to replace Pb-based alloys as solder materials for metallic connections under high temperatures. However, a lack of understanding regarding the effects of solidification thermal parameters (growth rate - \( V_L \), the cooling rate - \( \dot{T} \)) on microstructural aspects is reported in literature. Another challenge is to improve properties and reliability. The results of the present study include the determination of the tip growth rate and the cooling rate by cooling curves recorded by thermocouples positioned along the casting length, metallography, X-ray fluorescence (XRF) and Vickers hardness. The entire directionally solidified Bi-1.5Ag microstructure was arranged by faceted Bi-rich dendrites surrounded by a eutectic mixture (Bi+Ag). The primary and secondary dendrite arm spacing (\( \lambda_1 \) and \( \lambda_2 \)), the interphase spacing (\( \lambda \)) and the diameter of Ag-rich particles were also measured along the casting length; and experimental growth laws. Relating these microstructural features to the experimental thermal parameters are proposed.

1. Introduction
During the last decades lead-based eutectic or near-eutectic alloys have been massively used as solders in electronic packaging and assembly. Due to the inherent negative impacts to human health and environment, nowadays lead (Pb) is intended to be banned from such applications. As a consequence, alternative solder alloys have to be selected and tested in order to replace the traditional lead-based material. In the case of high-temperature applications the usage of the Pb-5wt.%Sn solder alloy is still considered since lead-free alternative alloys do not achieve enough performance considering characteristics such as wettability, reliability and cost. As a consequence, further research is necessary since the use of high lead content alloys is growing considerably [1]. In this context, near eutectic Bi-Ag alloys become promising solder alternatives once Bi is the least toxic of the heavy metals, allowing its application as a substitute for Pb. This would become a step toward an environmentally friendly soldering technique. Further, the temperature criterion is achieved since the melting temperature of the eutectic Bi-2.5wt%Ag is quite close to that of the Pb-5wt.%Sn alloy. This criterion is based on the fact that high-temperature solders usually have melting temperature in the range between 260°C and 400°C. It is obviously realized that both cited characteristics are not enough to guarantee soundness for a candidate alloy in order to substitute high Pb-alloy solders.

The Bi-2.5Ag alloy is considered an interesting option due to compatible melting point and hardness as compared with Pb-based traditional solder alloys, with an actual possibility of having
ductility increased. As a consequence, a Bi-Ag alloy has already been developed as a die attach solder for power devices and light-emitting diodes (LEDs) [2].

In the case of Bi-Ag alloys, the development of non-equilibrium solidification microstructural features have been barely identified by some few studies [3,4]. It has been noted a lack of studies emphasizing the effects of the cooling rate variation on the final solder fillet microstructure. In this context, unidirectional solidification systems can be very useful for investigating the evolution of microstructures in solder alloys. Solder fillets develop an as-cast microstructure as a consequence of the solidification process. In this case, arrangements formed by dendrites and cells are well known to have significant influence on the final properties like mechanical strength and corrosion resistance [5,6]. The parameters characterizing such microstructures are the primary/secondary dendrite arm spacings ($\lambda_1$, $\lambda_2$) and the cell spacing ($\lambda_c$).

The results reported by Masayoshi and co-authors [7] demonstrated a gradual increase in the tensile strength with the increase in the alloy Ag content. In this study, the dispersed Ag phase with average size of 18$\mu$m is reported to act as an effective arrester against propagating cracks. Recently, the examination of the Bi-1.5, 2.5 and 3.5wt.%Ag alloys [2] revealed that the wetting angle decreases as the silver content increases. A 11.17° wetting angle is reported for the Bi-3.5wt.%Ag alloy, which means that it could easily spread on a Cu substrate surface.

The aim of this study is to correlate the microstructural parameters such as primary/secondary dendrite arm spacing ($\lambda_1/\lambda_2$) and eutectic spacing ($\lambda$) with the solidification thermal parameters during directional solidification of the Bi-1.5wt%Ag alloy. This will allow realizing which experimental growth laws may be fitted for this alloy. Examination of the combined effects of macrosegregation and microstructure parameters on the microhardness profile along Bi-1.5wt.%Ag alloy is also planned.

