Study of the interface reactions between two lead-free solders and copper substrates

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Resumo

As ligas tradicionais para solda, à base de Sn-Pb, estão a ser substituídas devido ao impacto, causado pela toxicidade do chumbo, no ambiente e na saúde humana. Entre os sistemas alternativos de ligas sem chumbo, as ligas à base de Sn-Zn e Sn-Cu apresentam propriedades promissoras. As características da ligação produzida dependem do tipo de reacções que ocorrem entre a solda e o substrato, durante a operação de soldadura.
As reacções solda/substrato foram estudadas neste trabalho, para diferentes ligas dos sistemas Sn-Zn e Sn-Cu, relativamente à morfologia e composição química da interface. Foram caracterizadas as fases formadas entre a solda no estado líquido e o substrato de cobre, à temperatura de 250 ºC, para diferentes composições químicas da solda e tempos de estágio. As temperaturas de transformação das ligas ensaiadas foram determinadas por Calorimetria Diferencial de Varrimento (DSC).
A caracterização morfológica da interface criada foi efectuada por Microscopia Electrónica de Varrimento e a análise química por Espectroscopia de Dispersão de Energias (SEM/EDS). Os resultados obtidos, para as ligas sem chumbo, foram comparados com os obtidos para a solda tradicional, à base de Sn-Pb. Foram obtidos diferentes tipos de morfologia de interface, nomeadamente, para os sistemas contendo zinco.

Abstract

Traditional Sn-Pb solder alloys are being replaced, because of environmental and health concerns about lead toxicity. Among some alternative alloy systems, the Sn-Zn and Sn-Cu base alloy systems have been studied and reveal promising properties. The reliability of a solder joint is affected by the solder/substrate interaction and type of layers formed at the interface.
The solder/substrate reactions, for Sn-Zn and Sn-Cu base solder alloys, were evaluated in what concerns the morphology and chemical composition of the interface layer. The phases formed at the interface between the Cu substrate and a molten lead-free solder were studied, at 250 ºC, with different stage times and alloy compositions. The melting temperatures of the studied alloys, were determined by Differential Scanning Calorimetry (DSC).
Identification of equilibrium phases, formed at the interface layer, and the evaluation of their chemical compositions were performed by Scanning Electron Microscopy (SEM/EDS). Results of the studied systems were compared with the interface characteristics obtained for a traditional Sn-Pb solder alloy. Different interface characteristics were obtained, namely for the alloys containing Zn.

Introduction

New lead-free alloys for solders application in the electronic industry are being developed to substitute 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 [1,2,3,4].

The Sn-Zn and Sn-Cu based alloys, with chemical compositions close to their eutectic points, are potential candidates to substitute the traditional alloys [1,5]. The Sn-Zn alloy system has several interesting properties for solder applications, namely, the low melting point, similar to the Sn-Pb alloys, and good mechanical properties [6,7]. Alloys from the Sn-Cu based systems, although their higher melting temperature, are also an alternative for replacing the traditional lead containing alloys.

The wetting behavior of substrate by the solder is dependent of the interfacial reactions during the soldering process. The presence of Zn and Al may improve the wetting of copper or nickel substrates by the solder [1].

The study of the interfacial zone is important to explain the reactions that occur during the soldering process and the intermetallic compound phases (IMC) formed. The reliability of a solder joint is affected by the solder substrate interaction and by the 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. The IMC constitution is also important in the definition of the thermal and electrical conductivity through the solder contact.

Experimental procedure

The solder alloys used in this work were melted from pure elements (≥99.9 wt. %) in a resistance furnace under inert atmosphere (obtained by a constant flow of argon) and cast in a steel mold, pre-heated up to 100 ºC. After melting and pouring, each alloy was heat treated using the following cycle: heating up to 120 ºC, at 10 ºC/min, stage of 60 min,. and cooling to room temperature, at 10 ºC/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 µm diamond paste, cleaned with ethylic alcohol, dried 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 a constant flow of pure helium (99,999% purity).

After the diffusion experiments, samples were cut through a section normal to the diffusion path and polished, in order to study the interface layers produced during the experiments. The samples microstructures were characterized by means of optical and electronic microscopy and the chemical composition of the interface phases determined by Energy Dispersive Spectrometry at Scanning Electron Microscopy (SEM/EDS).

Results and discussion

The chemical composition of the alloys (in wt.%) used in this work, obtained by XRF spectrometry, is presented in table 1 as well as the melting temperatures obtained by DSC. The DSC experiments were made with a heating/cooling of 10 ºC/min in an inert atmosphere of high purity helium.

