MICROSTRUCTURAL DEVELOPMENT OF A DIRECTIONALLY SOLIDIFIED HYPEREUTECTIC Sn-2.8wt%Cu SOLDER ALLOY

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Abstract. *Nowadays several trends of laws have been employed as guidelines to restrict the use and application of certain hazardous substances applied in manufacturing processes of components in general. Some examples of such components are the products containing cadmium, mercury and lead. Because of these constraints, electronics manufacturers must tailor their products to new guidelines and develop new lead-free solder alloys. Near-eutectic and eutectic Sn-Pb are the traditional solder alloys used to connect microelectronic devices. Some alternative lead-free solder alloys have been studied and used to replace lead-containing components. Some alternatives are Sn-Ag alloys, Sn-Bi alloys, Sn-In alloys, the eutectic Sn-9wt% Zn and Sn-Cu alloys. The latter metallic system is characterized by a eutectic reaction at 0.7wt% Cu, whose eutectic temperature is 227°C. The eutectic reaction occurs between Sn and intermetallic* Cu_6Sn_5*. Sn-Cu alloys have received attention due to their low production costs compared with other alternative alloys. Thus, the Sn-Cu alloys are promising alternatives to replace lead-based solder alloys. However, little is known of the effects of cooling rate on the solidification microstructure of these alloys. This study aims to examine, through the use of an upward unidirectional solidification system, the evolution of solidification thermal parameters, the development of the microstructure and microhardness along a Sn-2.8wt%Cu alloy casting. Equiaxed grains have prevailed along the entire casting since the bottom up to the top. An experimental power law function was able to characterize the evolution of microhardness as a function of microstructure. Higher hardness values were found in regions with more refined microstructure.*

Keywords: *soldering, microelectronics, Sn-Cu alloys, unidirectional solidification, microhardness.*

1. INTRODUCTION

Solder alloys containing tin and lead, for metallic interconnects, were first used about 2000 years ago. Currently, the solder has become indispensable for interconnection of virtually all devices and electronic circuits. Solders containing lead, especially in the composition of eutectic or near eutectic composition (Sn-40wt.% Pb) have been widely used in modern electronic circuits Union (Wu et al., 2004). The tin-lead solders have been the first to be used to attach electronic components because they had low cost and high availability: basis for high-volume manufacturing. According to Pareck (1996), extensive knowledge of their properties also motivated their use.

Lead is considered one of the most toxic substances used nowadays. No matter its toxicity, lead is extensively used in the global electronics industry. About 65,000 (sixty five thousand) tons per year are used in solders (LQES, 2007). The situation becomes more complicated when it increasingly appears that more than 40% of lead used, found in waste treatment centers, come from electronics or electrical equipments. This residue of lead can be considered a threat not only to the people responsible for recycling, but also to the environment that surrounds the place of storage before starting the re-treatment of lead.

Some alternative lead-free alloys have been studied and used to replace lead-containing components. Sn-Ag alloys, for example, are characterized by a dispersion of Ag_3Sn particles which gives good mechanical properties to these alloys. However, in spite of being one of the best options, Sn-Ag alloys have a relatively higher melting point compared with the other alternatives, i.e., around 216 to 221°C. These higher values require adjustments in the industrial operations, since the melting point of conventional alloys containing lead (Sn-40wt.% Pb) is 183°C. Such limitation can cause serious problems for electronic components (Wu et al., 2002). On the other hand, the Sn-Bi and Sn-In alloys have too low melting points: 139°C and 120°C, respectively (Cheng and Lin, 2002). The development of alloys with eutectic composition like the Sn-9wt% Zn alloy seems to be a good choice since its melting point is close to that of the lead-based alloy used so far, which avoid any significant changes in the industrial operations for interconnections. Sn-Zn alloys are also known by their excellent mechanical properties. These alloys, however, are very susceptible to corrosion (Yu et al., 2000), having low wettability. The Sn-Cu eutectic composition is 0.7wt% Cu and melting point of 227°C.