2. Experimental procedure

A directional solidification setup was used so that heat was directionally extracted only through a water-cooled bottom made of low carbon steel. Further details about the solidification system used in the present research have been described in a previous study [8]. The Bi-1.5wt%Ag, alloy was melted in situ by controlling the power of the radial electrical wiring. The electric heaters were disabled so that solidification could be initiated, and at the same time the controlled water flow was opened. Continuous temperature measurements in the casting were performed during solidification by fine type J thermocouples (0.2mm diameter wire sheathed in 1.0mm outside diameter stainless steel tubes) placed along the casting length.

The data acquisition system employed allows accurate determination of the slope of the experimental cooling curves. Hence, the cooling rates associated with the liquidus isotherm have been determined by considering the thermal data recorded immediately after the passage of this isotherm by each thermocouple.

An etching solution of 96% (vol.) $C_2H_5OH$ and 4% (vol.) $HNO_3$ applied during 30s was used to reveal the microstructures. The primary dendrite arm spacing ($\lambda_1$) was measured on transverse sections of the casting. The triangle method was used in order to perform such measurements [9]. Further, the intercept method was adopted (also on transverse specimens) in order to determine the interphase spacing ($\lambda_c$), which is in brief the distance between two adjacent Ag spheroids positioned side by side inside the eutectic mixture. The ImageJ software for processing and analysis was used to measure the cited spacings and their distribution ranges. At least 30 measurements were performed for each selected position of each examined Bi-Ag alloy. Microstructural characterization was completed using a Field Emission Gun (FEG) - Scanning Electron Microscope (SEM-EDS) Philips (XL30 FEG). Vickers microhardness tests were performed on the cross sections of the samples using a test load of 500 g and a dwell time of 15s. The adopted hardness value of a representative position was the average of at least 10 measurements on each sample. Samples for segregation analysis underwent a fluorescence spectrometer (FRX), model Shimadzu EDX-720 to estimate local average concentration through an area of 100 mm$^2$ probe.
3. Results and discussion

The temperature-time profiles registered for the hypoeutectic Bi-1.5wt%Ag alloy are depicted in figure 1. The experimental cooling curves refer to thermocouples located at specific distances from the cooled surface of the directionally solidified casting, i.e., 3mm, 8.5mm, 13.5mm, 18.5mm, 23mm and 42.5mm. Such thermal readings have been treated to provide plots of position from the metal/mold interface and the corresponding time of the liquidus isotherm passing by each thermocouple. The derivative of a generated function with respect to time gave values for the tip growth rate, which varied from 0.07 to 0.4mm/s. A large cooling rate spectrum was allowed to be obtained due to the employed directional solidification technique. The cooling rates varied from 0.03 K/s to 9.7K/s which is a range that encompasses the typical values applied during reflow procedures in industrial practice. Preceding studies give complete information about the experimental set-up used in the directional solidification trials [5] [8].

![Figure 1. Cooling curves acquired for the Bi-1.5wt%Ag alloy at different positions from the cooled bottom of the casting. $T_L$ means liquidus temperature.](Image)

Some representative transverse and longitudinal microstructures are depicted in figure 2a and figure 2b, respectively. The solidification thermal parameters like growth rate and cooling rate were included inside each microstructure. It can be noted that the size of the microstructure is connected with these parameters. Thus, as the cooling rate is high close to the bottom of the casting and decreases toward the top, the microstructural length scale increases as a result. Bi-rich $\beta$ phase dendrites prevail for the entire range of experimental growth rates (0.4mm/s – 0.07 mm/s) determined during solidification of the hypoeutectic Bi-1.5wt%Ag alloy. The light regions are constituted by the primary solid formed ($\beta$ phase) and the eutectic mixture is represented by the dark interdendritic regions.

The dendrites appear as anomalous broken microstructures (see figure 2). This kind of feature was reported earlier by Song and Chuang [10], which considered such appearance as a consequence of non-equilibrium solidification conditions. The average primary dendritic spacing determined for the hypoeutectic Bi-1.5wt%Ag was found to vary between 121$\mu$m and 1024$\mu$m while the average eutectic interphase spacing measured based on the presence of Ag-rich spheroids in the interdendritic regions was in the range 0.3$\mu$m to 2.2$\mu$m.

