

## EFFECT OF TRACE ELEMENTS ON THE INTERFACE REACTIONS BETWEEN TWO LEAD-FREE SOLDERS AND COPPER OR NICKEL SUBSTRATES

D. Soares\*#, C. Vilarinho\*, J. Barbosa\*, F. Samuel\*, L. Trigo\* and P. Bré\*\*

University of Minho, Azurém, 4800-058 Guimarães, Portugal

\*TecMinho - Associação Universidade Empresa para o Desenvolvimento

\*\* Peixinhos, Lda.

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### 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 the nature of the 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 layers. The effect of the addition of P, at low levels, on the chemical composition of the layers present at the interface was studied. The phases formed at the interface between the Cu or Ni substrate and a molten lead-free solder at 250° C, were studied for 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 composition were performed by Scanning Electron Microscopy (SEM/EDS). Different interface characteristics were obtained, namely for the alloys containing Zn. The obtained IML layer thickness was compared, for both types of alloy systems.*

Keywords: *lead free, electronics, solder, interface, reaction*

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### 1. Introduction

Recently, lead-free solders are being introduced to replace traditional Pb-

containing solders because of environmental concerns. Among other alternatives, solders based in the Sn-Cu and Sn-Zn systems are being studied.

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# Corresponding author: [dsoares@dem.uminho.pt](mailto:dsoares@dem.uminho.pt)

During the soldering process one or more interface layers usually form between the solder and the substrate (IML - intermetallic layer), constituted by one or more intermetallic compounds (IMC), which composition and morphology are crucial factors in the definition of the electronic systems reliability.

During the soldering process, mainly in what concerns to the wave process, elements present at the surface of the electronic components can dissolve in the liquid solder, changing its chemical composition. The introduction of these elements, namely phosphor from the Ni-P coatings, even in small amounts, can change the characteristics of the soldering process, namely, the solder/substrate IML (intermetallic layer) constitution, and thus, the joint reliability, as well as its electrical properties. As an example of that, it has been reported that the formation of some P-rich compounds (ex: Ni<sub>3</sub>P), at the interface, can degrade the joint reliability, namely, because this phase easily cracks [1,2,3].

In this work, the effect of small amounts of some alloying elements in the morphology of the reaction layer formed between two types of lead-free alloys, Sn-Cu and Sn-Zn, and two types of substrates, Cu and Ni, was investigated.

Copper is widely used as a substrate in the electronic components. Ni is used as a diffusion barrier layer to prevent the rapid interfacial reaction between lead-free solder and the Cu layer in the electronic components. So, the study of the interfacial reaction between lead-free solders and these substrates can be helpful for the understanding of the soldering process.

## 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 cast 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 diffusion experiments were conducted, for both kinds of alloys, on copper and nickel substrates. Pure copper or nickel wires were polished up to 1.0  $\mu\text{m}$  with diamond paste, cleaned with ethylic alcohol and dried. For the diffusion experiments themselves, the wires were cleaned with one flux (RF800 no clean flux, from Alpha Metals), heated for the flux evaporation and then immersed in the liquid solder, at  $250 \pm 3$  °C, for the selected times of reaction. After extraction from the liquid solder, the wires were air cooled to room temperature. During the experiments, the assembly was under an inert atmosphere, obtained by a constant flow of argon. Three contact times (reaction times) between the solid wire and the molten solder, were used: 5, 600 and 3600 seconds. The selection of the more prolonged stage time (3600 seconds) -, much longer than that used in a normal soldering process, was done in order to verify the stability of the interface structure.

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). The samples were examined, by SEM/EDS, without chemical etching. The DSC experiments were made with a heating/cooling of 10 °C/min in an inert atmosphere of high purity helium.

### 3. Results and discussion

The chemical composition of the alloys (in atomic %) used in this work, obtained by XRF spectrometry, is presented in table 1 as well as the melting temperatures obtained by DSC.

Table 1. Chemical compositions (in at. %) and melting temperatures of the alloys used in the diffusion experiments

| Solder | Zn    | Cu   | Bi   | P    | % Sn | Melting temp. (°C) |
|--------|-------|------|------|------|------|--------------------|
| LF32   | 14.92 | -    | 1,53 | -    | rest | 198,0              |
| LF34   | 12.11 | -    | 1.31 | 0.06 | rest | 198,5              |
| LF35   | 11.07 | -    | 1,26 | 0.34 | rest | 199,1              |
| LF37   | -     | 1.31 | 1.54 | -    | rest | 225,5              |
| LF38   | -     | 1.21 | 1.39 | 0.28 | rest | 225,6              |
| LF39   | -     | 1.21 | 1.31 | 0.70 | rest | 225,7              |

Results of the thermal analysis, for alloys of the Sn-Zn and Sn-Cu base systems are presented in figure 1.

