UNIDIRECTIONAL SOLIDIFICATION OF THE EUTECTIC Sn-0.7wt%Cu

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Abstract. *An unidirectional upward solidification system was used to obtain the eutectic Sn-0.7wt%Cu. This alloy is an important alternative to the application of Sn-Pb alloys in the welding / brazing of microelectronic components. It is worth mentioning that the lead is going through the process of replacing due to its harmfulness to human health. In order to conduct a complete evaluation of the solidification thermal parameters (cooling rate and eutectic front velocity), seven thermocouples were placed in the following positions: 3, 7, 11, 21, 37, 52 and 88 mm from the chilled surface. So, the cooling curves of each position have been recorded during solidification process. The dendritic / cell spacings were measured after a complete evaluation of the as-cast microstructures. A cellular-to-dendritic transition was found to happen along the Sn-0.7wt%Cu alloy casting. Also, the correlations between these microstructural parameters and solidification thermal parameters were determined. The microstructures were captured by light microscopy and scanning electron microscopy (SEM). These image data were essential to characterize the growth behavior from both transversal and longitudinal sections along the casting. The dependence of microhardness on microstructure along the casting was analyzed, and from the results it may be noted a slight increase in hardness to the lower values of primary dendritic / cell spacing.*

Keywords*: Unidirectional Solidification; Sn-Cu solder Alloy, soldering, solidification thermal parameters, microhardness*

1. INTRODUCTION

Nowadays, the manufacturing processes of components in general tend to fit new laws and guidelines, which govern the application and use of certain substances that come to be harmful to human health. Some examples are products containing cadmium, mercury, hexavalent chromium, ethers and lead. Such situation has generated a need to develop new alloys such as lead-free solder. The traditional solder material used by manufacturers of electronic components is the Sn-Pb eutectic composition (60-40 wt%Pb), which has been used extensively to weld different types of components, which in turn, should be urgently replaced in view of a new European law which came into force on 1st. July 2006, seeking to minimize the environmental impact generated by its overuse. Based on this, lead-free alternative alloys have been studied, appearing numerous choices of materials with higher melting temperature than tin-lead alloys (Garcia et al., 2010).

The ternary systems based on binary Sn-Ag with the addition of Cu, Bi and Sb are considered favorites. The alloys Sn-Ag-Cu are classified as the most appropriate and compatible with electronic components that are usually covered with tin-lead. The evaluation of different compositions has been a promising proposal. The preference of U.S. developers is Sn-3.9wt%Ag-0.6wt%Cu, since the Europeans indicate Sn-4.0wt%Ag-0.5wt%Cu and Sn-3.7wt%Ag-0.7wt% Cu alloys. In Japan the most suggested is Sn-3.0wt%Ag-0.5wt%Cu alloy, which is considered an adequate strong replacement for eutectic tin-lead alloy. It can be noted a significant variation between the use of silver and copper in such alloys. Preliminary studies indicate that Sn-Zn alloys, Sn-Bi, Sn-Ag, Sn-In, Sn-Cu, Sn-Ag-Cu and Sn-Ag-Bi consist of promising alternatives for the replacement of solder alloys containing lead. However, it is necessary to evaluate the influences of cooling rates of the process on the microstructure formed and the mechanical properties of these alloys. The use of binary or ternary alloys near the eutectic composition in the welding of components is desirable since a low number of elements can propitiate relatively small compositional changes. Such heterogeneities may affect the weld performance (Çadirli et al., 2009; Cheng and Lin, 2002).

Unidirectional solidification techniques have been widely employed in characterization studies such as macrostructure, microstructure local and large scale segregation. Such techniques can be divided into two categories:

those dealing with solidification under steady heat flow and solidification occurring in stationary regime. In the stationary regime, the temperature gradient G and growth velocity, v, are managed independently and kept constant throughout the experiment. In contrast, the transient solidification allows free variation of solidification parameters such as growth rate, v, G and the cooling rate ($\dot{T}$), which approximates the experimental method with the reality of many industrial processes involving the solidification of metals.

