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Fluidity on Metallic Eutectic Alloys

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Abstract

Eutectic alloys have a great importance both from academic as technological point of view. For technological applications such casting, welding and joining, these systems offer lower melting point than the pure elements and good fluidity. This property is the distance travelled by the liquid metal until it is stopped by solidification when is forced to flow through a channel of small cross section and is called Fluidity Length (L_F).Physical variables associated with the process are: metallostatic pressure, heat extraction rate at the metal-mold interface, overheating of the liquid metal and the physico-chemical properties of metal or alloy (latent heat of fusion, density, viscosity, surface tension and solidification mode). In general, pure metals and alloys of eutectic composition have the highest values of fluidity, whilst intermediate composition alloys with greater solidification range show lesser fluidity lengths. Taking into account that the chemical composition plays a fundamental role in the fluidity length by its relation with the resulting microstructure, the aim of this work is to obtain fluidity values of binary and ternary metallic alloys, with different eutectic morphology, in order to determine the relationship between such morphology and the fluidity length and consequently the influence on binary and ternary proeutectic alloys. Fluidity tests were carried out in a linear fluidity device, using alloys of the AlAgCu system in the Al-rich corner and Lead free Sn based alloys, extensively used for important industrial applications. The samples were characterized using Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Microanalysis (EDAX). Usually, Fluidity Length (L_F) depends on solidification mode, latent heat of fusion of the alloy and the fluidity of the phases present in the microstructure.

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Keywords: fluidity; eutectic alloys; solidification structures; Lead Free Solders LFS.

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1. Introduction

Eutectic alloys have a great importance both from academic as technological point of view. For technological applications such casting, welding and joining, these systems offer lower melting point than the pure elements and good fluidity. The fluidity is the distance travelled by the metal until it is stopped by solidification when the liquid metal is forced to flow through a channel of small cross section, is called Fluidity Length (L_F). The process that takes place is a combination of the dynamic progress of the vein with the solidification of liquid metal. Physical variables associated with the process are: metallostatic pressure, heat extraction rate at the metal-mold interface, overheating of the liquid metal and the physico-chemical properties of metal or alloy (latent heat of fusion, density, viscosity, surface tension and solidification mode). Also, the alloy chemical composition plays a fundamental role on the resultant fluidity length and has been extensively studied in the literature by Flemings (1974), Campbell (1991) and Garbellini et al. (1990). In general, pure metals and alloys of eutectic composition have the highest values of fluidity, whilst intermediate composition alloys with greater solidification range show lesser fluidity lengths. This behavior also shows a relation with the solidification structures.

Biloni and Boettinger (1996) classified eutectic systems in two groups: regular and irregular. The criteria used for this are: the entropy of fusion and the volume fraction of phases. If both phases have low entropy of fusion exhibits a regular or nonfaceted-nonfaceted morphology. If one phase has high and the other low entropy then the eutectic morphology results irregular or faceted-nonfaceted type.

Based on the results obtained by the authors in previous works for the AlCuSi system, Garbellini et al. (1990 and 2004), the aim of this work is to analyze the fluidity of binary and ternary metallic alloys, with composition close to the eutectic composition, in terms of solidification microstructure. The fluidity measurements were carried out in linear fluidity tests corresponding to the Al-rich corner of the AlAgCu diagram and Sn based alloys extensively used for important industrial applications. The purpose was to determine the physical mechanism involved in experiments and the relationships between morphology of growth, microstructure and fluidity length, and consequently the influence on binary and ternary proeutectic alloys.

2. Experimental

2.1. Materials

Binary and ternary alloys were prepared by melting pure elements (4N) in an electric resistance-type furnace under inert Ar gas atmosphere, stirred for adequate homogenization and cast in stainless steel molds. The nominal compositions of the alloys are expressed as weight % of solute.