The melting temperature, shown in table 1, was determined considering the curve peak temperature, corresponding to the end of the melting, for the experimental heating rate (only the heating cycle was considered).

For the Sn-Zn base alloys, there is a small decrease in the melting temperature that should be associated with the zinc content. The presence of Bi can, also, decrease the melting temperature [4]. Sample LF32, with the higher Bi content, has a melting temperature very close to the traditional Sn-Pb alloy. However, higher Bi contents might be detrimental for the mechanical behavior of the bulk alloy [5]. The melting

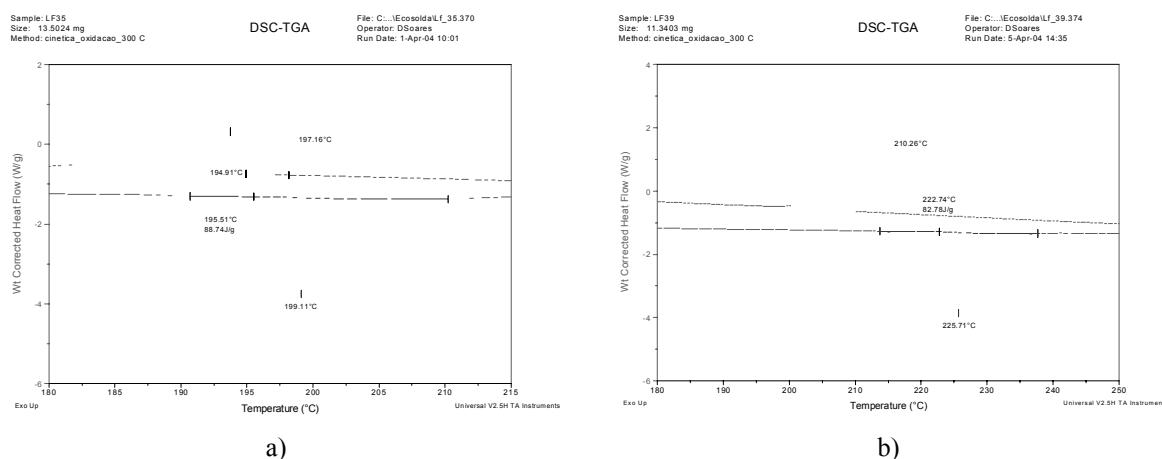


Fig. 1. Detail of the DSC curves, at the melting range, for alloys of the Sn-Zn (LF35) a) and Sn-Cu (LF39) b) based systems

temperature, of the Sn-Cu base alloys, was almost constant for all the tested chemical compositions.

### 3.1. Copper substrate

The interface structure obtained with the Sn-Zn based alloys, with P additions, is constituted by a single IMC compound, with a chemical composition close to the  $\text{Cu}_5\text{Zn}_8$  phase (table 2), as presented in figures 2a) to 2c), for the three times of reaction tested. Figure 2 presents the microstructure obtained in the alloy with the highest P addition.

Although almost no P was detected at the IML, it seems to have a significant effect on the IML formation. Previously reported

results [4, 6, 7], refer the presence of more complex IML, constituted by several sub-layers, for the same solder/substrate couple. The changes in the IML constitution, when compared with the results obtained with Sn-Zn alloys without P, could be explained by the change of the elemental interfacial energy (tin, ..), caused by the presence of P. Concerning the IML thickness, a continuous increase with the reaction time was obtained, as presented in figure 4a).

The Sn-Cu based alloy interface with the Cu substrate is constituted by a single IMC compound (table 3), of the  $\text{Cu}_6\text{Sn}_5$  type, as presented in Figures 2d) to 2f), for the three times of reaction tested. Similar IML constitution was obtained by Yoon et al. [8]. The phase  $\text{Cu}_3\text{Sn}$  was not detected at the IML, even in samples with the longest