Structural parameters such as grain size, dendritic spacing, cellular spacing, interphase spacing, porosity are directly influenced by the thermal behavior of metal/mold system during transient solidification, consequently imposing a close correlation between solidification kinetics and the resulting microstructure. The dendritic microstructure, for example, can be characterized by the quantification of the experimental primary or secondary dendritic spacing. Several studies have been carried out in order to determine the evolution of primary and secondary dendrite arm spacings in the as a function of the solidification thermal parameters v, G and $\dot{T}$ (Berry, 1970; Donelan, 2000; Goulart et al., 2010; Canté et al., 2010; Osório et al., 2006;. Cruz et al., 2010).

In this paper, transient unidirectional solidification tests have been conducted to obtain Sn-0.7wt%Cu solder alloy as well as the experimental thermal profiles along the casting. The solidification thermal parameters v, G and $\dot{T}$ were determined and correlated with the microstructural parameters measured along the casting. The main purpose of this study is to determine the Vickers microhardness (HV) evolution along the casting and its dependence on the as-cast microstructure of the eutectic Sn-0.7wt%Cu solder.

2. EXPERIMENTAL PROCEDURE

Details describing the used directional solidification assembly may be found in previous articles (Osório et al., 2006; Silva et al., 2010). Heat is directionally extracted only through a water-cooled low carbon steel bottom, promoting vertical upward directional solidification. The eutectic Sn-0.7wt%Cu eutectic alloy was used in the experiment, which was performed under thermally and solutally stable solidification conditions.

Fig. 1 shows the partial Sn-Cu phase diagram obtained by the software Thermo-Calc. As indicated in Fig. 1, the stable eutectic reaction gives raise to the transformation of a liquid phase into a mixture of a solid Sn-rich phase (BCT_A5) and Cu_6Sn_5 intermetallic particles.

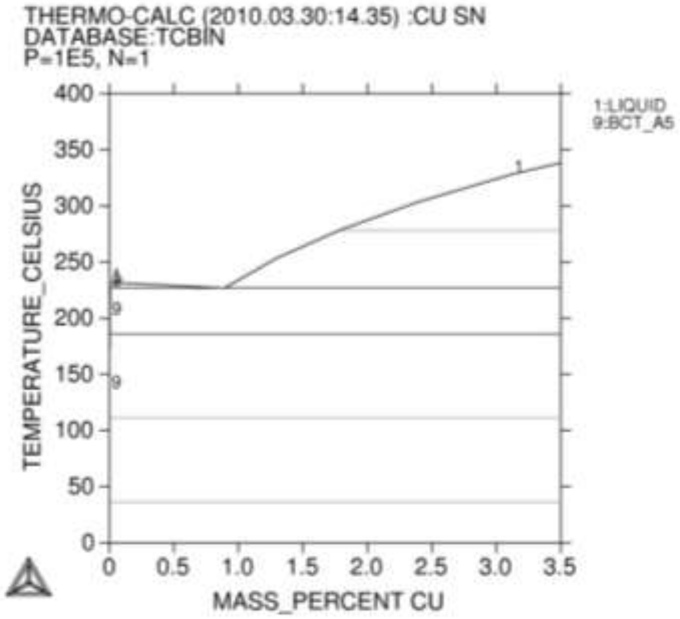


Fig. 1. Sn-Cu phase diagram taken from USLD1 Thermo-Calc data base.

The eutectic composition of the alloy is 0.7wt%Cu, which is the chemistry chosen for this study. In order to obtain the desired composition of such alloy, the melting of tin was firstly performed. Secondly, an electrolytic copper bar was placed into the molten tin, being consumed until eutectic composition was ensured.

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, i.e., 250°C.

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. Higher immersion times of about 40s permitted to examine the eutectic phase.

The triangle method was employed to measure λ_1 and λ_c on transverse sections of the directionally solidified casting (Gunduz and Çadirli, 2002). At least 40 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. The microstructure was also characterized by scanning electron microscopy (Philips, XL-30, Netherlands).

