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## Directional Solidification of Sn-Ag-Cu Alloys

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### Abstract

The alloys of Sn-Ag-Cu family (SAC) are candidates for lead-free replacement of Sn-Pb eutectic used in welding processes of electronic devices. These alloys, with eventual adding of Zn, In and Bi highly improves the morphological stability and the corrosion resistance. Close to the eutectic ternary composition, the solidification occurs with three distinct phases: Sn-rich dendritic primary phase, Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> intermetallic phases, which have limited solubility in the Sn phase, in such a way that some authors consider these alloys as compounds of Sn with the mentioned intermetallic phases. In this aspect, the directional solidification is a suitable tool to study the solidification under strictly controlled conditions. In this work, samples of Sn-Ag-Cu composition were grown to analyze the mechanisms involved in the solidification of these alloys. The typical microstructure agrees the above description, with a spacing that depends mainly on the advance interface velocity of the growth.

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### 1. Introduction

Ternary eutectic Sn-Ag-Cu have receipt particular attention due to this system is a main candidate to be a lead-free solder alloy replacement. Microstructural characteristics are reported as containing a homogeneous primary

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phase coupled with binary eutectics (Kurz and Fisher, 2009). The extent of primary phase affects the mechanical properties, fundamentally under moderate and high working temperatures. Previous studies of binary and ternary eutectics are based on the fundamental works of Jackson and Hunt (1966) and McCartney et al. (1980 and 1980a). According to these models or descriptions, a microstructure of columnar cells and lamella secondary phases in middle of a homogenous primary phase is expected. The Sn-Ag-Cu ternary eutectic shows this type of microstructure, with a homogeneous primary phase of Sn with small quantities of Ag and Cu in solution, and the intermetallic phases  $\text{Cu}_6\text{Sn}_5$  and  $\text{Ag}_3\text{Sn}$ .

Solidification of Sn-Ag-Cu ternary system is a bit more complex than that of Sn-Pb eutectic traditionally used. Firstly, this is a ternary system, which implies more diffusion paths between species both during the cooling and solidification as in the alloy working life at high temperature. Also, whilst Sn-Pb is formed by two non-faceted phases, the ternary Sn-Ag-Cu is formed by two faceted phases into a non-faceted matrix, which means that the growth could be more influenced by crystallographic effects (Shaeffer and Lewis, 2005).

Process parameters that affect the microstructure during the soldering process, where the solder is cooled generally through the substrate and the environment while occurs the solidification, are still unknown. In this sense, directional solidification let us to control the process variables such as and advance velocity and thermal gradient in front of the interface that affect the resultant microstructure. The aim of this work is to perform directional growth of Sn-Ag-Cu ternary eutectics to study the formation of microstructures during the solidification of this alloy to eventually apply these results during the soldering process.

## 2. Experimental

The alloys were prepared starting from 99.99 % analytical purity elements melted in an electrical furnace under a protective Ar atmosphere. Pre-ingots were poured into a 10 mm internal diameter by 120 long cylinders. Firstly the binary eutectics Sn-0.9%Cu and Sn-3.5%Ag were obtained and used as mother alloy, Morando et al. (2012). Ternary eutectic composition Sn-3.5%Ag-0.9%Cu was obtained by the addition of Ag and Cu to the previously

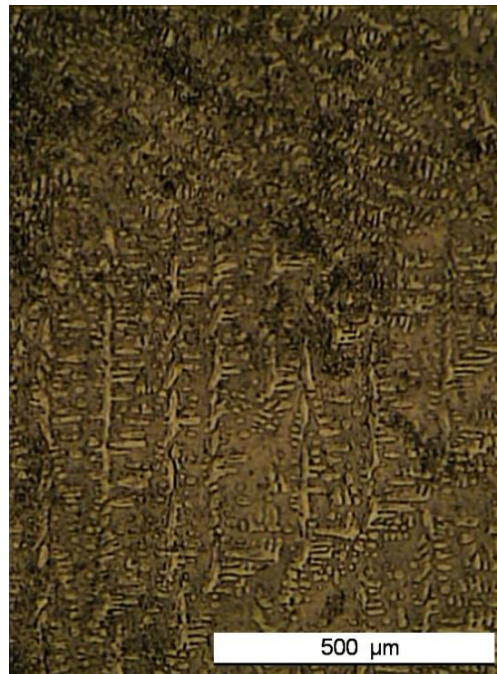


Fig. 1. Macrography of a solid-liquid quenched interface,  $V = 1 \mu\text{m/s}$   $G_L = 2,5 \text{ K/mm}$

obtained binary eutectics and poured in a similar way. These ingots were located into quartz tubes of 8 mm internal diameter, to be directionally grown.