2.2. Fluidity Tests

Fluidity Tests were carried out in a vacuum linear device described by Garbellini et al.(1990) and Morando et al.(2007), molten alloys were forced to flow on a rectangular sectioned channel under depress-casting. The distance travelled by the alloy until it is stopped by solidification is called Fluidity Length (L_F). As the solidification microstructures depend on the cooling conditions, fluidity values were determined under two different cooling conditions: refractory sand mold giving a heat transfer coefficient at the metal-mold interface h_i = 0.2 x103 J/m^2.s.K (slow cooling) and h_i = 5x103 J/m^2.s.K (fast cooling) for cooper mold. In each experience the liquid alloy is forced to flow in the channel under constant metallostatic pressure ΔP=2mmHg or 15mmHg for sand or Cu mold respectively to a casting temperature. The mold is cooled in air. The sample was removed and longitudinally sectioned. We measured the distance travelled by the metal until it is stopped by solidification: L_F. Each data represents the average of at least 5 experiments performed under the same experimental conditions. The dispersion range was 5%.

2.3. Metallographic Study

The solidified samples were polished for microstructural observations. Both Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) were used to characterize the microstructure. Energy dispersive X-ray microanalysis (EDAX) was used to characterize the compositions. Microstructural analysis was performed on metallographic specimens that were polished following standard metallographic procedures, etched with a solution of 0.5ml of HF in H_2O and then 42.5 ml of HCl + 42g FeCl3 in 5 ml of alcohol (Al alloys) and 2% HCl in alcohol (Sn based alloys) and electrolytically polished with butilcelosolve80cc, 10cc glycerin and 10cc perchloric acid.

2.4. Thermal Properties

Computer-aided cooling curve analysis (CA-CCA) was used to determine solidus and liquidus temperatures, the range of solidification and the amount of undercooling associated with the solidification of the alloys and DSC (Differential Scanning Calorimetry) was used to determine latent heat of fusion. Cooling curves were carried out using small samples between 50 and 80g in an electric furnace, electronically controlled. Chamber and sample temperatures were taken by using K type thermocouples wired to a NI-USB 9211 acquisition data interface, connected to a personal computer. The latent heat of fusion (H_F) was determined using a scanning calorimeter Heat Flux DSC Rheometric Scientific SP, with a stability of line better than 1mW in the measurement range used. The samples used are 6mm in diameter and 20mg of weight. The curves were obtained for scan rates of 5 and 10K/min.

3. Results and Discussion

3.1. AlAgCu alloys

Table 1 contains the nominal composition of the AlAgCu alloys expressed as weight % of solute, Fluidity Length obtained for the two cooling conditions: slow cooling (refractory sand mold) L_{FS} and fast cooling (Cu mold) L_{FF}, Latent Heat of fusion (H_F), constituent phases (according to the equilibrium diagram, Mondolfo (1976), and the microstructures analysis by EDAX) and the melting temperature (T_M) determined experimentally.

Table 1. Composition, Constituent phases, Fluidity Length (L_F), Latent Heat of fusion (H_F) and Melting Temperature (T_M) of the AlAgCu alloys.

Alloy	Composition	Constituent phases	L_{FS} (cm)	L_{FF} (cm)	H_F (J/g)	T_M(ºC)
1	Al-33%Cu	BE: Al+Al_2Cu	33	35.3	331	548
2	Al-70%Ag	BE: Al+Ag_2Al	23	24.6	230	565
3	Al-32%Ag-20%Cu	TE: Al+Al_2Cu+Ag_2Al	13	14	373	502
4	Al-5%Ag-10%Cu	Al+Al_2Cu+ET	15	16.2	387	622
5	Al-10%Ag-10%Cu	Al+Al_2Cu+ET	11.5	12.5	380	612
6	Al-40%Ag-10%Cu	Al+Ag_2Al+ET	16	17.3	290	566

BE: binary eutectic
TE: ternary eutectic

It is observed that general behaviour is similar for both cooling rates, the results obtained for the refractory sand mold (L_{FS}) are similar to those obtained for the Cu mold (L_{FF}).

Typical optical micrographs (OM) of Al-33%Cu and Al-70%Ag binary eutectic alloys are shown in Figure 1. The alloy Al-33%Cu (Alloy 1 in Table 1) exhibits a regular lamellar morphology consisting of two non faceted phases: α-Al (white phase) and θ-Al_2Cu (black phase) as shown in Figure 1a).Figure 1b)is an OMof the Al-70%Ag (Alloy 2), exhibits a regular lamellar morphology consisting of two non faceted phases: α-Al (white phase) and ξ-Ag_2Al (black phase).

