

# Effect of the bismuth content on the interface reactions between copper substrate and Sn-Zn-Al-Bi lead-free solder

D. Soares\*, C. Vilarinho\*, J. Barbosa\*, R. Silva\* and F. Castro\*

## Abstract

Because of environmental and health concerns, some alternative solder alloys, named lead-free ones, are being developed. Among them, the Sn-Zn-Al system has been studied and reveals promising properties. In this work the presence of bismuth, in the range of 0 -8 wt%, was evaluated in what concerns to the chemical interactions between solder/substrate and the equilibrium phases present at the interface. The phases formed at the interface between the copper substrate and a molten lead-free solder were studied with different time of stage and alloy compositions. The effect of bismuth content on transformation temperatures of a Sn-9Zn-1Al base alloy was studied by Differential Scanning Calorimetry (DSC). For each alloy the solidification range was determined, which is an important characteristic regarding the application of these materials in the electronic industry. Identification of equilibrium phases and their chemical composition evaluation was performed by scanning electron microscopy (SEM/EDS). The interface thickness and chemical composition profiles were also evaluated.

## Keywords

Solder. Interface reactions. Bismuth effect.

## Efecto del contenido en bismuto sobre las reacciones en la superficie de contacto entre el substrato de cobre y la soldadura Sn-Zn-Al-Bi sin plomo

## Resumen

Debido a las preocupaciones ambientales y sanitarias, se están desarrollando aleaciones alternativas para soldadura sin plomo. Entre ellas se ha estudiado el sistema Sn-Zn-Al, que revela propiedades prometedoras. En este trabajo se evalúa la presencia de bismuto, en el rango de 0 a 8 % en peso, en relación con las interacciones químicas entre soldadura y substrato y con las fases de equilibrio presentes en la superficie de contacto. Se han estudiado las fases formadas en la superficie de contacto entre el substrato de cobre y una soldadura fundida sin plomo en función del tiempo de mantenimiento y de la composición de la aleación. Se ha evaluado el efecto del contenido en bismuto sobre las temperaturas de transformación de una aleación de base Sn-9Zn-1Al mediante Calorimetría de Barrido Diferencial (DSC). Se ha determinado el rango de solidificación para cada aleación, lo que es una característica importante en relación con la aplicación de estos materiales en la industria de la electrónica. Se ha llevado a cabo la identificación de las fases de equilibrio y su composición química mediante microscopía electrónica de barrido (SEM/EDS). También se han evaluado los perfiles de la composición química y el espesor de la interfase de reacción.

## Palabras clave

Soldadura. Reacciones en la interfase. Efecto del bismuto.

## 1. INTRODUCTION

New lead-free alloys for solders application in the electronic industry are being developed to substitute the traditional Sn-Pb base alloys. Because of lead toxicity, health concerns, environmental and legislation reasons (Directive

2002/96/EC) efforts have been done to substitute the traditional alloys<sup>[1-4]</sup>.

The Sn-Zn based alloys, with chemical compositions close to the eutectic point, are potential candidates to substitute the traditional alloys<sup>[1 and 5]</sup>. This alloy system has several interesting properties for solder applications, namely, the low

(\*) University of Minho, Azurém, 4800-058 Guimarães, Portugal.

melting point, similar to the Sn-Pb alloys, and good mechanical properties<sup>[6]</sup>. These alloys, because of Zn presence, might oxidize during soldering or after that, in service.

The wetting behavior of substrate by the solder is dependent of the interfacial reactions during the soldering process. The presence of Zn and Al might improve the wetting of the copper substrate by the solder<sup>[1]</sup>. The study of the interfacial zone is important to explain the reactions that occur during the soldering process and the intermetallic compound phases (IMC).

The reliability of a solder joint is affected by the solder substrate interaction and type of layers formed at the interface. The microstructure type and phase chemical composition are important factors to anticipate the solder mechanical behavior in service. Heat dissipation in the components, in service, is another aspect to be studied because it might change the interface layers with the formation of different equilibrium phases.

## 2. EXPERIMENTAL PROCEDURE

The solder alloys used in this work were melted from pure elements ( $\geq 99.9$  wt. %) in a resistance furnace under inert atmosphere (obtained by a constant flow of argon) and casted in a steel mold pre-heated up to 100 °C.

