Effect of Thermal Aging on the Interfacial Reactions of Tin-Based Solder Alloys and Copper Substrates and Kinetics of Formation and Growth of Intermetallic Compounds

(Efeito do envelhecimento térmico nas reações interfaciais de ligas de soldagem branda a base de estanho em substratos de cobre e cinética de formação e crescimento de compostos intermetálicos)

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ABSTRACT

The formation and growth of intermetallic compounds at the interface between four solder alloys, Sn-3.5Ag, Sn-0.7Cu, Sn-3.2Ag-0.8Cu and Sn-9Zn, and Cu-plated substrates have been studied. Thermal aging tests for 20, 100, 200, 500 hours at 70, 100 and 150 °C were carried out. As expected, results indicate that the formation of the intermetallic layer is a diffusion-controlled process. Nevertheless, migration and dissolution of Cu into the solder was observed, especially at lower temperatures. The thickness of the layer of intermetallic compound increased with increasing aging temperature and time. The Sn-3.5Ag alloy showed the smallest intermetallic growth and the Sn-9Zn alloy the highest, compared to the other alloys. The results also show definite morphological differences between the Cu/Cu₃Sn, the Cu₃Sn/Cu₆Sn₅, and the Cu₆Sn₅/solder-matrix interfaces.

Key Words: Tin-based solder alloys, Intermetallic compounds, Isothermal aging, Morphology, Interface, IMC layer growth front.

1. Introduction

Health and environmental concerns in the electronic packaging industry regarding the use of lead-based alloys led to the search for lead-free substitute alloys. Previous studies have shown that Sn-based alloys such as Sn-3.5Ag, Sn-0.7Cu, Sn-3.2Ag-0.8Cu and Sn-9Zn exhibit promising mechanical properties [1-3] and can be considered as serious candidates to replace the Sn-Pb alloy. Nevertheless, more information is needed before life and reliability predictions can be made for joints using these materials. During reflow soldering, a layer of intermetallic compound (IMC) is formed between the substrate and the solder alloy. In solid-state this layer continues to grow and may react to produce additional IMC layers [4]. The concern about these IMCs is that at high operating temperatures they may grow to become detrimental to the mechanical integrity of the solder joints [3,5]. This study provides information about the effects of annealing on the solder/substrate interface morphology and microstructure. For that purpose, the formation and growth of intermetallic layers between the copper-plated substrates and the Sn-3.5Ag, Sn-0.7Cu, Sn-3.2Ag-0.8Cu and Sn-9Zn alloys is investigated.

2. Experimental Procedure

2.1. Production of copper/solder joints

The melting temperatures of the solder alloys utilized in this study are shown in Table 1. The number in front of each element symbol represents its weight percent in the alloy. For example, there is 0.7 wt. pct. of copper in Sn-0.7Cu alloy. The substrate was a commercial Cu-plated printed circuit board (PCB). The PCB board was cut in pieces of 25.4 x 25.4 mm (1 x 1 inch). Prior to producing the joints, the Cu substrates were cleaned with a water-based solution of ammonium hydroxide, trisodium phosphate and sodium tetraborate pentahydrate (also known as M-prep neutralizer). For Sn-3.5Ag, Sn-0.7Cu and Sn-3.2Ag-0.8Cu alloys, after letting the copper surface dry for a few seconds, a solution of water-based phosphoric acid (M-prep conditioner) was applied. These solutions removed
any impurities, dirt, and oxide layers present on the surface and promoted wetting. In the case of the Sn-9Zn alloy, a commercial zinc chloride and ammonium chloride based paste was applied to the copper surface, which provided better wetting than the phosphoric acid-based solution applied to the copper substrate for the three previous solder alloys. The solder drops were melted on the substrate at a temperature 50°C above their respective melting temperatures indicated in Table 1, under argon gas. The joints, with approximately 3mm thick solder, were cooled in air to room temperature.