The eutectic reaction occurs between Sn and the intermetallic Cu_6Sn_5 phase. This alloy has received special attention due to its low production costs compared with other alternative alloys (Çadirli et al., 2009). Additions of small amounts of nickel (between 20 and 1000 ppm) can strongly increase the wettability of the filler metal (alloy) and the base metal (electronic circuit, for example) (Nogita et al., 2005). Mainly due to cost issues, the eutectic Sn–Cu alloy is becoming an interesting lead-free solder alternative (Li et al, 2010). Also, it has been successfully transferred to practical production. The Sn-Cu eutectic reaction is between the faceted eutectic Cu_6Sn_5 phase and the non-faceted Sn-rich phase and occurs at 227°C (Nogita et al., 2010). The Cu_6Sn_5 phase grows in the form of rods embedded in a continuous Sn-rich matrix.

In a recent study, the as-cast microstructure of a Sn-2wt.%Ag solder alloy was characterized and the resulting scale of the dendritic matrix and the morphology of the Ag_3Sn intermetallic particles have been correlated to the corresponding solidification cooling rate (Garcia et al., 2011)

In order to prohibit the use of lead in solder for electronics, the European Union (EU) has adopted new directives to restrict the market in Europe for electronic products that contain heavy metals like lead, cadmium, mercury, among others. As a consequence, several electronic industries located in Manaus, Brazil, which provide services to European companies, have been required to adapt their manufacturing processes to the use of lead-free solders. Alternative lead-free alloys have been studied in the last years, appearing several options to be used. One of these options is the Sn-2.8wt% Cu alloy. The attributes to be encompassed are: low toxicity to the environment, good electrical and thermal conductivity, low cost, availability of base metals, low melting point (or similar to tin-lead alloy), easy repair, adequate mechanical strength.

The present work aims to determine solidification thermal parameters, microstructure evolution and microhardness profiles along a Sn-2.8wt%Cu alloy casting. An upward directional solidification experiment under transient conditions of heat extraction was carried out to permit the mentioned examinations.

2. EXPERIMENTAL PROCEDURE

The basic steps performed along this experimental study were: i) Stoichiometric calculation and formulation of the used alloy; ii) Melting, homogenization and standardization of the obtained alloy; iii) Assembly of the solidification system with thermocouples positioned at strategic positions; iv) Pouring of the molten alloy inside the solidification setup; v) Remelting and stabilization of the liquid metal; vi) Start the experiment by initiating water flow at the bottom part of the system; vii) Acquisition of the temperature profiles during solidification; viii) Macrostructure etching; ix) Cut of the directionally solidified Sn-2.8wt%Cu casting in transversal and longitudinal specimens for microstructure examination, chemical analysis by x-ray fluorescence (XRF) and for measurement of microhardness along the casting. Figure 1 shows a flowchart containing all stages the experimental study.