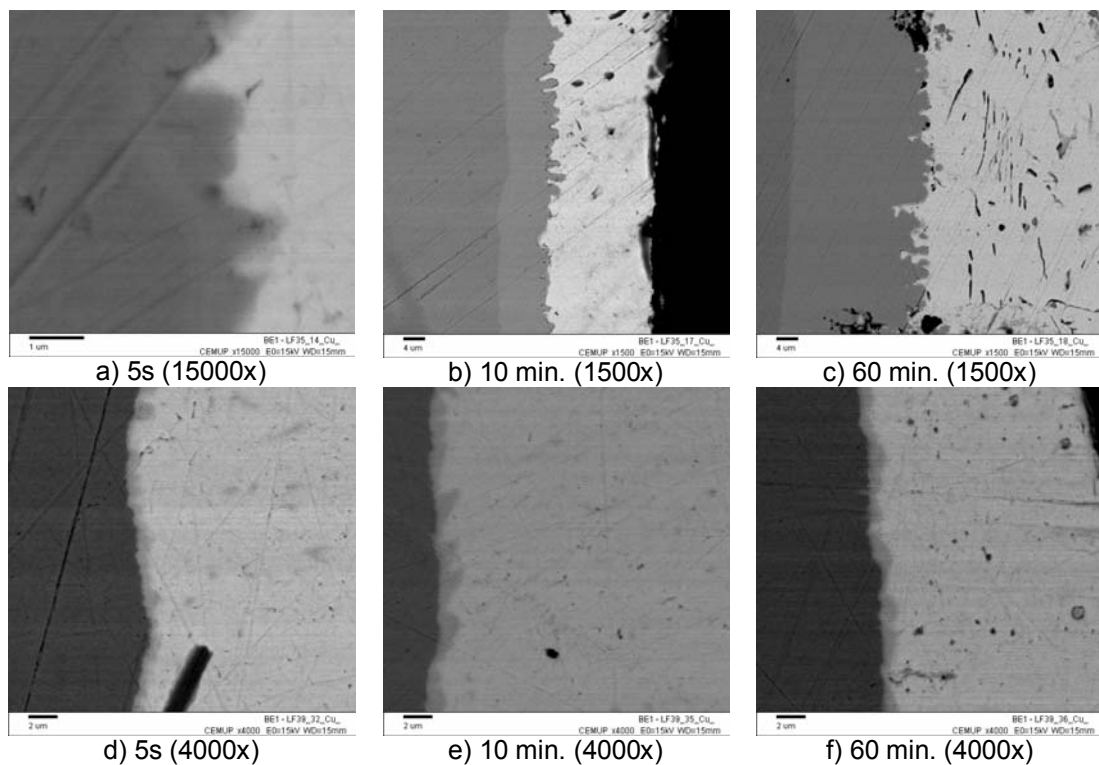


Fig. 2. Microstructure of the IML, for the three times of solder/substrate reaction, for solders LF35 (a, b and c) and LF39 (d, e and f) and the copper substrate

reaction time (60 minute). The presence of P in the alloy seems to have no significant effect on the IML formation. Almost all the P appears in an independent phase inside the solder (table 4).

The IML thickness is thinner then the obtained for the Sn-Zn alloys and has a small change with the reaction time (figure 4a).

*Table 2. Chemical composition (in at.%) of the IMC obtained in the diffusion experiments of Sn-Zn based solders in copper substrate, as presented in figures 2a) to 2c)*

|    | Substrate | IMC   |
|----|-----------|-------|
| Sn | -         | -     |
| Zn | -         | 67.27 |
| Bi | -         | -     |
| Cu | 100       | 32.73 |
| P  | -         | -     |

*Table 3. Chemical composition (in at.%) of the IMC obtained in the diffusion experiments of Sn-Cu based solders in copper substrate, as presented in figures 2d) to 2f)*

|    | Substrate | IMC   |
|----|-----------|-------|
| Sn | -         | 48.62 |
| Bi | -         | -     |
| Cu | 100       | 51.38 |
| P  | -         | -     |

### 3.2. Nickel substrate

Concerning the Sn-Zn based alloys, the obtained IML constitution is presented in Figures 3a) to 3c). A single IMC was obtained with the chemical composition presented in table 5. The IMC formed is constituted by Zn and Ni, with a chemical composition close to the  $\gamma$ -Ni<sub>5</sub>Zn<sub>21</sub> compound, with small contents of Cu and

Sn. Kim et al. [9] reported the formation of three IMC, with zinc contents from ~79 to 85 at.%. These results were not confirmed in this work. No P was detected at the interface (table 5), as it appears as an independent phase inside the solder (table 7).

In the Sn-Cu alloys, the presence of P seems to have an important effect in the IML constitution in opposite with the results obtained with the other systems. The obtained interface is presented in figures 3d) to 3f). The IML is constituted by two different layers, refereed as IMC-I and IMC-II in table 6, and identified in Figure 3e).