Results of the thermal analysis, considering the melting range temperatures of the heating cycle, for alloys of the Sn-Pb (alloy P1), Sn-Zn (alloy LF1, LF24 and LF6) and Sn-Cu (alloy LF27, LF22 and LF23) base systems, are presented in figure 1. Melting range, shown in table 1, was determined considering the start of melting, determined as the onset point in the DSC curve, and the curve peak temperature, corresponding to the end of the melting, for the used heating rate. When compared with traditional alloy (P1 in table 1) lead-free alloys have higher melting range temperatures, as shown in table 1 and figure 1.

For both systems of alloys, the introduction of Bi lowers the melting temperature. For the lead-free alloys, systems based on the Sn-Cu system have higher melting temperatures, above 200 ºC. The melting temperatures are higher than 20ºC above the traditional Sn-Pb alloys.

Table 1 – Chemical compositions (in wt.%), determined XRF, of the alloys used in the diffusion experiments.

Solder	% Zn	% Cu	% Pb	% Al	% Bi	% Sn	Melting range (ºC)
P1	-	-	34.7	-	2.6	rest	174-181
LF1	8.3	-	-	0.9	-	rest	196-200
LF24	9.8	-	-	0.1	3.3	rest	181-197
LF6	9.5	-	-	1.1	7.6	rest	173-189
LF27	-	0.6	-	-	-	rest	226-230
LF22	-	0.8	-	-	5.6	rest	204-221
LF23	-	0.7	-	-	7.5	rest	207-226

Table 2 – Chemical composition (in wt.%), obtained by SEM/EDS, of the layers obtained in diffusion experiments for tested solders, in copper substrate, as presented in figures 3a) to 3d).

Zone	Solder	Z1	Z2	Z3	Z4	substrate
Al	0.5	36.1	26.0	15.5	1.8	-
Zn	1.6	6.4	5.8	14.4	41.9	-
Sn	96.4	4.6	1.8	0.1	0.9	-
Cu	1.5	52.9	66.4	70.0	55.4	100.0

a) Sn-Zn-Al solder system (LF1)

Zone	Solder	Z1	Z2	Z3	Z4	Substrate
Al	0.2	31.0	24.4	14.9	1.8	0.2
Zn	4.9	9.7	6.1	15.0	44.3	-
Sn	83.7	6.3	2.2	1.0	0.0	0.3
Bi	10.1	0.5	0.4	0.3	0.4	-
Cu	1.1	52.5	66.9	68.8	53.5	99.5

b) Sn-Zn-Al-Bi solder system (LF6)

Zone	Z1	Z2	Z3	substrate
Sn	89.5	63.4	38.1	0.5
Bi	9.8	-	0.2	-
Cu	0.7	36.6	61.7	99.5

c) Sn-Cu-Bi solder system (LF 22)

Zone	Z1	Z2	Z3	substrate
Sn	62.4	65.8	40.1	0.3
Bi	2.7	0.3	-	-
Cu	-	33.9	59.8	99.6
Pb	34.9	-	0.1	0.1

d) Sn-Pb-Bi solder system (P1)

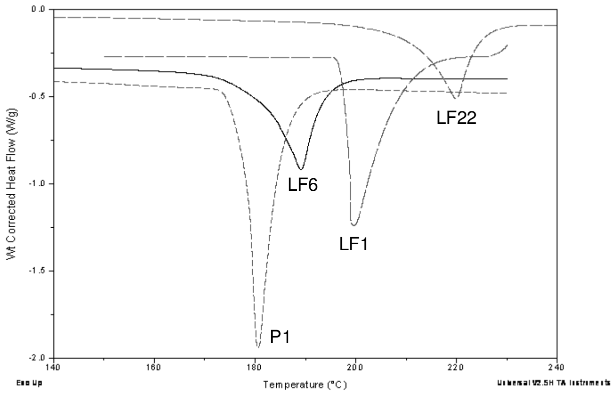
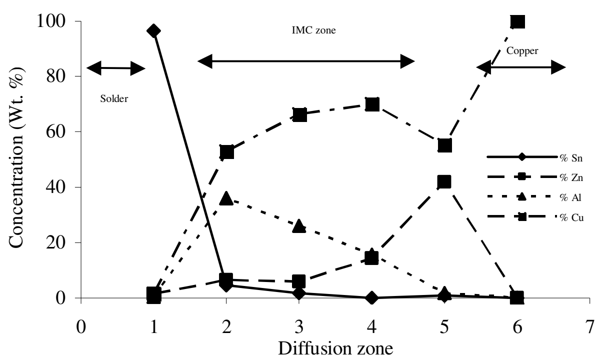
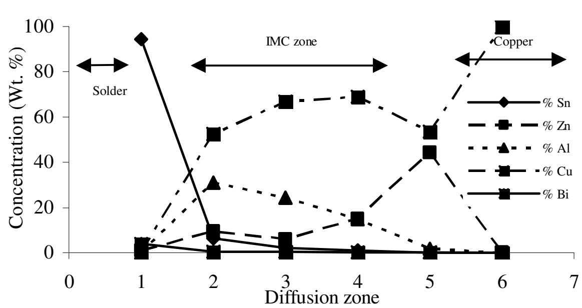


Figure 1 – DSC curves, at the melting range in the heating cycle, for the studied alloys.