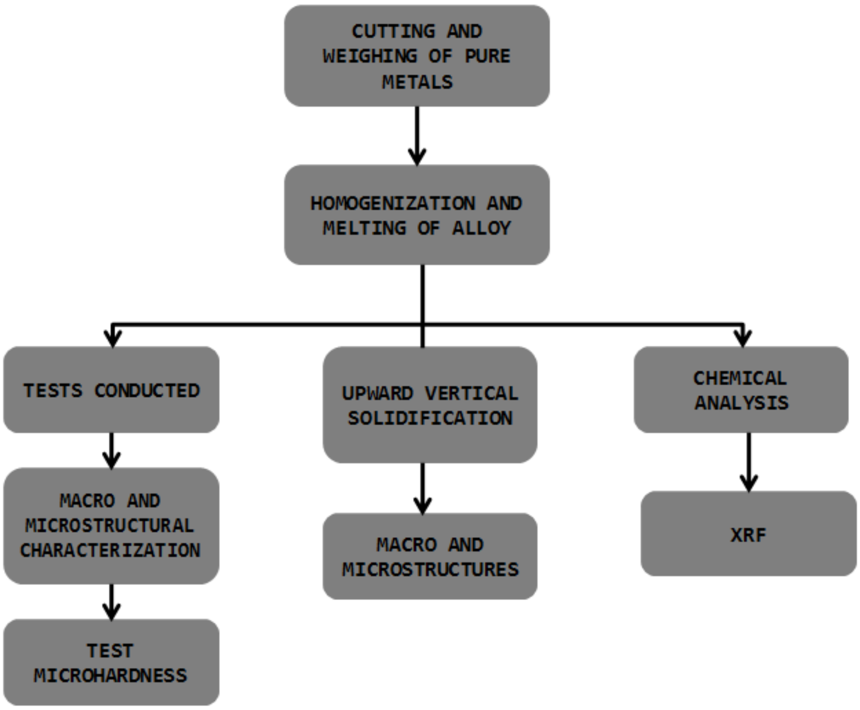


Figure 1. Flowchart of experimental procedure.

The Thermo-Calc software was used to calculate the equilibrium diagram for the Sn-Cu metallic system. The *liquidus* temperature of the studied alloy was also determined; whose value is 317°C. The partial phase diagram is shown in Figure 2.

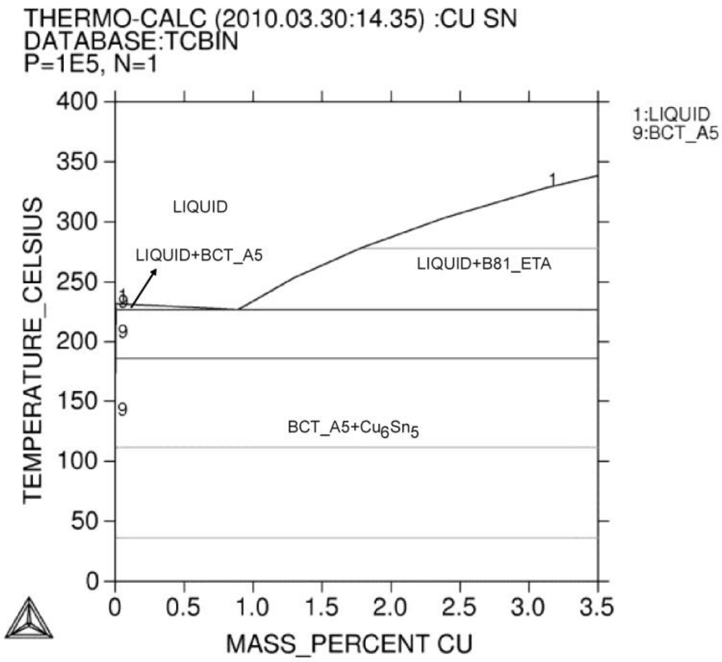


Figure 2. Partial phase diagram of the Sn-Cu system.

Chemical analysis was performed in order to verify the alloy composition. Twelve samples have been selected along the casting to be tested by X-ray fluorescence, which permitted an additional verification of the final alloy composition. The samples used in the XRF analysis were ground sequentially by sanding with particle sizes of 180, 320, 400 and 600, respectively. The device used was a fluorescence spectrometer, model Shimadzu EDX-720. Figure 3 shows a typical XRF result for one of the specimens. This analysis shows a copper content of about 3.1wt% close to that expected by stoichiometric calculation, which confirm the initial formulated solute content of 2.8wt%Cu.

Quantitative Result

Analyte	Result	Std.Dev.	Proc-Calc	Line	Int.(cps/uA)
Sn	96.898 %	(0.109)	Quan-FP	SnKa	440.9483
Cu	3.103 %	(0.012)	Quan-FP	CuKa	44.9695

Figure 3. XRF result found for Sn-2.8% Cu solder alloy.

Details of the directional solidification setup are shown in Figure 4. Heat is directionally extracted only through a water-cooled low carbon steel bottom, promoting vertical upward directional solidification. Continuous temperature measurements in the casting were monitored during solidification via the output of a bank of fine type J thermocouples sheathed in 1.6 mm outside diameter (O.D.) stainless steel tubes, and positioned at 3, 7, 11, 21, 37, 52 and 88 mm from the heat-extracting surface at the bottom of the casting. All thermocouples were connected by coaxial cables to a data logger interfaced with a computer and the temperature data were acquired automatically. The cooling water was started when the melt temperature was about 10% above the eutectic temperature.