Directional growth was performed in a Bridgman like apparatus, as has been previously reported by Fornaro et al. (2006) and Ochoa et al. (2012). The device consists of two chambers located in a cylindrical symmetry. Upper chamber consist of an alumina core with a heating coil with electronic temperature control. The lower section is refrigerated by water circulation. This disposition brings a fixed thermal gradient where the samples were located to be directionally grown. The pulling system of the samples was based in a stepper motor and a gear box, which permitted a translation velocity in the range of 0-10  $\mu\text{m/s}$  range. The displacement velocity was measured and controlled with a linear variable differential transformer (LVDT) and a signal conditioning interface. The data was sent to a personal computer which drives the motor. This scheme provides a very precise motion, resulting with a precision of  $\pm 0,1 \mu\text{m/s}$ .

The temperatures in the sample were taken using a double K-type (CrNi-AlNi) thermocouple, which let us determine temperature and thermal gradient simultaneously. Measuring was made by an Acquisition Data logger system, with an experimental error of  $\pm 0.5 \text{ }^\circ\text{C}$ . In this work, we fixed the thermal gradient in each set of experiences, taking the velocity as the control parameter of the problem.

The set up process of the surface for optical microstructural observation and analysis requires particular attention, because this alloy can show plastic deformation during the mechanical polishing giving place to twinning formation and the re-precipitation of small grains on the surface. To avoid these effects, an extremely slow and continuously refrigerated mechanical polishing was made. The microstructure was observed both in longitudinal views (in direction of the growth) and in cross sections. The surface was set up by mechanical polishing with up to 1000 grit SiC abrasive paper lubricated with water, and then with 6 and 3  $\mu\text{m}$  diamond powder refrigerated with alcohol. In some opportunities, chemical polishing and electrolytic polishing were also used. Electro-polishing also generates a thick surface oxide which allows us to detect changes in crystallographic orientation when it is observed under polarized light. The samples were observed using optical microscopy under bright field, polarized light and differential interferometry contrast conditions. While different grains were observed with slight lighting changes, the grain boundaries were no revealed. [Morando et al. (2012), Castro and Fornaro (2009)].