It can be seen that the Bi-rich phase tends to grow anisotropically as faceted crystals. A SEM image is depicted in figure 3 so that the contour formed between a secondary dendrite arm (Bi-rich dark region) and a eutectic portion could be appreciated. Nodules at the interface between the phases (indicated by black arrows) are homogeneously spaced between each other. This is in disagreement with previous studies [11]. The referred results on the literature were conducted under stationary heat flow conditions, permitting long periods of temperature maintenance on levels above the eutectic point. Transient conditions enabled in the present experimental conditions together with the high cooling rates may allow Bi to grow in a faceted manner.
Figure 2. (a) Transverse and (b) longitudinal microstructures of the directionally solidified Bi-1.5wt%Ag alloy.

(a)

(b)

Figure 3. SEM image detailing the faceted contour between a Bi-rich secondary dendrite branch (dark gray region) and the eutectic region found in the Bi-1.5wt%Ag alloy.

Figures 4a and 4b show average microstructural spacing values ($\lambda_1$ and $\lambda_2$) and their standard deviation for the Bi-Ag alloy examined, plotted as a function of cooling rate and growth rate, respectively. The exponents usually reported for the growths of single-phase dendrites [12] were considered representative for the near eutectic Bi-Ag composition. These exponents are -0.55 and -2/3 and they have been found to apply for experimental power growth laws relating the spacings to the growth rate ($\lambda_2 = A \gamma^{-2/3}$) and the cooling rate ($\lambda_1 = B \dot{T}^{-0.55}$), respectively, for the examined alloy.

The effects of growth rate and temperature gradient on the eutectic interphase spacing have been determined as can be seen in figure 4c. Points are experimental results and line represents an empirical
fit to the experimental points, with spacing being expressed as a power function of $G \times v$. The main theoretical models for cellular/dendritic growth, which were developed for steady-state conditions, propose specific exponents to be used in this kind of correlation ($-1/2$ for $G$ and $-1/4$ for $v$) [13,14].

In the present experimental investigation, which was conducted under conditions of unsteady-state growth, the exponents $-1/2$ for $G$ and $-1/4$ for $V_L$ were found to be appropriate for the eutectic growth of the Bi–1.5 wt%Ag alloy. The same exponents have been adopted by Goulart and co-authors [15] for eutectic growth of the directionally solidified Al–1.5wt%Fe alloy. As can be seen through the SEM images in figure 4c finer Ag spheroids are associated with regions close to the cooled surface of the casting. Figure 5a shows the experimental macrosegregation profile of Ag along the length of the directionally solidified Bi–1.5wt%Ag alloy casting. This segregation profile has the typical trend of a normal segregation distribution for a solute redistribution coefficient ($k_0$) less than unity. Hardness is affected by both the dendritic spacing evolution (figure 5b) and the silver (Ag) distribution along the casting length. Lower dendritic spacings allow a more extensive distribution of the Ag-rich spheroids. Higher hardness values are associated with regions where such distribution is optimized together with the lower silver content, i.e., regions close to the bottom of the casting.

**Figure 4.** (a) Primary and (b) secondary dendritic spacings as a function of tip cooling rate and growth rate for the Bi–1.5wt%Ag alloy. (c) Interphase spacing as a function of the $G^{-1/2} \times V_L^{-1/4}$. $R^2$ is the coefficient of determination.
Figure 5. (a) Experimental Ag segregation profile along the length of the directionally solidified Bi-1.5wt%Ag alloy; (b) Vickers microhardness as a function of $\lambda_1^{-1/2}$.

4. Conclusions
Experimental power growth laws relating $\lambda_1$ and $\lambda_2$ to the cooling rate and the growth rate, respectively, are proposed. A modified Hall-Petch equation was able to represent the experimental hardness scatter of the Bi-1.5wt%Ag alloy. This has been attributed to both the primary dendritic spacing evolution and the silver distribution along the casting length.

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