Microhardness tests were performed on the longitudinal sections of the samples by using a test load of 10g 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 15 measurements on each sample.

3. RESULTS AND DISCUSSION

Fig. 2 represents the experimental result of the cooling curves for respective thermocouples placed on the molten alloy soldering Sn-0, 7wt% Cu. The thermocouples readings have also been used to generate a plot of position from the metal/mold interface as a function of time corresponding to the eutectic front passing by each thermocouple. A curve fitting technique on these experimental points yielded a power function of position as a function of time (Fig 3a). The derivative of this function with respect to time gave values for the eutectic growth velocity, v. Fig. 3b shows the experimental evolution of v for the experimentally examined alloy. The experimental cooling rate (Fig. 3c) was then determined by considering the thermal data recorded immediately after the passing of the eutectic front by each thermocouple.

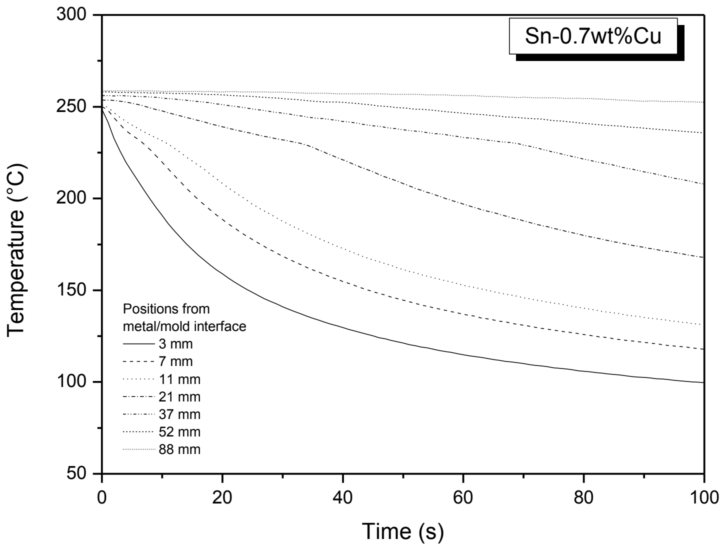
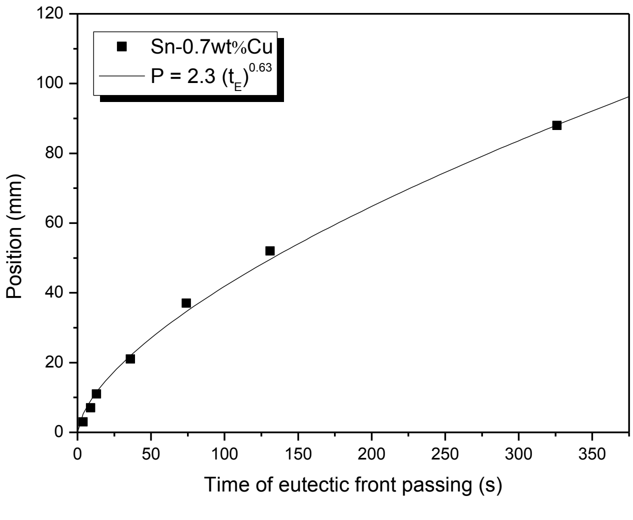
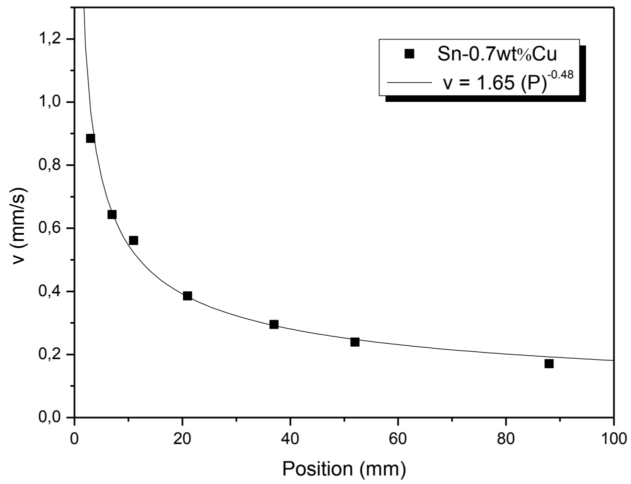