Figure 2a and b) shows an OM and Scanning Electron Micrograph (SEM) of the alloy 3, Al-32% Ag-20% Cu, corresponding to the ternary eutectic composition. Presents a Semi regular or Brick type structure (Mc Cartney et al. 1980) composed by α-Al primary dendrites (phase 1) and two phase dendrites Ag_2Al (phases 2 and 4) and Al_2Cu (phase 3). These phases are marked in Figure 2b), the composition were determined by energy dispersive X-ray microanalysis (EDAX).

Figure 3shows an OM and SEM micrographs of the alloy 4, Al-5% Cu-10% Ag. The microstructure consists of α-Al primary phase dendrites (clear phase) and a fine interdendritic phase (dark phase) composed of binary eutectic Al-Al_2Cu and ternary eutectic. The detail of the microstructure is shown in Figure 3b) in which are marked the different phases whose compositions were determined by EDAX: α-Al (phase 1), Al-Al_2Cu (phase 2) and Al-Ag_2Al Al_2Cu (phase 3).

Figure 4 shows OM and SEM micrographs of alloy 6 whose composition is Al-40% Ag-10% Cu. Presents in its microstructure primary dendrites α-Al (dark phase), binary degenerated eutectic Al-Ag_2Al (clear phase) and fine ternary eutectic in the interdendritic spaces. The detail of this microstructure is shown in Figure 4b) (SEM) in which are marked the different phases whose compositions were determined by EDAX: α-Al (phase 1), Al-Ag_2Al (phase 3) and Al-Al_2Cu-Ag_2Al (phase 2).

Regular or non faceted-non faceted binary eutectics alloys, 1 and 2, flow better than the ternary eutectic alloy 3 because of solidification mode. In the first group liquid-solid interface is flat as in pure metals and the latter is irregular. In ternary non eutectic AlAgCu alloys, 4, 5 and 6 alloys, flow values depend on the fluidity of the phases present in the microstructure. These results agree with those obtained in previous works for AlCuSi system by Garbellini et al. (1990 and 2004).

In Figure 5, we can appreciate the thermograms obtained at a rate of 5K/min for the non-eutectic composition alloys Al-5% Ag-10% Cu, Al-10% Ag-10% Cu and Al-40% Ag-10% Cu. The first two concentrations correspond to the same primary zone on the phase diagram (Mondolfo 1976), this is observed in the generation of a primary phase at a similar temperature labeled (α) and the appearance of the binary eutectic (1) before the most important reaction (2) (ternary eutectic). The third studied composition is the nearest to the ternary eutectic composition so that the contribution of the primary phase is less compared to the other two curves, increasing the area corresponding to the ternary eutectic reaction in comparison with the other two processes.

Figure 6 shows a thermogram obtained by DSC (Differential Scanning Calorimetry) for the Al-40% Ag-10% Cu alloy where the heat released during solidification is shown as the area enclosed under the curve. In (a) starts the primary phase formation in small amount, whereas (b) highlight the ternary eutectic reaction at 774K. In the same figure shows the evolution of the solid fraction as a function of temperature for the same alloy. We analyzed the various alloys listed in Table 1 using this method.