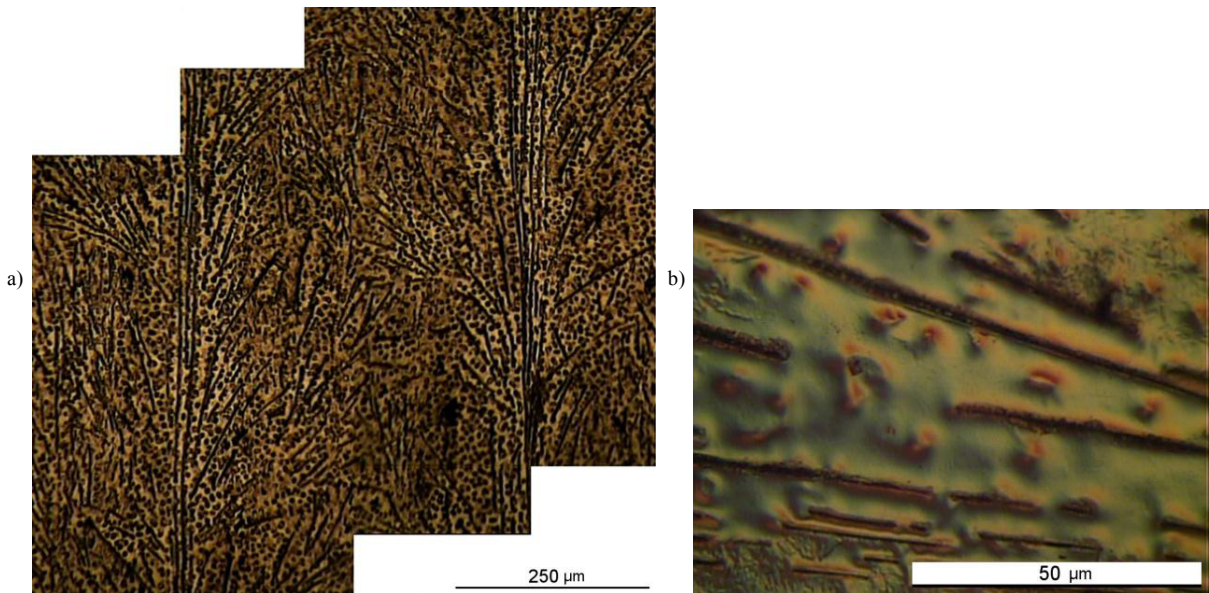


Fig. 2. Directional growth of Sn-3.5%Ag-0.9%Cu, grown at  $V = 0,5 \mu\text{m/s}$ ,  $G_L = 2.5 \text{ K/mm}$ . a) longitudinal view, b) detailed view of present phases.



### 3. Results and Discussion

Directionally growth experiences were developed under velocities of 0.5; 1; 2; y 5  $\mu\text{m/s}$ . The growths were not quenched allowing the crystal to grow in all the sample, that is approximately 80 mm long. However some experiences were quenched to allow the observation of the microstructure at the interface during the crystal growth and to verify the directionality of growth [Ochoa et al. (2012)]. The Figure 1 shows a directional growth of the ternary Sn-0.9%Cu-3.5%Ag as quenched. The morphology in this case is dendritic, showing a primary spacing of approximately  $\lambda_1 = 100 \mu\text{m}$ . In the bottom part of the sample the crystal grown upward is observed, whilst in the superior part can be seen the quenched liquid.

Regarding the microstructure description, in general lines is formed in a fashion has been mentioned before, that is in a primary homogeneous phase, composed by Sn, Ag and Cu in solution, and the intermetallic phases  $\text{Cu}_6\text{Sn}_5$