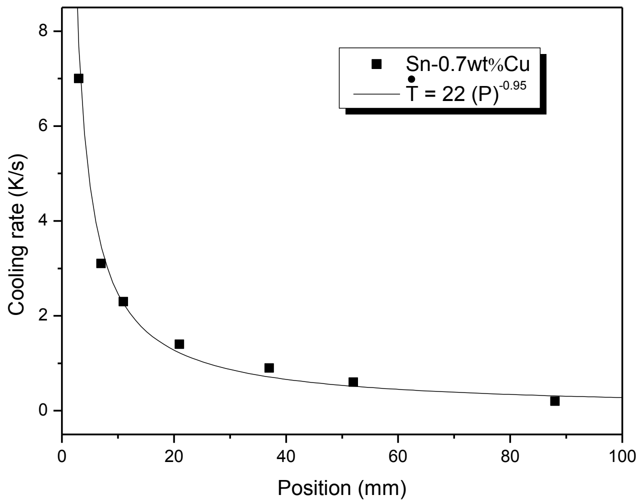
Fig. 2. Experimental cooling curves obtained for the eutectic Sn-0.7wt%Cu alloy.



(a)



(b)

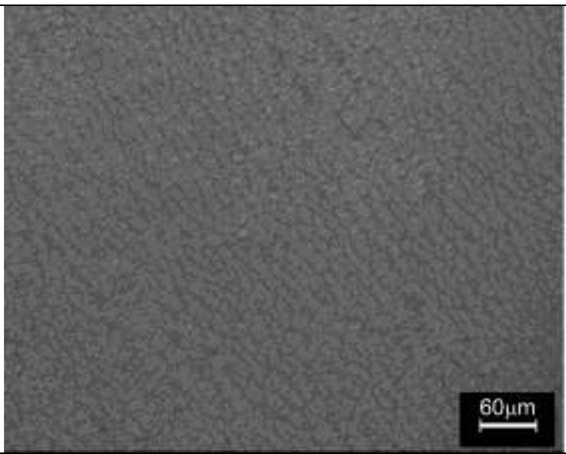
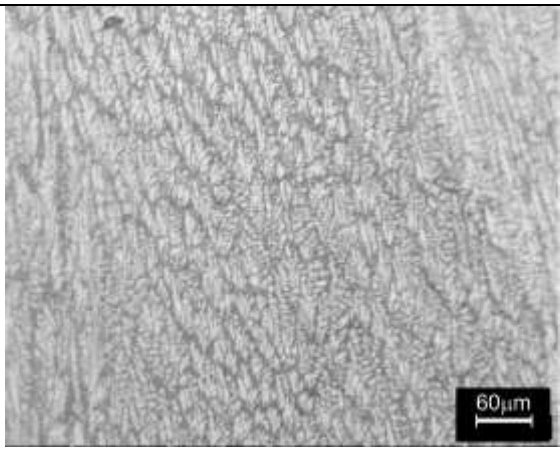
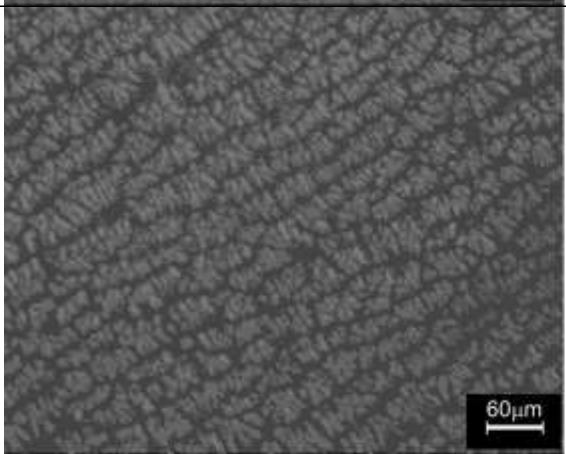
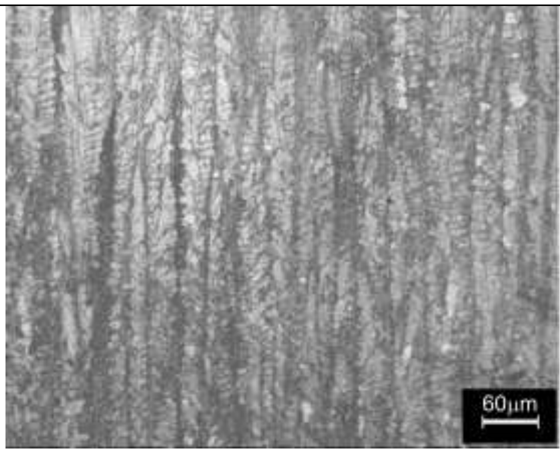
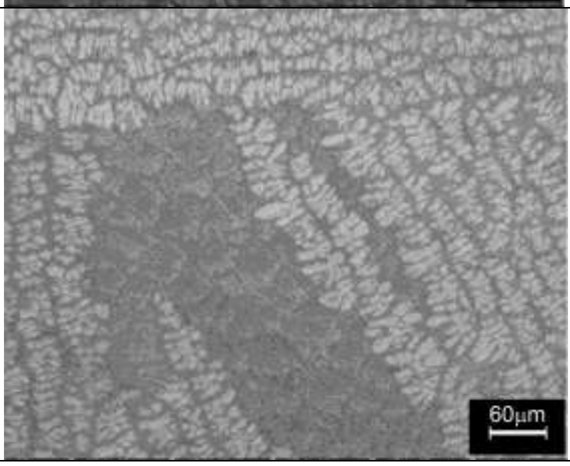
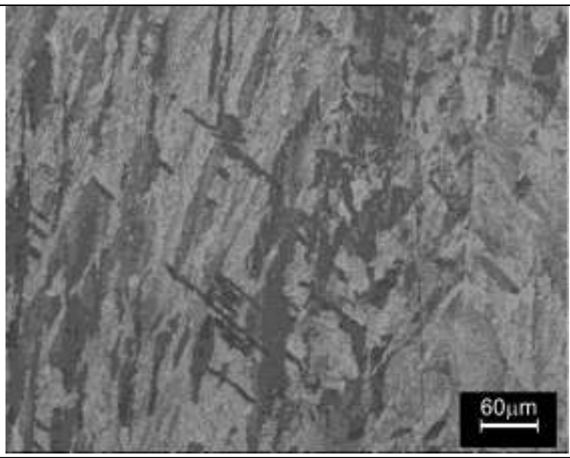


(c)

Fig. 3. (a) Evolution of the eutectic front along the casting; (b) Experimental values of eutectic growth rate and (c) cooling rate as a function of position from the metal/mold interface for a eutectic Sn-0.7wt%Cu alloy.

Fig. 4 shows the typical microstructures of the Sn-0.7wt%Cu solder alloy in both transverse and longitudinal position. It is noted an increase in the size of the structures along the casting, which are more refined near the bottom of the casting and coarser in the upper regions. This is due to the fact that the eutectic growth rate decreases with increasing solidified layer, as observed in Fig. 3.

This observed microstructure is barely seen in the equilibrium solidification of binary eutectic alloys, however, solute additions and non-equilibrium solidification conditions can promote instability at the planar liquid-solid interface resulting in the formation of two-phase eutectic colonies (Tewari et al., 2004). The microstructural transition does not occur abruptly. It happens in between of the positions 15 mm to 25mm. After transition region, it can be seen that the cell boundaries are parallel and well delineated, having intermetallic particles inside the cells generally well aligned along the growth direction (Fig. 4).