### Table 1. Melting and furnace temperatures for the solder alloys used in this study.

<table>
<thead>
<tr>
<th>Solder alloy</th>
<th>Melting Temperature, (°C)</th>
<th>Furnace Temperature ± 1°C, (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.2Ag-0.8Cu</td>
<td>217</td>
<td>267</td>
</tr>
<tr>
<td>Sn-3.5Ag</td>
<td>221</td>
<td>271</td>
</tr>
<tr>
<td>Sn-0.7Cu</td>
<td>227</td>
<td>277</td>
</tr>
<tr>
<td>Sn-9Zn</td>
<td>198.5</td>
<td>248</td>
</tr>
</tbody>
</table>

### 2.2. Thermal aging test

The thermal aging tests of the copper/solder joint coupons were done using furnaces with temperatures controlled to ± 1°C. To avoid oxidation during thermal aging, a continuous flow of industrial grade argon gas was provided to the furnaces. The copper/solder joints were thermally aged at 70, 100 and 150 °C for 20, 100, 200 and 500 hours. The specimens were water-quenched as they were removed from the furnaces.

### 2.3. Interface characterization

Each sample was cut in half and cold mounted using epoxy for metallographic analysis. The reason for using cold mounting instead of hot mounting is that cold mounting undergoes a lower curing temperature. The mounted samples were ground and polished using standard metallographic techniques, first to 0.5 mm with diamond slurry, and then to 0.05 mm for 45 minutes using colloidal silica. Polishing the samples in a vibratory machine with colloidal silica resulted in a good etched surface.

The samples were analyzed using light microscopy and scanning electron microscopy (SEM) to characterize the different microstructural features and energy dispersive spectroscopy (EDS) to identify the intermetallic compounds. Quantification of IMC thickness was done by measuring the linear distance from the edge of the copper substrate to the IMC layer growth front. In the same manner, the measurement of the average total IMC layer thickness when two layers were present was done measuring the linear distance from the edge of the copper substrate to the second IMC layer growth front. Eighty thickness readings along the interface at consistent intervals were averaged to obtain the average IMC layer thickness for each of the solder alloy-substrate combinations. The IMC thickness measurements were performed using the image analysis software incorporated in the scanning electron microscope.

### 3. Results And Discussion

#### 3.1. Joint interface characterization

Micrographs of the Cu/Solder alloy interface after soldering, such as the one in Figure 1, indicate the existence of a very small Cu$_6$Sn$_5$ intermetallic layer visible only at high magnifications [5, 6]. In the tin/copper and tin-rich-alloys/copper joint systems, the intermetallic Cu$_6$Sn$_5$ (h’-phase) formed immediately upon contact of the liquid solder with the copper substrate [7, 8]. Then, the intermetallic compound grew rapidly [9,10].

![Figure 1. Micrograph of the Cu/Sn-3.5Ag interface after soldering, showing the presence of the Cu$_6$Sn$_5$ intermetallic layer.](image)

The interface after thermal aging was found to be very different compared to the initial observations immediately following soldering, as shown in Figure 2, in the micrographs of the Cu/Solder interface at 150 °C for 500 hours. Beginning from the bottom, in Figures 2(a), (b) and (c), the visible layers are the epoxy board, the copper substrate, the intermetallic compounds (IMCs), Cu$_6$Sn$_5$ and Cu$_3$Sn$_2$, and finally the solder matrix. It was observed that the layer of Cu$_6$Sn$_5$ formed at the Cu/solder interface when the joint was under thermal aging, and the layer of Cu$_3$Sn$_2$ resulted on top of Cu$_6$Sn$_5$. This sequence is true for the three solder alloy systems, Cu/Sn-3.2Ag-0.8Cu, Cu/Sn-3.5Ag, and Cu/Sn-0.7Cu. In the case of Cu/Sn-3.5Ag, a few small particles of Ag$_3$Sn can also be observed along the Cu$_6$Sn$_5$/Sn-3.5Ag interface. Different from the previous joint systems, the Cu/Sn-9Zn system displayed only one intermetallic layer, Cu$_5$Zn$_8$, as evidenced in Figure 2(d).