The IMC-I is of the Ni<sub>3</sub>(Sn,P)<sub>4</sub> type [10]. The Ni<sub>3</sub>Sn<sub>4</sub> phase was already detected in Sn-Cu/Ni systems IML [10,11]. The chemical composition of the IMC-II could be associated with a Ni<sub>6</sub>Sn<sub>5</sub> type of phase, with some dissolved P. The Ni<sub>3</sub>P phase, also referred in the literature, was not detected in none of the studied alloys.

Phosphorus is present in the IML with a higher concentration at the IMC-II, which is in the solder side. The rest of the P is, inside the solder, in a phase of the CuP<sub>3</sub> type (table 7).

The total thickness of the IML, presented in figure 4, decreases after 10 min. of reaction time. The thickness of IMC-I seems to change, with reaction time, more significantly then the IMC-II. However, more experiments (with more intermediate reaction times) are needed to determine if the IMC-I is growing or, in opposite, if this phase is disappearing with the reaction time.

The thickness of the obtained IML, for both the Sn-Zn and Sn-Cu solder alloys, is presented in Figure 4. The Sn-Zn base alloys have an IML that reveals a continuous increasing with the reaction time for both types of substrates. In opposite, the Sn-Cu

Table 4. Chemical composition (in at.%) of the matrix and the P rich phases obtained in the solder after the diffusion experiments

|    | Sample LF35 |              | Sample LF39 |              |
|----|-------------|--------------|-------------|--------------|
|    | Matrix      | P rich phase | matrix      | P rich phase |
| Sn | 98.58       | 0.86         | 98.81       | 3.28         |
| Zn | -           | 58.30        | -           | -            |
| Bi | 1.42        | -            | 1.19        | 0.19         |
| Cu | -           | -            | -           | 28.75        |
| P  | -           | 40.84        | -           | 67.78        |

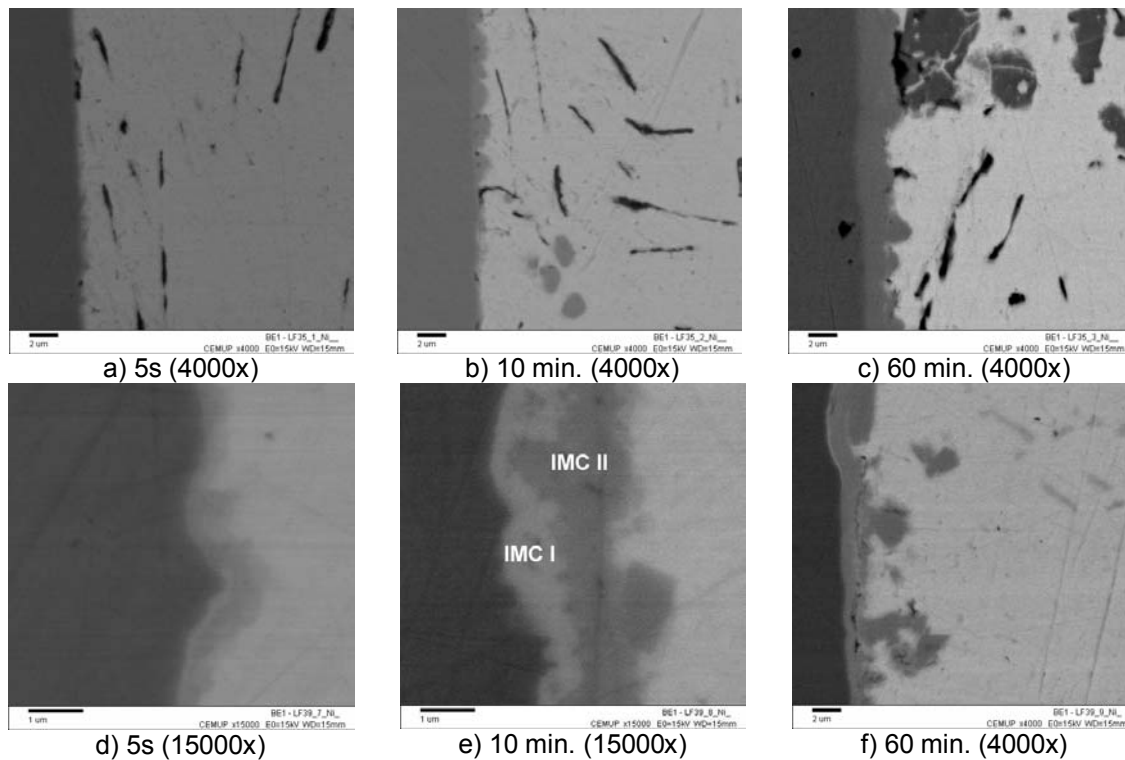


Fig. 3. Microstructure of the IML, for the three times of solder/substrate reaction, for solders LF35 (a, b and c) and LF39 (d, e and f) and the nickel substrate

alloys IML thickness stops growing after some time of solder/substrate reaction. It seems that the lower diffusivity of Sn through the IML, when compared with the Zn diffusivity, is the controlling mechanisms for the IML growing rate.