Position from metal/mold interface	Cross section	Longitudinal section
5mm		
15mm		
Transition		

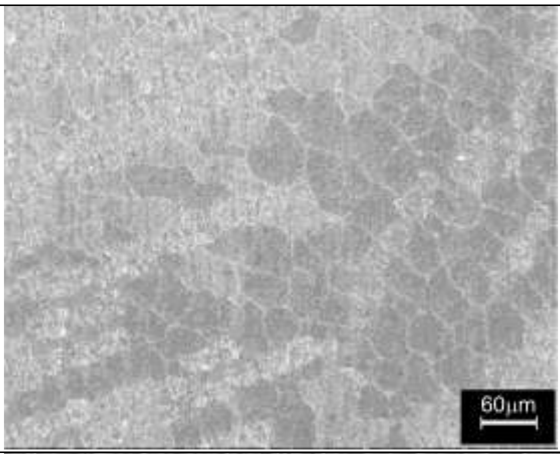
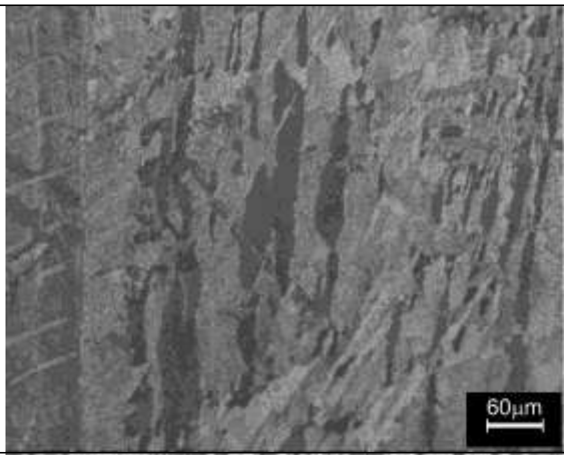
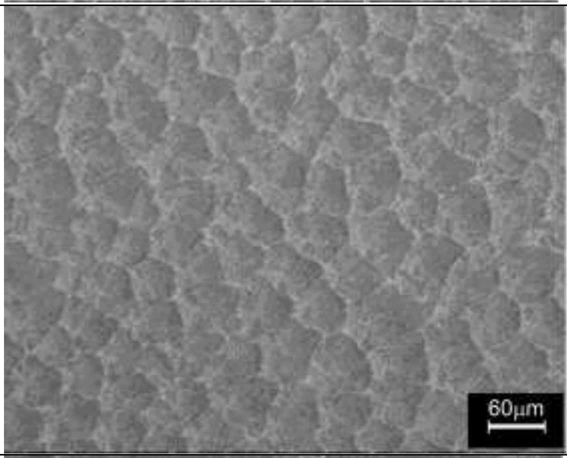
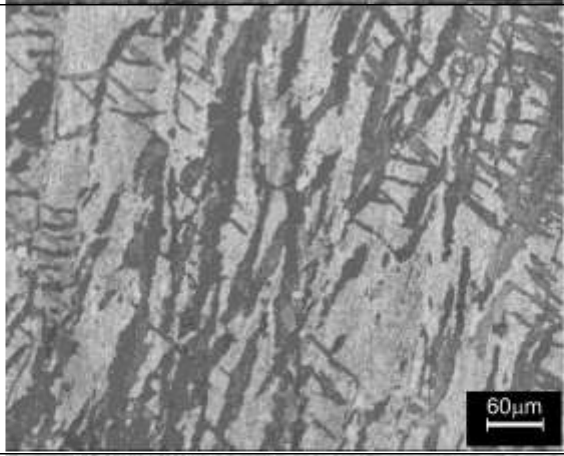
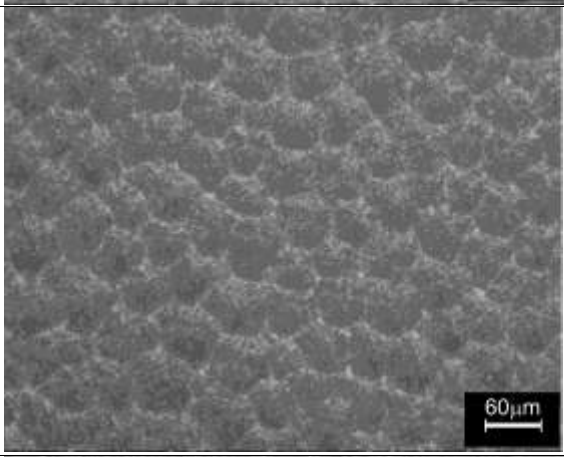
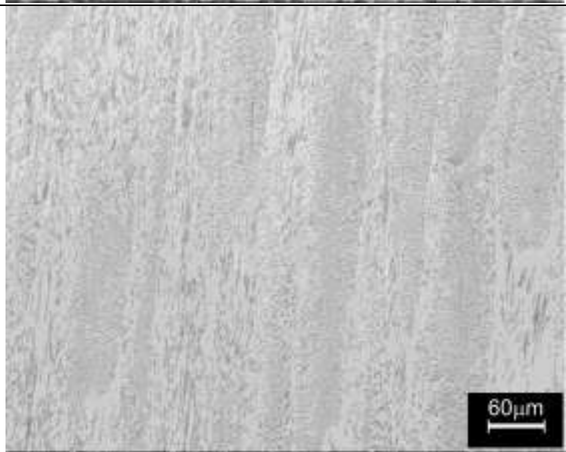
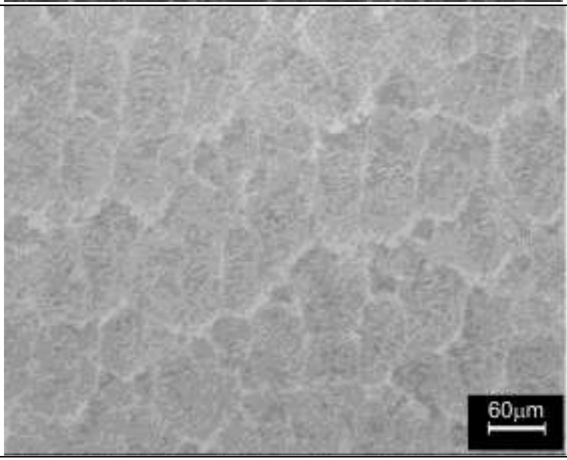
region		
30mm		
45mm		
60mm		