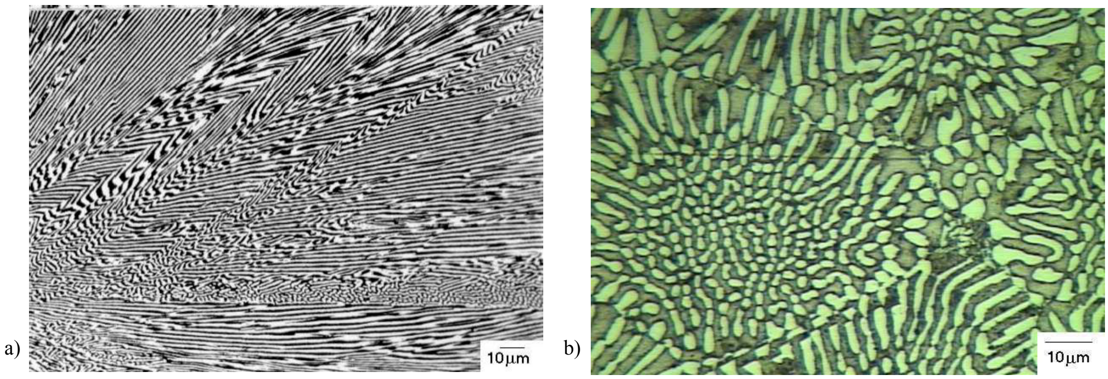
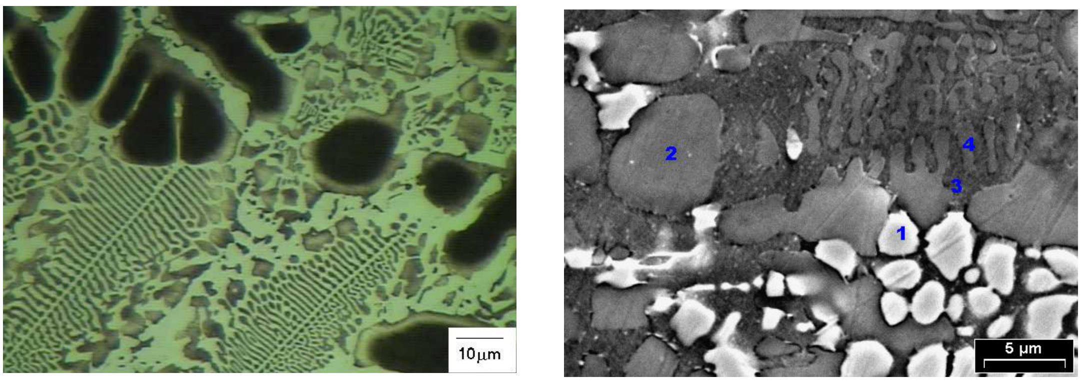
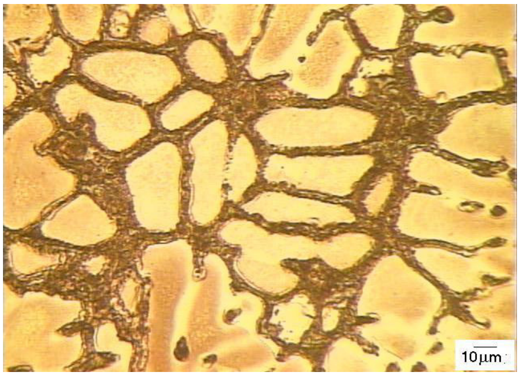


Fig. 1.Optical micrographs of the (a) Al-33%Cu and (b) Al-70%Ag eutectic alloys.



a) b)

Fig.2.(a) Optical and (b) Scanning Electron Micrographs of theAl-32%Ag-20%Cu ternary eutectic alloy.

a) 

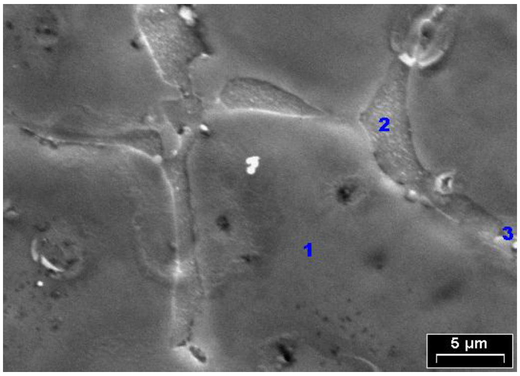
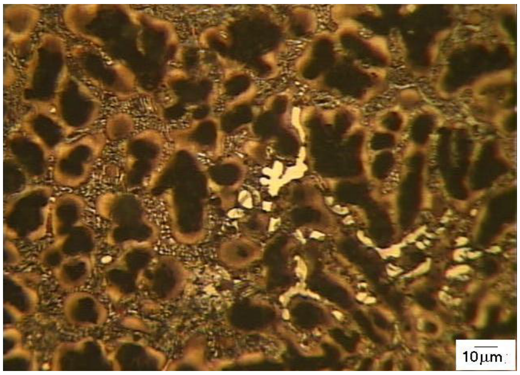
b) 

Fig. 3. (a) Optical and (b) Scanning Electron Micrographs of theAl-5%Ag-10%Cu alloy.