After melting and pouring, each alloy was heat treated using the following cycle: heating up to 120 °C at 10 °C/min, stage of 60 min and cooling to room temperature at 10 °C/min. The chemical composition of the produced alloys was determined by XRF Spectrometry.

The solder alloy and the pure copper sheet substrate were polished up to 1.0  $\mu\text{m}$ , cleaned with ethylic alcohol, and pressed to improve the surface contact between the two materials. For the diffusion experiments the assembly was placed in a furnace, under inert atmosphere obtained by the constant flow of pure helium. The following thermal cycle was employed: heating up to 250 °C, at 10 °C/min, stage time of 30 or 120 min and cooling to room temperature, at 10 °C/min.

After the experiments, the samples were cut in a normal section to the diffusion path and polished, in order to study the interface layers produced during the experiments. The samples microstructures were characterized by optical and electronic microscopy and the chemical composition of the phases was determined by EDS by scanning electron microscopy.

## 3. RESULTS AND DISCUSSION

The chemical composition of the alloys (in wt. %) used in this work, obtained by X-ray Fluorescence Spectrometry (XRF), is presented in table I as well as the melting temperatures obtained by DSC. The experiments were made with a heating/cooling of 10 °C/min in an inert atmosphere of high purity helium.

The interface microstructures, obtained in the diffusion experiments for alloys LF1 and LF6, are presented in figures 1a) and 1b), respectively. These alloys have the lower and higher bismuth contents used in the present work. For both alloys, four layers were detected at the interface between the solder and the substrate. The chemical composition of the phases formed at the interface is presented in tables I and II.

The chemical composition profile at the interface, as presented in figures 1b), 1c) and in table II, shows that the first layer (in the copper side) is, essentially, constituted by copper and zinc. The formation of the  $\gamma$  phase at the interface close to the copper side, as proposed by some authors<sup>[7 and 8]</sup>, cannot be confirmed by the results obtained in this work. The formation of the peak, in the Zn content at zone Z5, could explain the difference in the chemical composition.

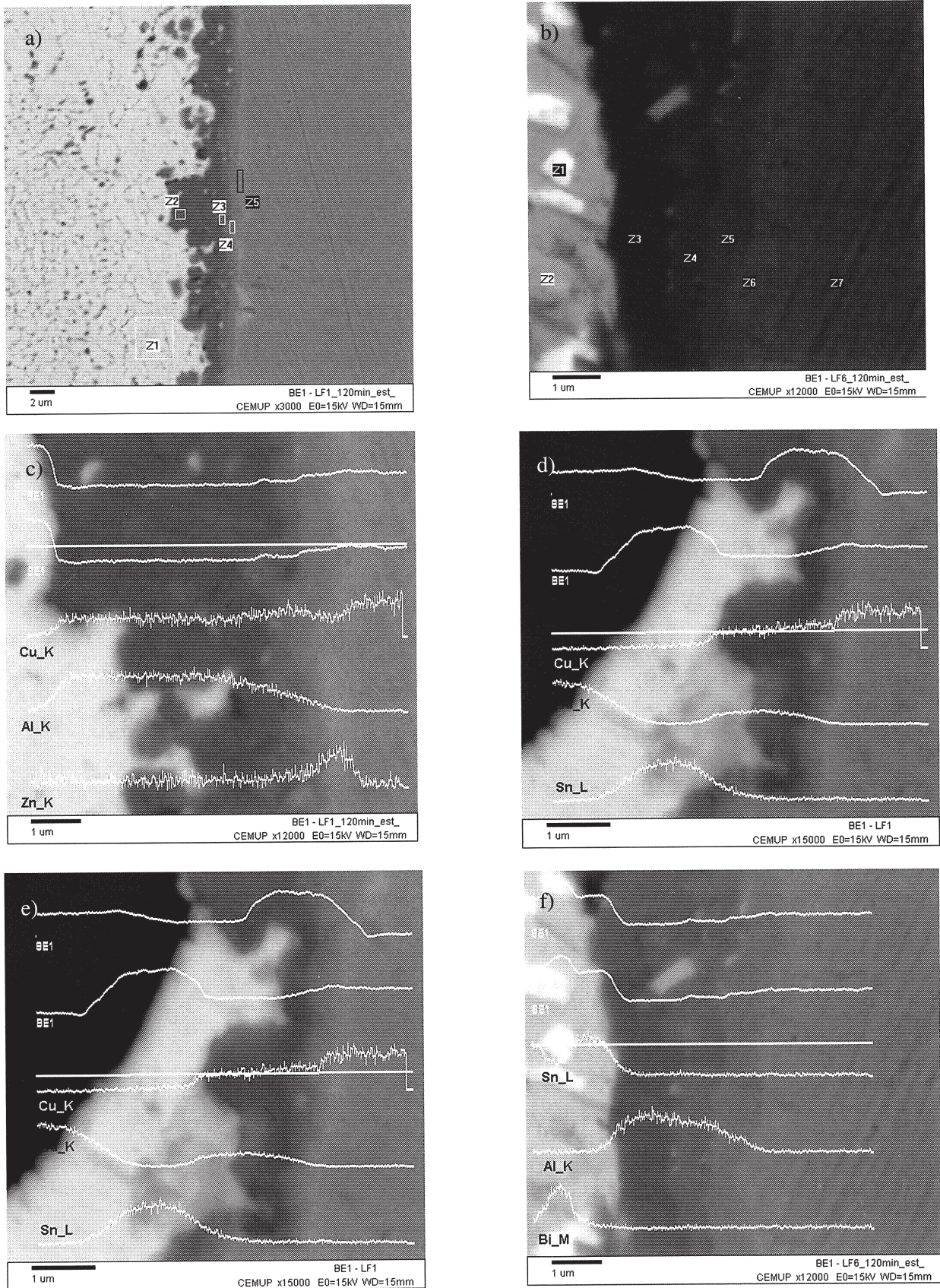
In zone Z5 there is a decrease in the curve representing the copper content at the interface, as presented in figure 2. This behavior shows that the driving force for phase formation at the interface is the thermodynamic equilibrium and not the elements diffusivity, as proposed by Kwang *et al.*<sup>[1]</sup>.