Fig. 4. Typical microstructures found along the Sn-0.7wt%Cu solder casting (Magnification 200x).

Fig. 5 shows that the same power-function exponent used for single-phase growth can be applied to the growth law of a directionally solidified eutectic Sn-0.7wt%Cu solder alloy under unsteady-state heat flow conditions. This exponent is -1.1 for the growth rate and is in agreement with previous studies concerning single-phase alloys structures [Rocha and co-authors, 2003; Spinelli et al., 2008).

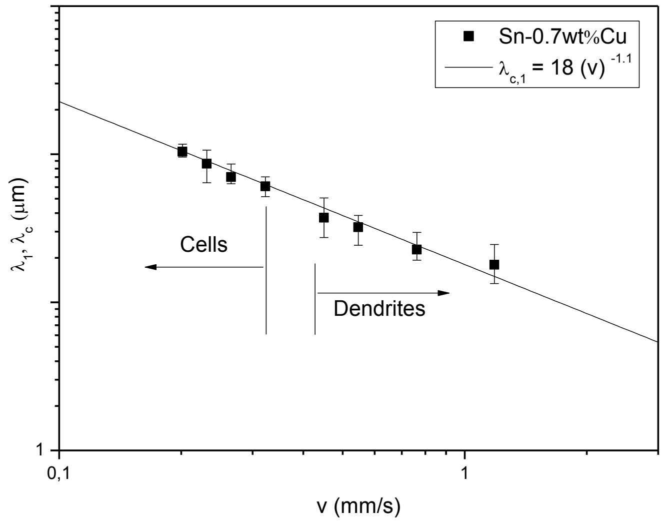


Fig. 5. Cell and primary dendritic spacings as a function of growth rate for a Sn-0.7wt%Cu alloy.