The obtained solder/substrate interfaces, for the tested Sn-Zn, Sn-Cu and Sn-Pb base solder alloys, are different concerning the number and morphology of IMC at the interface layer, as presented in figures 2 and 3. The chemical compositions of intermetallic compounds (IMC) found at the interface, are presented in table 2.



a)



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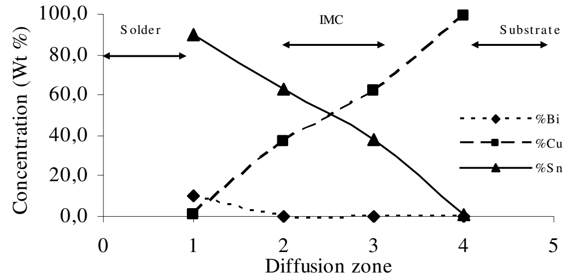

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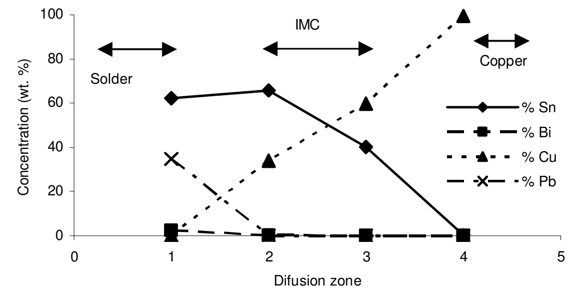

d)

Figure 2 – Chemical composition profile in the diffusion zone, established between the copper substrate and the solder alloys LF1 a), LF6 b), LF22c) and P1 d).

The interface microstructure, for alloys of the Sn-Zn-Al-Bi and Sn-Zn-Bi systems (samples LF1 and LF6), is presented in figures 1a) and 1b), respectively. These alloys have respectively the minimum and the maximum bismuth contents used in the present work (table 1). 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 table 2a). The phase forming the first layer (zone Z4 in table 2a) has a chemical composition close to the β' phase. The results are different from those obtained by Kivilahti [8], for alloys with 3.5at.% Zn, who obtained a first layer constituted by the γ phase, with approximately 65 at.% Zn. These differences might be explained by the presence of Al and/or Bi in the solder alloys, which could change the interface equilibrium. Bi content in the formed interface layers is very low, and within the chemical analysis error of the SEM/EDS equipment. This means that the presence of Bi in the solder chemical composition is not a relevant factor in the definition of the solder substrate reactions. Aluminium is present at the interface intermetallic compounds (IMC), in zones Z1 to Z3, with a concentration several times higher than the existing in the solder base composition. However, as for bismuth, the presence of Al at the first interface layer is very low when compared with its content in the other layers.

A different interfacial behavior was obtained for alloys of the systems Sn-Pb and Sn-Cu. These alloys have a similar interface structure consisting of two intermetallic compounds. The first layer is constituted by the phase ε (Cu_3Sn) and the second layer corresponds to the intermediate η phase (Cu_6Sn_5) of the Cu-Sn phase diagram [2, 9, 10]. In both IMC obtained at the interface, Bismuth content is very low and it is under the error of the chemical analysis determined by EDS measurements. Like for the Sn-Zn systems, the presence of Bi in the solder doesn't affect the equilibrium at the interface.
The solder/substrate interface obtained for the Sn-Pb traditional alloy is, also, constituted by two layers, with morphology and chemical composition similar to the one obtained with the Sn-Cu base alloys [11]. In both systems, a low thickness first layer (phase ε, with about 2 μm of thickness) was obtained. These IMC are essentially formed by tin and copper with small traces of other elements present in the solder (Bi, Pb). No significant diffusion was detected in the direction of the substrate.