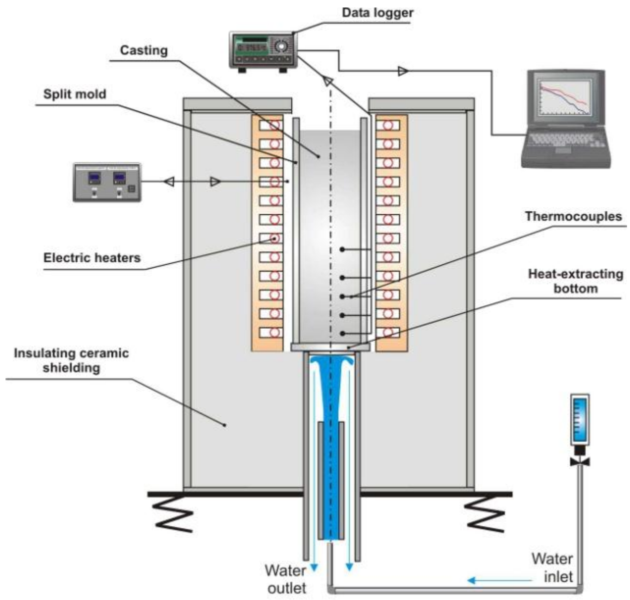


Figure 4. Schematic representation of the upward solidification setup (Rosa, 2007).

The casting was sectioned along the longitudinal direction and the macrostructure was revealed (2mL HCl; 10g $FeCl_3$ and 100 ml H_2O). An etching solution of 92% (vol.) CH_3OH, 5% (vol.) HNO_3 and 3% (vol.) HCl applied during 5s was used to reveal the microstructure.

The intercept method was employed in order to measure the inter-branches spacing (λ) of the Cu_6Sn_5 particles on longitudinal sections of the directionally solidified casting (Gündüz, 2002). At least 30 measurements were performed for each selected position along the casting length. An optical image processing system, Olympus GX51 (Olympus Co., Japan) was used to acquire the images.

Microhardness tests were performed on the samples by using a test load of 300g and a dwell time of 10s. A Shimadzu HMV model hardness measuring test device was used. The adopted Vickers microhardness was the average of at least 10 measurements on each sample.

3. RESULTS AND DISCUSSION

Figure 5 depicts the resulting experimental cooling curves for the thermocouples inserted in the Sn-2.8wt%Cu alloy casting.

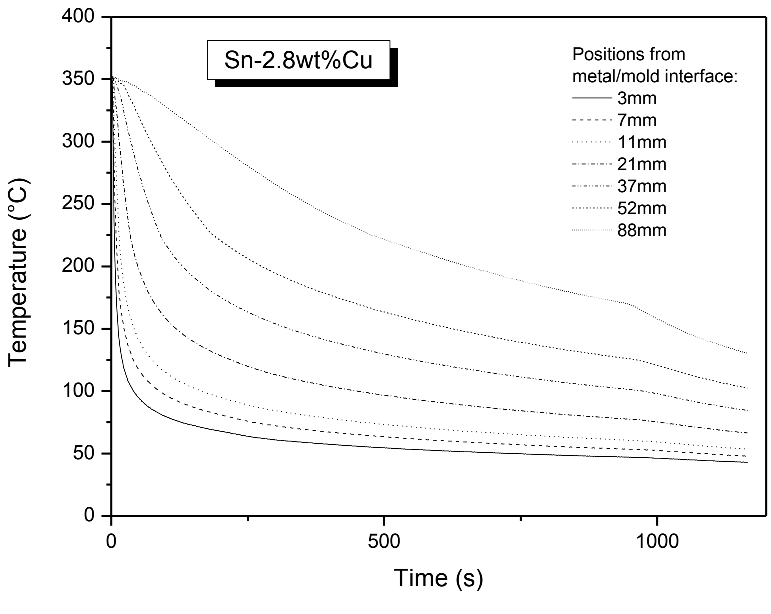
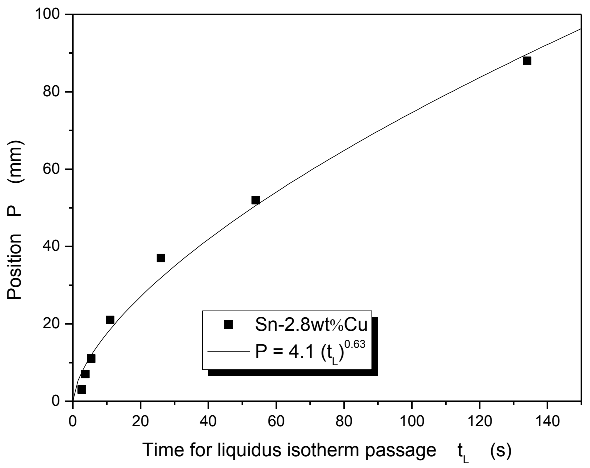