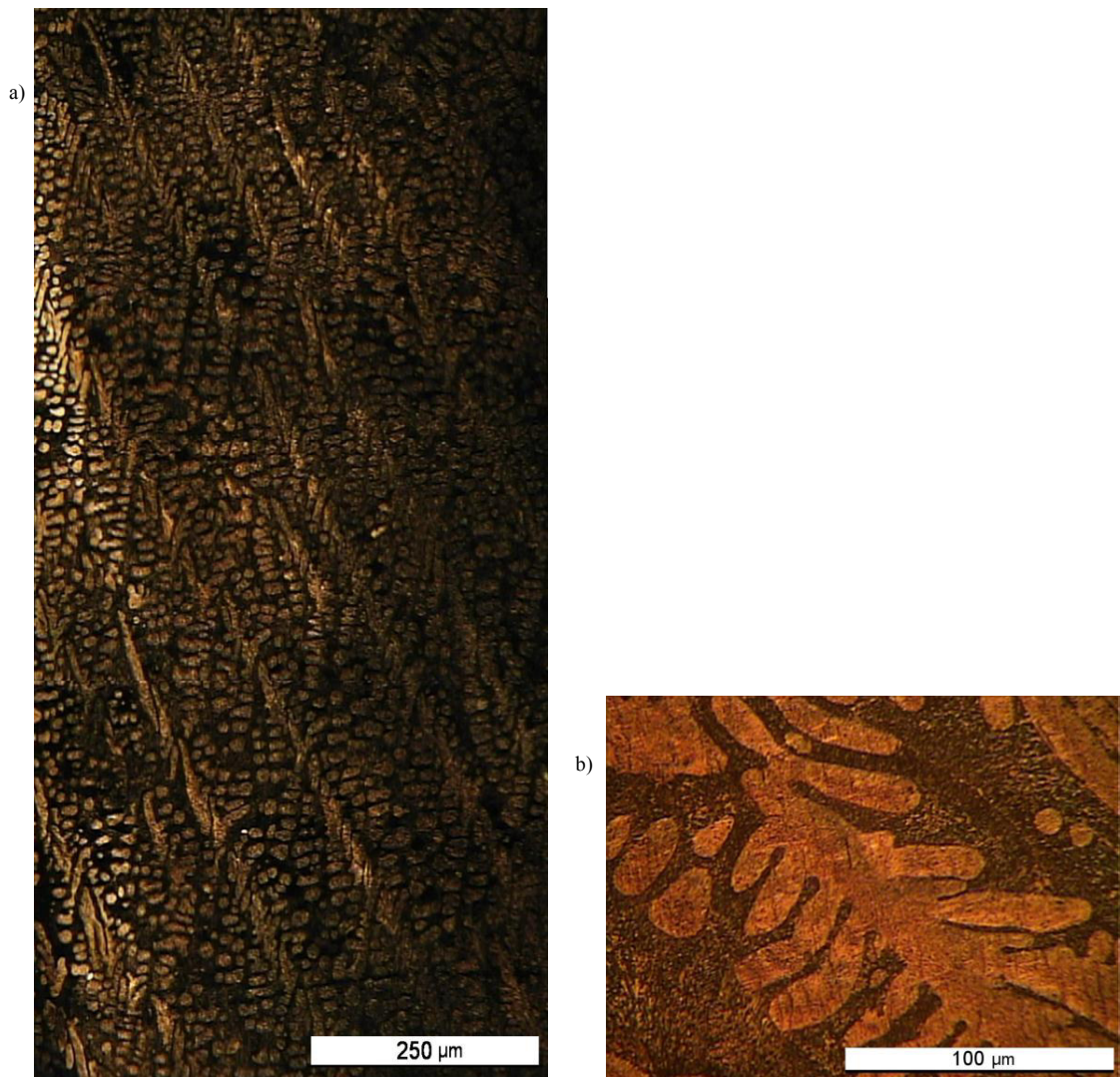


Fig. 3. Directional growth of Sn-3.5%Ag-0.9%Cu under  $V = 2 \mu\text{m/s}$ ,  $G_L = 2.5 \text{ K/mm}$ , a) longitudinal view, growth direction is upward; b) detailed view of the dendritic growth.

forming small precipitates and  $\text{Ag}_3\text{Sn}$  in a needle geometry.

The distribution of these intermetallic phases seems to be dependent of the interface growth velocity. At the smallest sample velocity of  $V = 0.5 \mu\text{m/s}$  and  $G_L = 2.5 \text{ K/mm}$  the microstructure is cellular, where the intercellular space is characterized fundamentally by a set of the intermetallic  $\text{Ag}_3\text{Sn}$  as can be seen in the Figure 2 a). Also it can be seen that the alignment of that phase gradually change forming secondary arms starting from a main fiber. In this way, the spacing is defined by the separation of these main fibers, independently of the secondary fibers.

The  $\text{Cu}_6\text{Sn}_5$  does not seem to take a relationship with the velocity, at least in this range of velocities. More well seem to locate in the spacing between the  $\text{Ag}_3\text{Sn}$  phase, without an evident order, as can be seen with a greater detail in Figure 2 b). This is against the reported by the binary eutectic Sn-0.9%Cu, for which the  $\text{Cu}_6\text{Sn}_5$  phase distribution shows a well determined spacing [Gruegel and Brush (1997)].

At a greater velocity, the typical microstructure is similar to a bi-phase dendritic growth morphology formed by a homogeneous primary phase of Sn-Cu-Ag in solution, and the interdendritic zone which is formed by three phases, the matrix and the other two intermetallic phases mentioned before. Figure 3 a) shows a longitudinal section grown at  $V = 1 \mu\text{m/s}$  and  $G_L = 2.5 \text{ K/mm}$ . The interdendritic zone can be seen in more detailed view at Figure 3 b). It can be noted that in this interdendritic zone the microstructure is finer than cellular growth. A similar behavior can be noted at  $V = 2 \mu\text{m/s}$  and  $G_L = 2.5 \text{ K/mm}$  as can be seen at Figure 4.