The formation of a first Zn rich layer is not in accordance with Kwang *et al.* experiments obtained with a similar solder composition<sup>[1]</sup>. These authors found an Al rich phase in contact with the copper substrate. The experiments were made at 325 and

**Table I.** Chemical compositions (in wt. %) and melting temperatures of the alloys used in the diffusion experiments

*Tabla I. Composiciones químicas (wt %) y temperaturas de fusión de las aleaciones usadas en los experimentos de difusión*

Solder	% Zn	% Al	% Bi	% Sn	Melting temp. (°C)
LF1	8.3	0.9	-	rest	198.7
LF3	8.2	0.6	1.8	rest	197.3
LF5	9.1	1.1	3.9	rest	188.5
LF6	9.5	1.1	7.6	rest	162 – 189



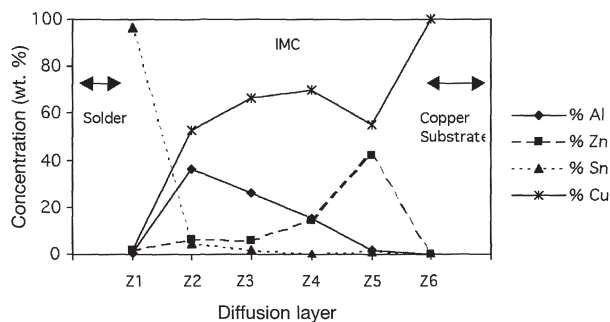
**Figure 1.** Microstructure of the diffusion layers, a) and b) and diffusion profile c-d) and e-f) obtained, respectively, in solder LF1 and LF6.

*Figura 1.* Microestructura de las capas de difusión, a) y b) y perfiles de difusión c-d) y e-f) obtenidos, respectivamente, para las aleaciones LF1 y LF6.