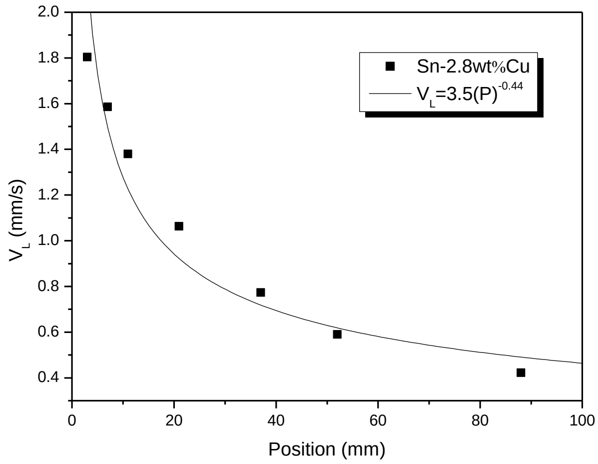
Figure 5. Experimental cooling curves for the hypereutectic Sn-2.8wt%Cu solder alloy.

The thermocouples readings have been used to generate a plot of position from the metal/mold interface as a function of time corresponding to the *liquidus* isotherm passing by each thermocouple (Figure 6a). A curve fitting technique on these experimental points yielded a power function of position as a function of time. The derivative of this function with respect to time gave values for the growth rate V_L. Figure 6b shows the experimental evolution of V_L for the experimentally examined alloy. The experimental cooling rate (Figure 6c) was then determined by considering the thermal data recorded immediately after the passing of the *liquidus* isotherm by each thermocouple.

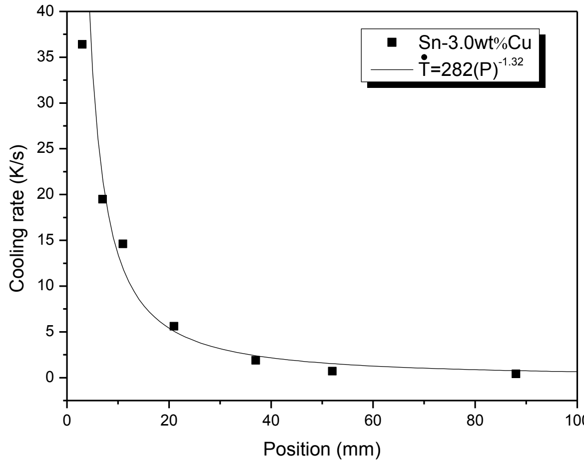
The complete volume of the casting was characterized by equiaxed grains as can be seen in the evaluated longitudinal section shown in Figure 7.



(a)



(b)



(c)

Figure 6. (a) Evolution of liquidus isotherm along the casting length; (v) Growth rate as a function of position and (c) cooling rate versus position.