Under the frame of this experiences, for velocities greater than  $1 \mu\text{m/s}$  the growth is developed as a coupled

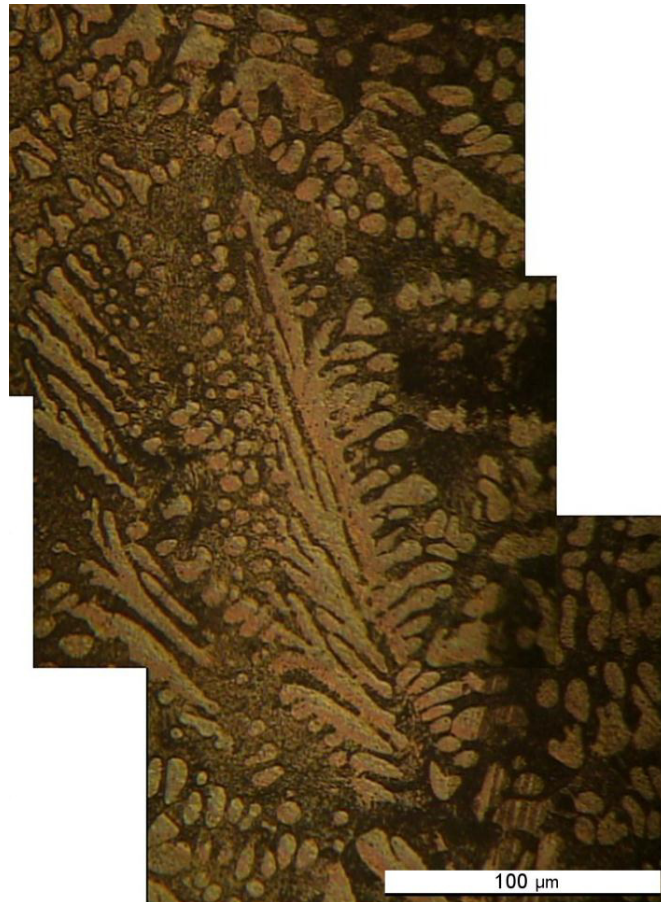


Fig. 4: Directional growth of Sn-3.5%Ag-0.9%Cu under  $V = 2 \mu\text{m/s}$  and  $G_L = 2.5 \text{ K/mm}$ .

Growth direction is upward

eutectic growth, where the primary phase is an homogeneous rich Sn phase with Ag and Cu in solution, that could be growing as non-faceted, while the other two present phases growth as faceted, in the interdendritic spacing. The precipitation of intermetallics  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  are well differentiated. At greater velocity the growth morphology changes dramatically, showing a bi-phase dendritic growth behavior, with a primary homogeneous phase and an interdendritic zone that contains the three phases of ternary eutectic.

This conclusion partially agree with the results reported by Schaeffer and Lewis (2005) who obtain a limit close to  $0,826 \mu\text{m/s}$  with a thermal gradient of  $7.5 \text{ K/mm}$  for a change in the growth mechanism reported in this work. In both cases the limit is determined by the velocities interval between the developed growths. Anyway, a zone where both mechanisms could coexist is expected.

#### 4. Conclusions

Directional growth of Sn-3.5%Ag-0.9%Cu ternary eutectic samples were developed in the range of advance velocities of the interface of 0.5; 1; 2 and  $5 \mu\text{m/s}$ , for a thermal gradient  $G_L = 2.5 \text{ K/mm}$ . It was found that there are at least two mechanisms of growth that could be identified. At low speed, formally below  $V = 1 \mu\text{m/s}$ , the growth is formed by a primary phase homogeneous Sn and Ag with Cu in solution, whereas  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  intermetallic phases are distributed in the resultant crystal. The first one is aimed partly allowing the growth direction define a cell type spacing, but also distributed in the form of needles away from this main fiber.  $\text{Cu}_6\text{Sn}_5$  phase appears homogeneously distributed in the form of small precipitates.

At higher speeds, the growth is characterized by a dendritic growth of Sn primary phase, with the interdendritic spacing formed by the two above-mentioned intermetallic phases and the Sn excess.

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