#### 3.2. Identification of the intermetallic compounds

Energy dispersive spectroscopy (EDS) analysis was used to identify the intermetallic compounds present in each of the joint samples. The characteristic x-ray intensity spectrum and the chemical data Sn = 46.33 at. pct. and Cu = 53.67 at. pct. (close to the 6:5 Cu/Sn molar ratio) in Figure 3(a) clearly show intensity peaks corresponding to the h’-phase in the copper-tin phase diagram (included as Appendix A), which is the Cu$_6$Sn$_5$ intermetallic compound. This IMC is present in the as-soldered and annealed samples.

Similarly the data in Figure 3(b) was analyzed. The high Cu and lower Sn x-ray intensity peaks indicate that copper is the major component of the compound. The chemical composition, Sn = 24.35 at. pct. and Cu = 75.65 at. pct., which is close to the 3:1 molar ratio of Cu/Sn, approaches the stoichiometric composition of Cu$_6$Sn$_5$. Using the atomic percent of the two elements given above on the copper-tin phase diagram in
Appendix A, the compound falls inside the e-phase region, which indeed is the Cu$_3$Sn intermetallic. The EDS spectrum in Figure 3(c) was obtained from area “A” in the micrograph in Figure 2(a), which indicates higher number of counts (peaks) of silver compared to those of tin. The data points indicate Sn and Ag in the amounts of 24.77 at. pct. and 75.23 at. pct., respectively. Locating these atomic percents on the tin-silver phase diagram in Appendix B, the intermetallic compound can be determined as Ag$_3$Sn (g-phase).

The EDS spectrum in Figure 3(d) indicates the presence of two elements, copper and zinc; the larger number of zinc peaks suggest higher amounts of zinc. Indeed, the atomic percent of copper and zinc, 35.10 at. pct. and 64.90 at. pct., respectively, confirm the existence of more zinc in the compound. Locating these amounts of copper and zinc on the copper-zinc phase diagram shown in Appendix C, it is found that the intermetallic is the Cu$_5$Zn$_8$ (g-phase). The intermetallic compounds identified in this study are in agreement with previous reports made by J.Y. Park et al. [11], and C. Hang et al. [12].

### 3.3. Morphology of the intermetallic layers

Evidence of interface morphological differences was found between the IMCs. The Cu$_3$Sn/Cu$_6$Sn$_5$ interface was observed to be irregular [11-13]. The thickness variation of the Cu$_3$Sn intermetallic layer was not as drastic as the thickness of the Cu$_6$Sn$_5$ intermetallic layer. In the case of the Cu$_3$Sn/solder-matrix, the interface is more irregular, with localized developments of elongated, needle-like, or elongated scalloped structures [14,15], growing far into the solder matrix. According
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Y.G. Lee et al. [6] the irregularity of the solder/IMC interface takes place during a liquid-solid reaction during soldering.

**Cu/Sn-3.5Ag System**

In the case of the Cu/Sn-3.5Ag system, the morphology of the Cu₆Sn₅ layer is significantly different from that of Cu₃Sn. Figure 4(a) clearly exhibits the irregular interface of the Cu₆Sn₅ intermetallic, protruding into the solder matrix. Some areas of this interface (growth front) developed into elongated, needle-like morphologies such as the one shown in the micrograph. In other areas, the initiation of the needle-like morphologies, “A”, and the formation of the scalloped structures [16], “B”, were observed, Figure 4(a). In addition, Ag₃Sn was found in the form of small particles at the Cu₆Sn₅/solder interface. It is plausible that these small particles of Ag₃Sn interrupted the fast growth of the Cu₆Sn₅ layer. The growth front of the Cu₃Sn layer is not as irregular as that of the Cu₆Sn₅ layer. For better visual clarification of the micrograph in Figure 4(a), the Cu₃Sn growth front has been outlined with a dash-dotted line, and the copper surface with a dashed line. It seems that the irregularity of the Cu₃Sn layer depended more on the original surface of the copper substrate.

**Cu/Sn-3.2Ag-0.8Cu System and Cu/Sn-0.7Cu System**

In the case of the Cu/Sn-3.2Ag-0.8Cu and Cu/Sn-0.7Cu system, the interface of the Cu₃Sn is smoother than that observed in the Cu/Sn-3.5Ag system. Evidence of this observation can be found in Figures 4(b) and (c). Figure 4(b) displays the Cu/Sn-3.2Ag-0.8Cu interface. The most noticeable feature of this interface is that the Cu₃Sn growth front was irregular but did not have sharp features as in the previous case of Cu/Sn-3.5Ag. For example, the needle-like and scalloped structures are not present here. The Cu₃Sn growth front was also irregular.