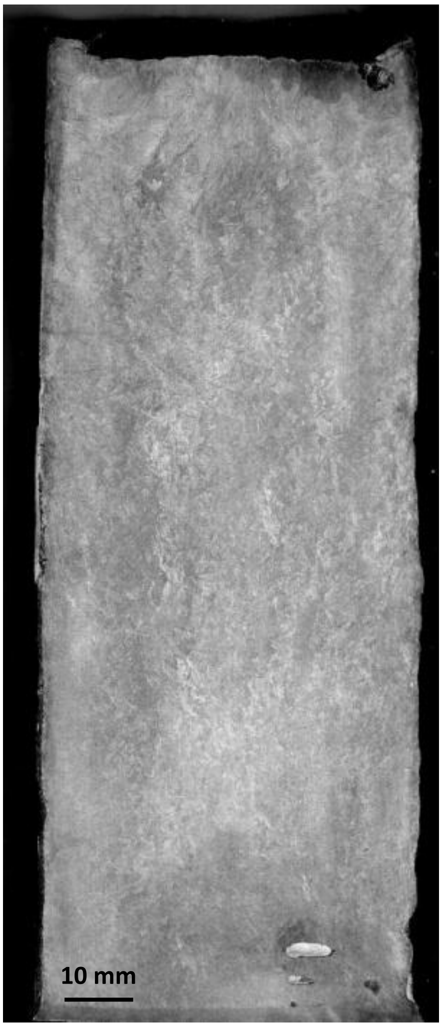


Figure 7. Directionally solidified macrostructure of the hypereutectic Sn-2.8wt%Cu alloy.

Both growth rate and cooling rate decrease as solidification progresses and this behavior is translated to the final as-cast microstructure for any examined alloy as can be seen in Figure 8. Typical longitudinal microstructures were inserted in such Figure in order to confirm the very different microstructure scales found for different positions along the casting. In general, the as-cast structure is composed by Cu_6Sn_5 particles embedded in the Sn-rich matrix. These intermetallics are normally found in the joints of commercial SAC alloys and are especially connected with final properties of the welded assembly. Thus, the control of distribution, size and morphology of Cu_6Sn_5 is essential to the final performance of a product.

The intermetallics developed branches whose section is similar to an "M". All the Cu_6Sn_5 particles in the casting are characterized by a similar morphology, with the particles having from two to three branches. Some arrows were included in the third image of Figure 8 in order to indicate the branches of the Cu_6Sn_5 particles.