#### 4. Conclusions

The effect of P addition in the solder/substrate reaction and the morphology of the intermetallic compounds, was investigated for two different lead-free alloys and two substrates.

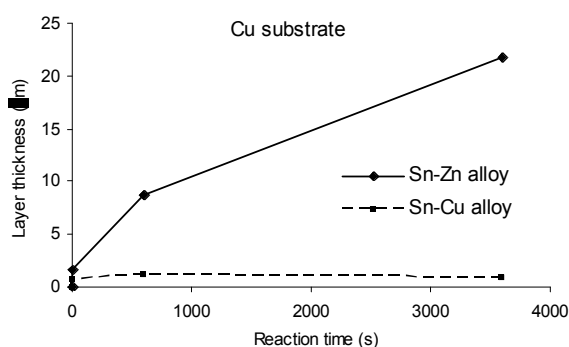
No significant changes were obtained in the alloys melting temperatures due to the P

Table 5 - Chemical composition (in at.%) of the IMC obtained in the diffusion experiments of Sn-Zn based solders in nickel substrate, as presented in figures 3a) to 3c)

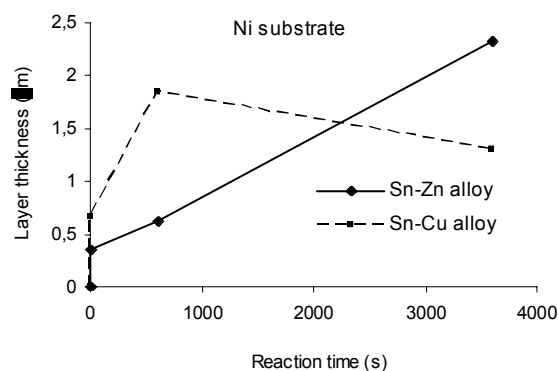
|    | Substrate | IMC  |
|----|-----------|------|
| Sn | -         | 3.1  |
| Zn | -         | 80.2 |
| Bi | -         | -    |
| Cu | -         | 2.0  |
| Ni | 100       | 14,7 |
| P  | -         | -    |

Table 6 - Chemical composition (in at.%) of the IMCs obtained in diffusion experiments of Sn-Cu based solders in nickel substrate, as presented in figures 3d) to 3f)

|    | Substrate | IMC-I | IMC-II |
|----|-----------|-------|--------|
| Sn | -         | 57.0  | 48.0   |
| Bi | -         | -     | 0.4    |
| Cu | -         | 14.0  | -      |
| Ni | 100       | 26.1  | 40.7   |
| P  | -         | 2.8   | 11.0   |



a)



b)

Fig. 4. Interface thickness for the different reaction times and solder alloys obtained with the copper a) and nickel substrates b)

Table 7. Chemical composition (in at.%) of the matrix and the P rich phases obtained in the solder after the diffusion experiments

|    | Sample LF35 |              | Sample LF39 |              |
|----|-------------|--------------|-------------|--------------|
|    | matrix      | P rich phase | matrix      | P rich phase |
| Sn | 92.5        | 4.27         | 97.23       | 4.41         |
| Zn | 2.3         | 69.15        | -           | -            |
| Bi | 2.2         | 0.93         | 1.01        | -            |
| Cu | 1.8         | -            | -           | 29.99        |
| Ni | 1.2         | 1.61         | 1.77        | -            |
| P  | -           | 24.04        | -           | 65.60        |

addition. In both alloy systems a P rich phase was obtained.

Concerning the solder/substrate reaction an important effect was detected, with the formation of a single IMC, for the reaction between the Sn-Zn alloys and the copper substrate. P was not detected in the IML. However, its presence should change the elements interfacial energy which could explain the formation of a different IML constitution.

Only in the IML obtained with the Sn-Cu alloys reacting with the Ni substrate was detected the presence of P in the IMCs chemical composition.

Concerning the IML thickness a very different behaviour was obtained for both alloy systems. For the Sn-Zn based alloys it continuously grows with the increase of the reaction time. For the Sn-Cu alloys the IML thickness seems to stop growing after the initial formation. The lower diffusivity of Sn, through the IML, when compared with the Zn diffusivity, seems to be the controlling mechanism for the IML growing rate.

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