**Table II.** Chemical composition (in wt.%), obtained by SEM/EDS, of the layers obtained in diffusion experiments for alloy LF1 in copper substrate, as presented in figure 1a)

*Tabla II. Composición química (wt %), obtenida por SEM/EDS, de las capas obtenidas en los experimentos de difusión para la aleación LF1 en el sustrato de cobre, según lo presentado en la figura 1a)*

Zone	Solder (Z1)	Z2	Z3	Z4	Z5	Substrate (Z6)
Al	0.5	36.1	26.0	15.6	1.7	-
Zn	1.6	6.4	5.8	14.4	41.8	-
Sn	96.4	4.6	1.8	0.1	0.9	-
Cu	1.5	52.9	66.4	70.0	55.3	100.0



**Figure 2.** Chemical composition profile in the diffusion zone between the copper substrate and the solder alloy LF1.

*Figure 2. Perfil de la composición química en la zona de difusión entre el sustrato de cobre y la aleación LF1.*

355 °C, with short contact time, under 3 s, between solder and substrate which might be not enough to form the equilibrium phases at the interface. However, as presented in figure 2, the Al rich phase obtained in this work appears close to solder zone and not at the copper side. The Al content at the Zn rich layer, zone Z5, is very low. The formation of phase  $\gamma$  as a first layer was predicted, by thermodynamic calculations, by Lee *et al.*<sup>[7]</sup> and confirmed by experimental work for the Sn-Cu-Zn system<sup>[8]</sup>.

The  $\eta$  -  $\text{Cu}_6\text{Sn}_5$  phase, that usually appears in the tin base alloys soldering process, was not detected in the diffusion layers.

The presence of tin at the interface layers is very low. The presence of Cu in the solder zone shows that the diffusivity of that element, through the interface, is higher than the Sn diffusivity. The obtained interface is not regular and no relationship was obtained between the layer dimension and the diffusion time. No significative

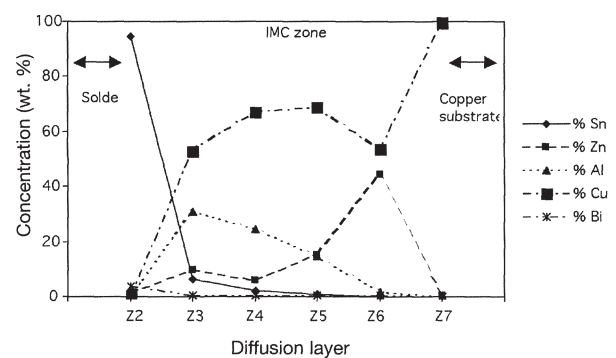
changes were detected in the thickness of the diffusion layer for the experiments with 30 and 120 min of stage, at 250 °C. The obtained diffusion interface varies between 2 and 10  $\mu\text{m}$ . These values are comparable with others obtained for the soldering processes of a Sn-Bi-In-Zn alloy, during ~10 s, with formation of a 3-10  $\mu\text{m}$  layer<sup>[3]</sup>. These results show that the interface layer is very stable and it is not significantly growing with time.

For the experiments with solders containing bismuth, a similar interface zone microstructure was obtained. Figures 1d) and 1f) present the interface constitution, for alloy LF6, which correspond to the highest bismuth content tested. As for alloy LF1, four layers were obtained at the interface. The interface chemical composition profile is presented in table III and figure 3. The

**Table III.** Chemical composition (in wt%), obtained by SEM/EDS, of the layers produced in the diffusion experiments, with 120 min of stage, for alloy LF6 in copper substrate, as presented in figure 1b)

*Tabla III. Composición química (wt %), obtenida por SEM/EDS, de las capas obtenidas en los experimentos de difusión, con 120 min de contacto, para la aleación LF6 en el sustrato de cobre, según lo presentado en la figura 1b)*

Zone	Solder (Z2)	Z3	Z4	Z5	Z6	Substrate (Z7)
Al	0.2	31.0	24.4	14.9	1.8	0.2
Zn	4.9	9.7	6.0	15.0	44.3	0.0
Sn	83.6	6.3	2.2	1.0	0.0	0.3
Bi	10.1	0.5	0.4	0.3	0.4	0.0
Cu	1.1	52.6	66.9	68.9	53.5	99.5



**Figure 3.** Chemical composition profile in the diffusion zone between the copper substrate and the solder alloy LF6.

*Figure 3. Perfil de la composición química en la zona de difusión entre el sustrato de cobre y la aleación LF6.*

layer close to the copper side is, as for the LF1 alloy, constituted, essentially by copper and zinc. The chemical composition layer profile is similar to the obtained for the Sn-Zn-Al solder alloy. The bismuth content at the interface layers is very low, as presented in table III, and does not change the interface constitution.