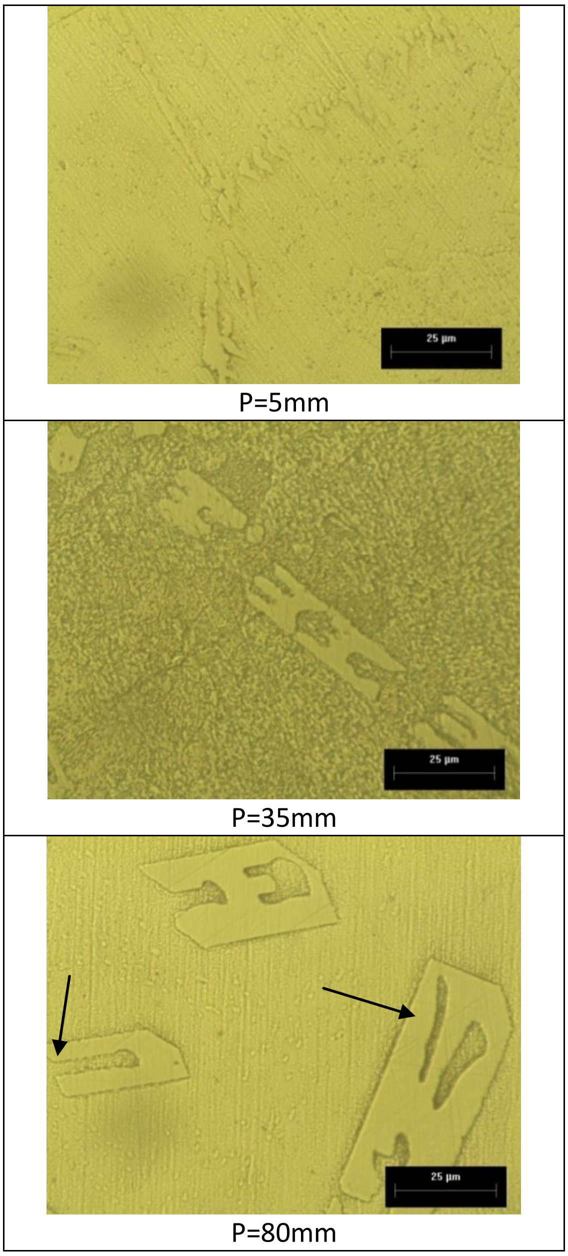
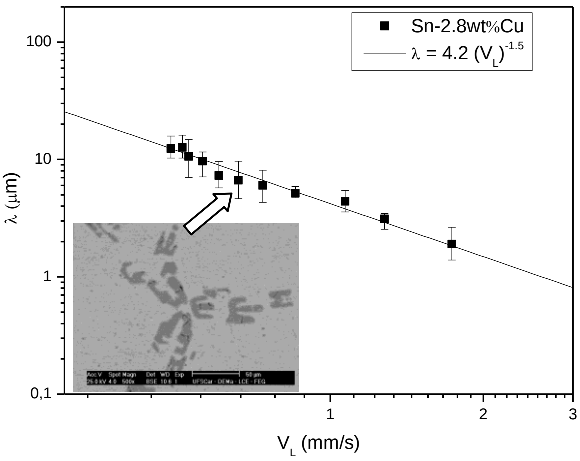
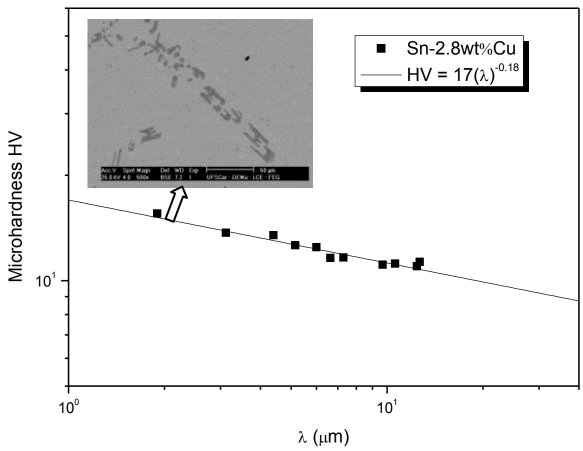


Figure 8. Typical microstructures of the hypereutectic Sn-2.8wt%Cu solder alloy (magnification 1000x).

Figure 9 shows the experimental correlations developed from original thermal, microstructure and hardness data. Fig. 9a shows the Cu_6Sn_5 inter-branch spacing evolution along the casting. The experimental average values are plotted along with the standard deviations. Finer Cu_6Sn_5 particles were found close to the casting cooled surface. The experimental equation expressing the inter-branch spacing dependence on growth rate is inserted inside the graph. The microindentation hardness as a function of λ for the examined alloy can be observed in Fig. 9b.



(a)



(b)

Figure 9. (a) Cu_6Sn_5 inter-branch spacing evolution with growth rate and (b) microhardness versus λ.

Linear regression analysis of these data were performed as proposed by Kaya et al. (2008) and Çadirli *et al.* (2009), resulting in expressions of the form: $HV = k\lambda^{-a}$. The exponent (a) was found to be 0.18. The hard intermetallic phase reinforces the ductile Sn-rich matrix, leading to improvements in the mechanical strength. Çadirli *et al.* (2009) reported an average exponent value of 0.14, which is in good agreement with the value found for the present results.

4. CONCLUSIONS

The distribution, size and morphology of Cu_6Sn_5 intermetallics found in the Sn-2.8wt%Cu directionally solidified solder alloy casting have been characterized. Correlations between solidification thermal parameters (growth rate and cooling rate) and microstructure parameters (inter-branch spacing) have been derived, yielding the following power function: $\lambda=4.2(V_L)^{-1.5}$. Furthermore, the microstructure dependence of a mechanical property for the studied alloy was obtained by measuring the Vickers microhardness (HV) profile along the casting, with the following final inter-relation: $HV=17(\lambda)^{-0.18}$.

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