a) 

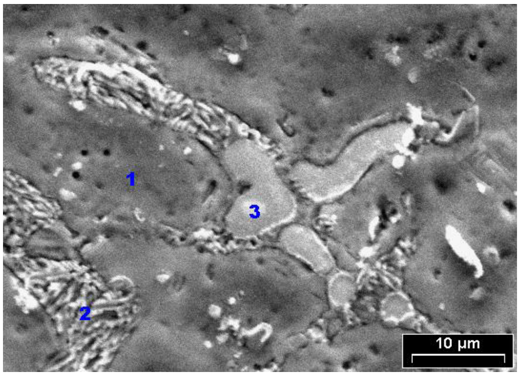
b) 

Fig. 4. (a) Optical and (b) Scanning Electron Micrographs of theAl-40%Ag-10%Cu alloy.

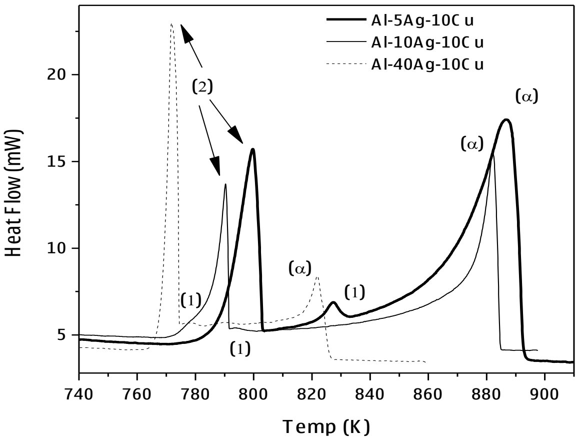


Fig. 5. Thermograms obtained by DSC for the AlAgCu non eutectic ternary alloys. In the curves is indicated the formation of the primary phase (α), binary (1) and ternary (2) eutectic.

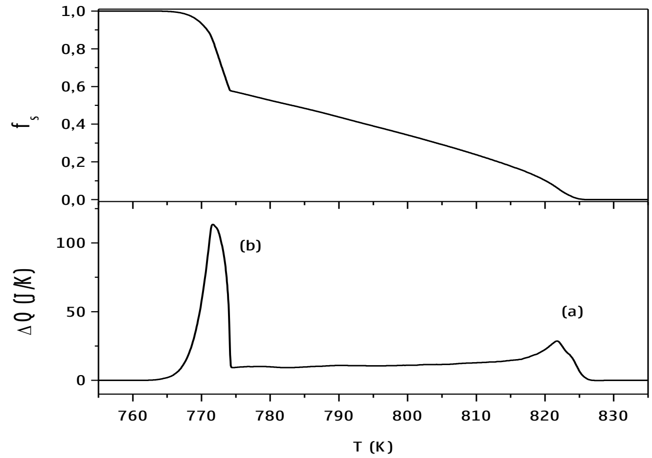


Fig. 6.Evolution of heat released during solidification for theAl-40% Ag-10% Cu alloy and the solid fraction changes *vs* temperature.

3.2. Sn based alloys

Table 2 contains the nominal composition of the Sn based alloys expressed as weight % of solute, Fluidity Length obtained for the two cooling conditions: slow cooling (refractory sand mold) L_{FS} and fast cooling (Cu mold) L_{FF}, Latent Heat of fusion (H_F), constituent phases (according to the microstructures analysis by EDAX) and the melting temperature (T_M) determined experimentally.

Table 2. Composition, Constituent phases, Fluidity Length (L_F), Latent Heat of fusion (H_F) and fusion Temperature (T_M) of the Sn Based alloys.

Alloy	Composition	Constituent phases	L_{FS} (cm)	L_{FF} (cm)	H_F (J/g)	T_M(ºC)
1	Sn		20.8	21.5	53.85	230.1
2	Sn-37%Pb	BE: Sn+PbSn	15	17.6	42.4	177.7
3	Sn-3.5%Ag	BE: Sn+Ag_3Sn	12.5	13.9	56.07	218.3
4	Sn-0.7%Cu	BE: Sn+Cu_6Sn_5	11.8	13.5	56.28	224.5
5	Sn-9%Zn	BE: Sn+ZnSn	14	16.4	56.2	196.9
6	Sn-57%Bi	BE: Bi+SnBi	20.5	21.5	52.1	134.7

BE: binary eutectic

As obtained for the AlAgCu alloys, the results for the refractory sand mold (L_{FS}) are similar to those obtained for the Cu mold (L_{FF}).