The high level of some alloying elements, at the formed interface, shows that the thermodynamic equilibrium is the driving force for the interface reactions. The formation of a zinc rich phase in equilibrium with the copper substrate is in accordance with the phase equilibria of the Cu-Sn-Zn system, proposed by Bau *et al.*<sup>[9]</sup>. Figure 4 presents a vertical section of the ternary Cu-Sn-Zn system for the zone of high copper content. The figure shows that at low temperatures, up to ~500 °C, the copper rich phase is in equilibrium with the  $\gamma$  phase.

The presence of bismuth in the solder composition, up to ~8 wt%, does not change the state of equilibrium at the substrate layer.

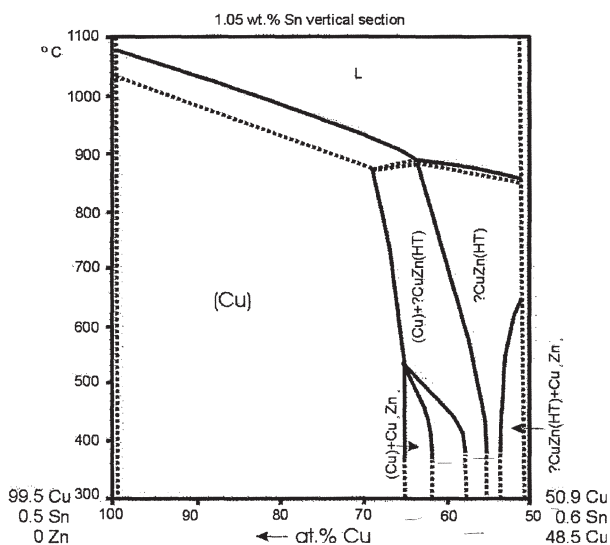


Figure 4. Vertical section of the Cu-Sn-Zn phase diagram<sup>[9]</sup>.

Figure 4. Sección vertical del diagrama de fases del sistema Cu-Sn-Zn<sup>[9]</sup>.

#### 4. CONCLUSIONS

The solder substrate interface was produced and characterized for alloys of the Sn-Zn-Al and Sn-Zn-Al-Bi systems. A similar interface profile, constituted by four layers, was detected for the two kind of alloy systems. The chemical composition profile has been determined by SEM/EDS analysis.

A first layer, in contact with the copper substrate, corresponding to the  $\gamma$  phase of the Cu-Zn system was obtained.

There is a high concentration of low content alloying elements, namely Al and Zn, at the interface. The presence of Al and Bi, in the solder, does not changes, the first layer next to the copper side, local equilibrium.

No significant effect was obtained between the diffusion time and the thickness of the solder/substrate interface or of the four layers produced.

#### REFERENCES

- [1] KWANG-LUNG LIN and LI-HSIANG WEN, *J. Mater. Sci. Mater. El.* 9 (1998) 5-8.
- [2] T. MASSALSKI, J. MURRAY, L. BENNETT and H. BAKE, *Binary alloy phase diagrams*, Vol. 1, ASM, 1986.
- [3] S. W. YOON, J.-R. SOH, B.-J. LEE and H. M. LEE, *Acta Mater.* 45 (1997) 951-960.
- [4] S. W. YOON, W. K. CHOI and H. M. LEE, *Scripta Mater.* 40 (1999) 327-332.
- [5] M. ABTEW and G. SELVADURAY, *Mat. Sci. Eng.* 27 (2000) 95-141.
- [6] T. SIEWERT, S. LIU, D. R. SMITH and J. C. MADENI, *National Institute of Standards and Technology – Properties of Lead-Free solders*, 2002.
- [7] BYEONG-JOO LEE, NONG M. HWANG and HYUCK M. LEE, *Acta Mater.* 45 (1997) 1867-1874.
- [8] S. W. YOON, R. J. LEE and B. J. LEE, 45 (1997) 951.
- [9] P. VILLARS, A. PRINCE and H. OKAMOTO, *Handbook of ternary alloy phase diagrams*, ASM International, 1997.