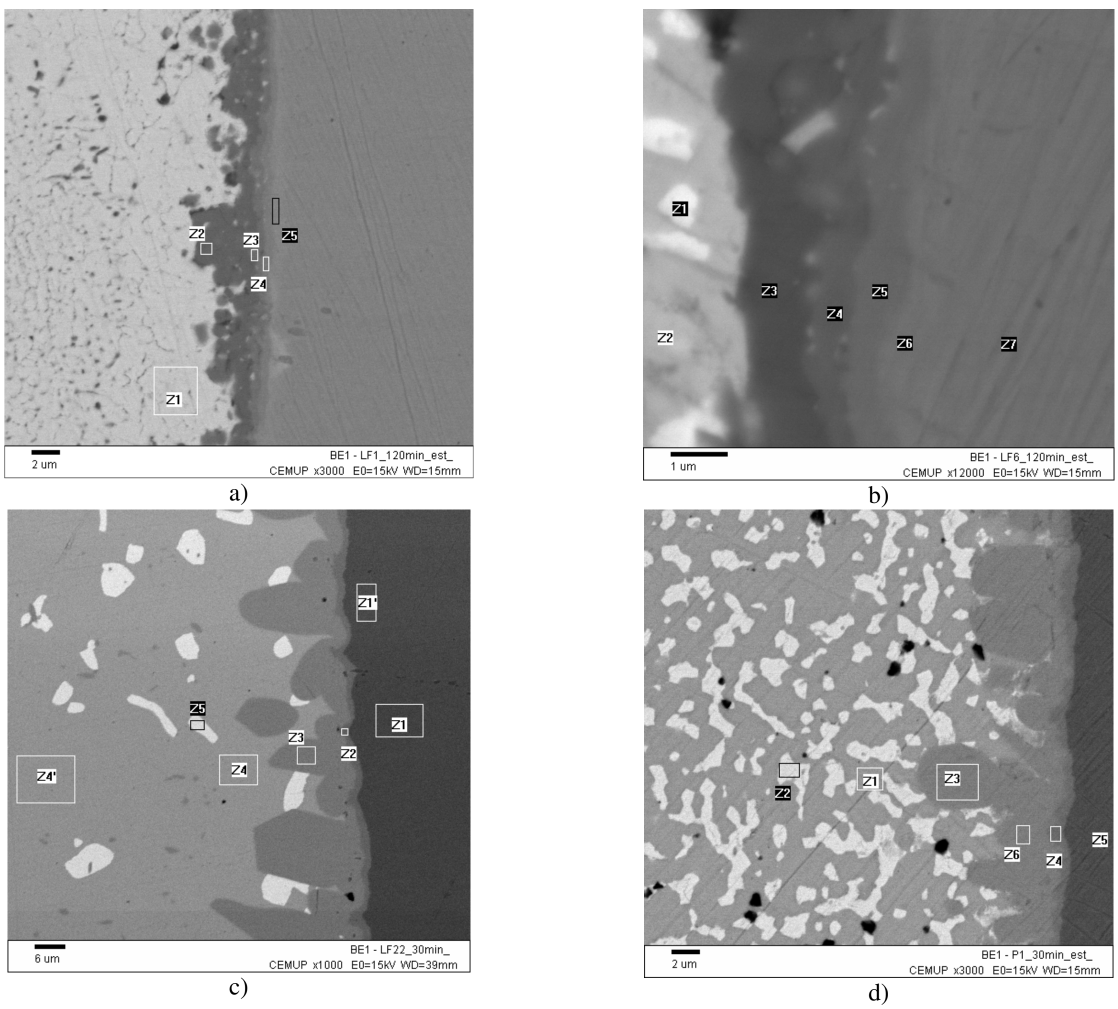

Figure 3 – Microstructure at the diffusion layers in solders LF1 a), LF6 b), LF22 c) and P1 d), with the copper substrate.

Conclusions

A very different solder/substrate interface constitution was obtained for solders of the Sn-Zn base systems when compared with those of the Sn-Cu or Sn-Pb systems, with copper substrates.

The alloys of the Sn-Zn system have lower melting range temperatures. The addition of Bi allows the reduction of that range of temperatures, approaching the working temperatures of the traditional Sn-Pb alloys. Alloys of the Sn-Cu system have higher melting range temperatures, above 200 ºC. The addition of Bi lowers those temperatures, but with smaller variations when compared with the obtained for the Sn-Zn lead-free system.

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 both alloy systems. The presence of Zn in the solder alloy avoids the formation of the Cu-Sn brittle phases (ε and η) as a first layer in contact with the copper substrate.

The first layer is essentially constituted by zinc and copper with some Al and Sn in the composition.

In the Sn-Cu base systems, a two layer structure was formed. These layers are essentially constituted by tin and copper with chemical compositions close to the intermediate phases (ε and η) of the binary phase diagram. This type of interface is similar to those obtained with Sn-Pb traditional alloys.

For all the studied systems, Bismuth is not present in the formed interfacial layers, meaning that it is not an important element in the definition of the interface local equilibrium.

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