Figure 7 is a summary of the cooling curves obtained for different eutectic Sn based alloys, pure Sn and Sn-Pb eutectic studied under controlled conditions. We can observe the typical aspect of Temperature-time curve, characteristic of the solidification. For some of these alloys we observed an initial undercooling at the start of the nucleation followed by a jump to reach the solidification temperature T_S. This shift reach up to approximately 5ºC, particularly in pure Sn, binary Sn-Cu, Sn-Ag and ternary Sn-Ag-Cu eutectics. As can be noted, the greater temperature corresponds to pure Sn, then binary Sn-Cu and Sn-Ag, ternary Sn-Ag-Cu, Sn-Zn and Sn-Pb eutectic. The lower temperature was obtained for binary eutectic Sn-Bi, even lower than traditionally used Sn-Pb. These data are summarized in the last column of Table 2.

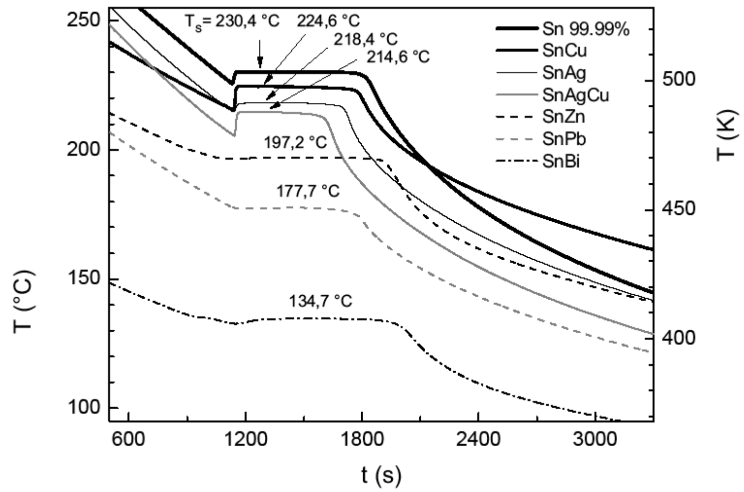


Fig. 7.Cooling curves Temperature vs time for the Sn based eutectic alloys and pure Sn.

Figure 8 shows Optical Micrographs (OM) of Sn-37%Pb eutectic alloy under different cooling conditions: a) fast cooling (Cu mold) and b) slow cooling (refractory sand mold). The microstructure consists on a mixture of fine Sn-rich (light regions) and Pb-rich (dark area) solid solutions forming a lamellar regular eutectic microstructure. The cooling rate affect significantly the microstructures of the solder alloys. Ochoa (2003) showed that an increase in solidification speed produces a refinement in the microstructure (Sn dendrites decrease in size). This is consistent with Fleming´s solidification theory (1974), which proposed that rapid solidification decreases the time needed for diffusion resulting in a finer dendritic microstructure.

Figure 9 exhibit OM of the microstructure of a) Sn-3.5%Ag and b) Sn-0.7%Cu binary eutectic alloys. The binary eutectic microstructure either in Sn-3.5%Ag or Sn-0.7%Cu is a mixture of the intermetallic particles, Ag_3Sn or Cu_6Sn_5, in the β-Sn matrix. Consists of two regions, i.e, white regions (primary Sn phase) surrounded by a dark network. These alloys exhibits a faceted-non faceted morphology corresponding to irregular eutectics, where the non-faceted phase is Sn and the faceted phase is Ag_3Sn or Cu_6Sn_5 respectively.

Figure 10 shows a) OM and b) Scanning Electron Micrographs (SEM) of Sn-9%Zn binary eutectic alloy. The structure corresponds to irregular eutectic, it is formed by a Sn-rich matrix and Sn-Zn needles, as can be seen in the micrographs. The constituent phases are marked on the SEM micrograph and were determined by EDAX.