In the case of the Cu/Sn-0.7Cu interface shown in Figure 4(c), the irregularity of the Cu₃Sn growth front was more than in the case of the Cu/Sn-3.2Ag-0.8Cu. This interface also exhibited small pieces of Cu₃Sn (~1 to 2 microns in size) detached from the Cu₃Sn layer, but they did not seem to grow far into the solder matrix. Again, the Cu₃Sn growth front exhibited irregular characteristics.

**Cu/Sn-9Zn System**

The most significant difference between the Cu/Sn-9Zn interface and the interfaces of the other three systems is that the Cu/Sn-9Zn interface exhibited only one intermetallic layer, which was identified as Cu₅Zn₈. The growth front of this layer, as seen in Figure 4(d), was irregular, finely jagged, but did not present sharp irregularities as in the case of the Cu/Sn-3.5Ag.
3.4. Kinetics of intermetallic layer growth

The growth kinetics of the IMCs as a function of aging time and temperature was analyzed by evaluating the thicknesses of the IMC layers. The method of determining the IMC thickness was presented in the experimental section of this document. The thicknesses of individual Cu$_3$Sn and Cu$_6$Sn$_5$ layers and combined (Cu$_3$Sn + Cu$_6$Sn$_5$) IMC layers were measured. The total intermetallic layer thickness measured in the four material systems at 150°C, the highest aging temperature used in the experiments, and for 500 hours were determined in the following: 13.3 mm for Cu/Sn-3.5Ag, 13.6 mm for Cu/Sn-3.2Ag-0.8Cu, 14.1 mm for Cu/Sn-0.7Cu, and 19.1 mm for the Cu/Sn-9Zn alloy.

A simple parabolic, diffusion-controlled growth model, represented by equation (1), was assumed in the analysis of these experiments.

\[ X = (kt)^{1/2} \quad (1) \]

\( X \) is the thickness of the intermetallic layer, \( k \) is the growth constant, and \( t \) the time. The observed total IMC thickness and time relationships at 70, 100 and 150 °C, shown in Figures 5(a), (b) and (c) respectively, were found to obey the parabolic relationship assumed previously. Other researchers such as Vianco et al.\(^7\) and Lee et al.\(^5\) have found similar relationships. The slopes of the lines in Figure 5 indicate the rate of IMC growth.
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growth; therefore, as the temperature increased, the rate of IMC layer growth increased. At the three temperatures, the Sn-9Zn alloy grew at the fastest rate. The Sn-3.5Ag alloy grew at the slowest rate at 70 and 100 °C, and the Sn-3.2Ag-0.8Cu alloy at 150 °C.

Similar analysis was conducted for each of the individual IMCs in each Cu/solder system. The general observation is that their growth also obeyed the parabolic growth as in the case of the growth of the total IMC. Figure 6 shows how the individual IMCs grew with time.

In the case of the Cu/Sn-3.2Ag-0.8Cu joint system, shown in Figure 6(a), the growth rate of the two intermetallic compounds, Cu₅Sn and Cu₆Sn₅, are statistically similar. In the case of the Cu/Sn-3.5Ag system, shown in Figure 6(b), the Cu₆Sn₅ layer grew at a faster rate than the Cu₃Sn layer. This observed trend can be explained as since abundant tin atoms are available they first react with the available copper atoms at the site and form Cu₅Sn. Cu₃Sn did not grow as fast as in the previous case because less Sn atoms were available to react with Cu atoms, since Sn would be reacting with Ag to form Ag₃Sn at the Cu₆Sn₅ growth front. The remaining tin atoms at the Cu₆Sn₅/solder interface would enhance the diffusion of tin through the Cu₆Sn₅ intermetallic layer to react with the copper atoms to form the Cu₃Sn intermetallic.