The microindentation hardness as a function of primary dendritic and cell spacing for the examined alloy can be observed in Fig. 6. The experimental average values are plotted along with the standard deviations. A slight increase in the hardness values can be observed for fine cell and dendritic spacing as indicated by arrows. It seems that the very low copper content inhibits the sensitivity of this alloy facing hardness indentations even for different microstructure scales and features. Further tensile mechanical tests are required in this case to confirm the present results. SEM images are inserted in Fig. 6 to illustrate the size and distribution of the Cu_6Sn_5 particles along the casting.

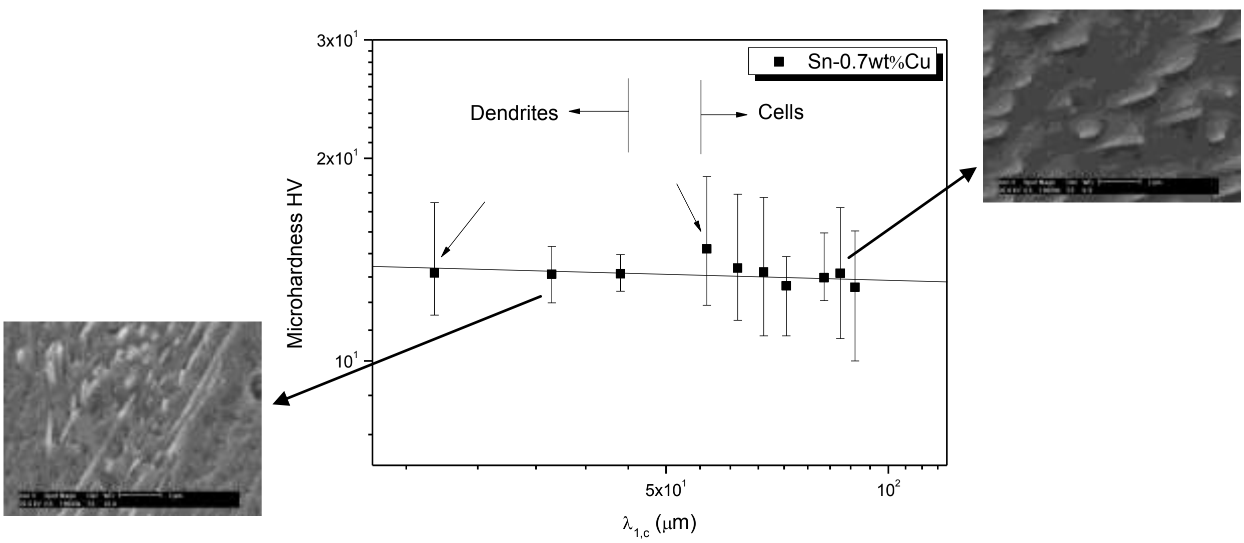


Fig. 6. Microhardness development along Sn-0.7wt%Cu solder alloy.

4. CONCLUSIONS

Even though the Sn-0.7wt%Cu solder alloy with eutectic composition was directionally solidified, a microstructural transition typically observed in single-phase alloys has happened in the examined casting. Both eutectic dendrites and cells were observed in distinct regions of the casting. A microstructural transition region occurs in between of dendritic and cellular features.

A single -1.1 power law characterizes properly both primary dendritic and cell developments with growth rate.

Fine dendrites and cells (each one identified for the distinct microstructural regions) propitiate a slight increase in HV hardness due to a better isolation of eutectic mixture and also a better solute distribution. However, hardness can be considered roughly constant along the casting due to the very low solute content present in the examined alloy.

The proposed experimental equations can be used in the control of the soldering process by manipulating solidification processing parameters such as growth rate in the preprogramming of a desired microstructural arrangement.

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