Figure 11 shows a) OM and b) SEM micrographs, the typical microstructure of Sn-57%Bi binary eutectic alloy. It is a regular globular type structure, consisting of a mixture of Bi-rich crystals in an eutectic matrix composed by Sn (light phase) and Bi (dark phase). The detail of this microstructure is shown in Figure 11b) in which are marked the different constituent phases. This is a lamellar regular eutectic like Sn-37%Pb.

Sn-3.5% Ag and Sn-0.7% Cu eutectic alloys have the lowest fluidity values of the Sn based alloys analysed. As mentioned above, both have a similar structure, with eutectic formation around the primary phase. The fluidity of Sn-9% Zn is greater, their morphology is irregular or non-faceted faceted type as in the case of Sn-3, 5% Ag and Sn-0, 7% Cu, although in this case has a greater percentage of eutectic phase, which could explain the higher fluidity. Sn-37% Pb and Sn-57%Bi binary alloys have a lamellar eutectic microstructure corresponding to a regular type eutectic and have fluidity greater than the fluidity of the irregular eutectics. These results agree with those obtained in previous works for other eutectic systems by Garbellini et al. (1990 and 2004) and Di Sabatino (2005).

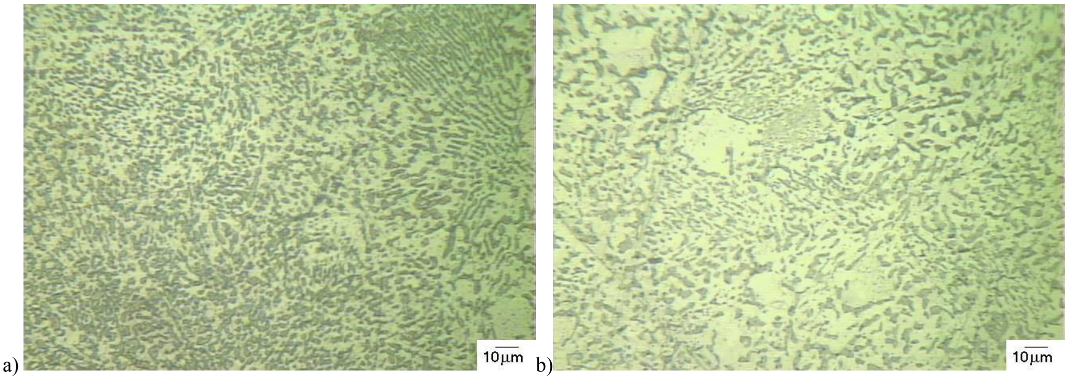


Fig. 8. Optical micrographs of the Sn-37%Pb eutectic alloy, (a) Cu and (b) refractory sand mold,at the same magnification for microstructure refinement comparison.

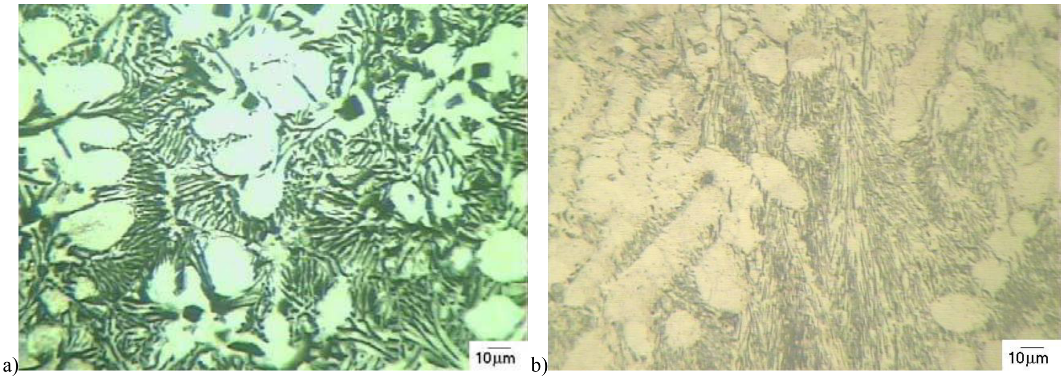


Fig. 9. Optical micrographs of the (a) Sn-3.5%Ag and(b) Sn-0.7%Cu eutectic alloys.