In the case of the Cu/Sn-0.7Cu system shown in Figure 6(c), larger amounts of Cu₃Sn formed but grew at approximately the same rate than Cu₅Sn. The Cu₅Sn layer grew because no Ag₃Sn were formed in this system. Therefore, more tin atoms would take part in the diffusion of tin through the Cu₆Sn₅ intermetallic layer to form Cu₃Sn. In the case of the Cu/Sn-9Zn system, only Cu₅Zn₈ formed. Therefore, Cu₅Zn₈ is considered as the total IMC layer. The results obtained in this study indicate that the IMCs were
formed by the reaction of tin and copper atoms at the solder/substrate interface and by the diffusion of copper and/or tin atoms through the layer. This IMC process formation is discussed by Vianco et al. [17]. The theory indicated by Flanders et al.[6], states that tin atoms travel towards the copper substrate, first to form Cu$_6$Sn$_5$ and then through the Cu$_6$Sn$_5$ layer to form Cu$_3$Sn. However, if that would be the case, the activation energy for the formation of Cu$_6$Sn$_5$ would have been lower but it is not, as is shown in Table 2. It should be noted that at lower activation energies the reaction would proceed easier than at higher activation energies. According to Y.G. Lee et al.[6] and D. Yao et al. [18] there are also different mass transport processes that occur at the solder/substrate interface, such as channels between grains serving as fast diffusion and dissolution paths of Cu in the solder to feed the reaction. However, they also recognize that during aging bulk diffusion is the dominant mechanism of mass transport for the growth of intermetallic compounds. Strong evidence of copper diffusion through the Cu$_6$Sn$_5$ layer to react with Sn-3.5Ag was reported by S.J Wang et al. [19]. For detailed description the reader is referred to reference 19.

![Figure 6. Individual IMC layers growth for samples aged at 150 °C, (a) Cu/Sn-3.2Ag-0.8Cu, (b) Cu/Sn-3.5Ag, and (c) Cu/Sn-0.7Cu.](image)
Table 2. Activation energy data for the Cu/Sn-3.5Ag and Cu/100Sn solder systems found in the literature compared to the data for the Cu/Sn-3.5Ag in this work.

<table>
<thead>
<tr>
<th>Joint System</th>
<th>Cu₃Sn (eV/atom)</th>
<th>Cu₆Sn₅ (eV/atom)</th>
<th>Total Q (eV/atom)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Sn-3.5Ag</td>
<td>---</td>
<td>1.20</td>
<td>1.20</td>
<td>Choi et al.²²</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>1.11</td>
<td>---</td>
<td>Flanders et al.¹³</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.93</td>
<td>0.85</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>---</td>
<td>0.80</td>
<td>Harris et al.⁵</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>---</td>
<td>0.67</td>
<td>Lee et al.²³</td>
</tr>
<tr>
<td></td>
<td>0.52</td>
<td>---</td>
<td>0.61</td>
<td>Vianco et al.¹⁷</td>
</tr>
<tr>
<td>Cu/100Sn</td>
<td>0.74</td>
<td>0.83</td>
<td>---</td>
<td>Vianco et al.²⁰</td>
</tr>
</tbody>
</table>

Figure 7. Experimental data for the Cu/Sn-3.5Ag system, (a) diffusion data for the individual Cu₃Sn and Cu₆Sn₅ IMCs plotted to determine the activation energy Q, and (b) diffusion data for the combined IMC (Cu₃Sn + Cu₆Sn₅) plotted to determine the activation energy Q, for the combined IMC growth.

The constant k in Equation (1) was determined from the slopes of the lines in the IMC thickness versus time⁴ plots, Figure 5. Using the Arrhenius equation below,

\[ k = k_0 \exp \left( \frac{-Q}{RT} \right) \]  

where \( k_0 \) is the pre-exponential term, \( Q \) the activation energy, \( R \) the Universal Gas Constant and \( T \), the absolute temperature. The log k versus \((1/T)\) plots for the individual phases and for the total IMC can be made. Both Figures 7(a) and (b) are for the Cu/Sn-3.5Ag system. The slopes of the lines in Figure 7(a) suggest higher activation energy for Cu₃Sn formation than for Cu₆Sn₅. The line in Figure 7(b) corresponds to the combination of the two intermetallic phases in one layer. As expected, its slope suggests intermediate activation energy value.