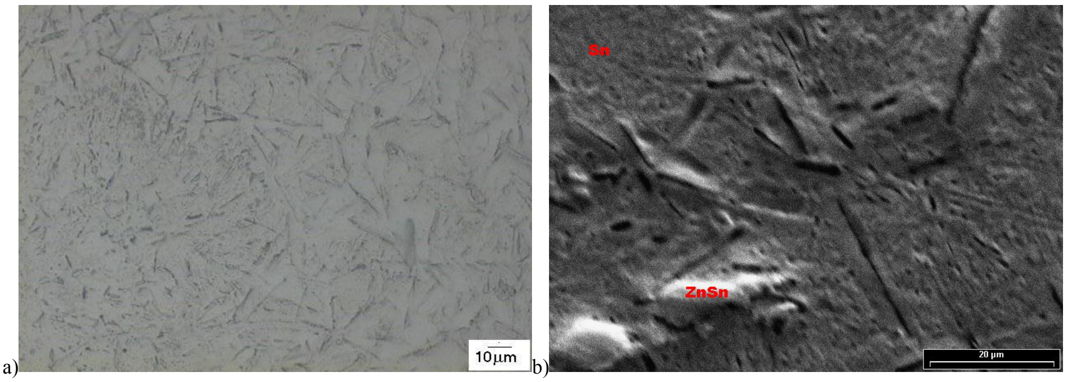


Fig. 10. (a) Optical and (b) Scanning Electron Micrographs of the Sn-9%Zn eutectic alloy.

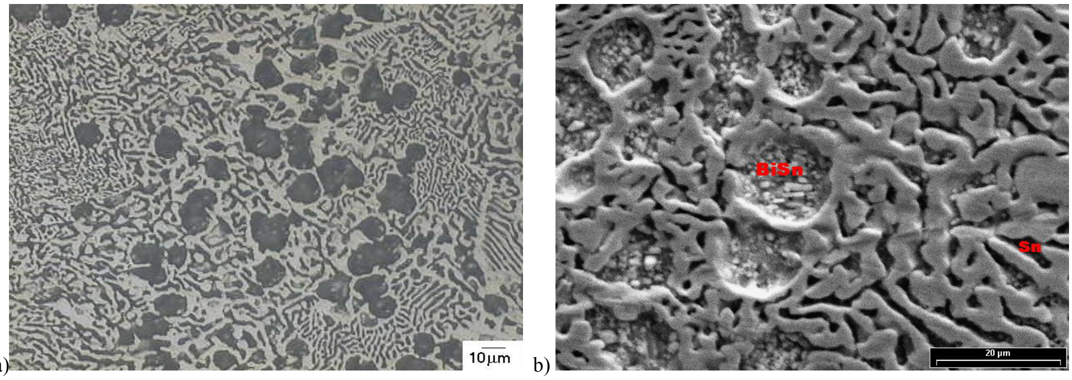
a) b)


Fig. 11. (a) Optical and (b) Scanning Electron Micrographs of the Sn-57%Bi eutectic alloy.

4. Conclusions

In this work we studied the fluidity of AlAgCu alloys in the Al-richcorner, within the primary phase fieldα-Al and Sn based eutectic alloys. The results were related to resultant microstructures:

Fluidity Length values obtained for the refractory sand mold (slow cooling) are similar for those obtained for the Cu mold (fast cooling).

The cooling rate affects significantly the microstructure of the alloys, an increase in that produces a refinement in the microstructure. This is consistent with the solidification theory, which proposed that rapid solidification decreases the time needed for diffusion resulting in a finer dendritic microstructure.

Regular or non faceted-non faceted binary eutectics alloys flow better than irregular or non faceted-faceted eutectics because of solidification mode. In the first group liquid-solid interface is flat as in pure metals and the latter is irregular.

In ternary non eutectic AlAgCu alloys, nº 4, 5 and 6 alloys, flow values depend on the fluidity of the phases present in the microstructure.

Analysis of the solidification microstructures of the samples permits the correlation of Fluidity Length with the solidification mode, latent heat of fusion of the alloy and the fluidity of the phases present in the microstructure.

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