The activation energies, Q, were calculated from the slope of the Arrhenius plot using a linear regression model. As the activation energy of a specific intermetallic compound increases, the formation and growth of this compound is expected to be more difficult. On the other hand, low activation energies indicate easier IMC formation and growth. The results of the activation energies for the total IMC thickness and for the individual phases for the four solder alloys are presented in Table 3. The activation energy data for the Cu/Sn-3.5Ag and Cu/Sn-0.7Cu joint systems are in good agreement with previous studies found in the literature [3,8]. In the case of the Cu/Sn-3.2Ag-0.8Cu and Cu/Sn-9Zn joint systems, no comparison data were found in the literature.
Table 3. Activation energies, $Q$, determined experimentally for the total (combined) and individual IMCs in the Cu/Sn-3.8Ag-0.8Cu, Cu/Sn-3.5Ag, Cu/Sn-0.7Cu, and Cu/Sn-9Zn joint systems.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>IMC</th>
<th>$Q$ (kJ/mol)</th>
<th>$Q$ (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.2Ag-0.8Cu</td>
<td>Total</td>
<td>70.9</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Cu$_3$Sn</td>
<td>69.2</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Cu$_6$Sn$_5$</td>
<td>72.2</td>
<td>0.75</td>
</tr>
<tr>
<td>Sn-3.5Ag</td>
<td>Total</td>
<td>81.6</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Cu$_3$Sn</td>
<td>69.2</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Cu$_6$Sn$_5$</td>
<td>90.0</td>
<td>0.93</td>
</tr>
<tr>
<td>Sn-0.7Cu</td>
<td>Total</td>
<td>65.5</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Cu$_3$Sn</td>
<td>59.2</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Cu$_6$Sn$_5$</td>
<td>72.2</td>
<td>0.75</td>
</tr>
<tr>
<td>Sn-9Zn</td>
<td>Cu$_5$Zn$_8$</td>
<td>33.8</td>
<td>0.35</td>
</tr>
</tbody>
</table>

As discussed earlier, data for the Cu/Sn-3.5Ag were collected from the literature [18,20-24] and reported in Table 2. Data obtained in this work were also included in the table for comparison. In this work the activation energies determined for the individual intermetallic compounds, Cu$_3$Sn and Cu$_6$Sn$_5$, are 0.72 and 0.93 eV/atom, respectively. Table 3 shows that Flanders et al. have obtained almost similar activation energy for Cu$_3$Sn (0.73 eV/atom) and much higher for Cu$_6$Sn$_5$ (1.11 eV/atom). The value of 0.8 eV/atom for the total activation energy reported by Harris agrees with the 0.85 eV/atom obtained in this work. Nevertheless, the values reported by Vianco et al. of 0.52 eV/atom for the Cu$_3$Sn IMC and 0.61 eV/atom for the total IMC are lower than all the data in Table 3. This difference may be due to the different processes utilized in the production of the joint specimens. It is shown by Lee et al. that furnace heating soldering process would produce higher amounts of IMCs than hot dipped and electroplating, in that order. Vianco [20] reported the behavior of IMCs in Sn-rich solder alloys in an electronic joint. Table 3 shows that the activation energies for this system are 0.74 eV/atom for the Cu$_3$Sn IMC and 0.83 eV/atom for the Cu$_6$Sn$_5$ IMC. These data is in close agreement with the data obtained in this work.

4. CONCLUSIONS

Two intermetallic compounds Cu$_3$Sn and Cu$_6$Sn$_5$ form at the Cu/Sn-3.5Ag, Cu/Sn-3.2Ag-0.8Cu, and Cu/Sn-0.7Cu interfaces. In the case of the Cu/Sn-9Zn system, the IMC is Cu$_5$Zn$_8$. The three intermetallic layers grew by thermal activation in a parabolic manner. If IMC formation were the sole criterion for determination of candidates for replacing the Sn-Pb alloys, the ranking would be: Sn-3.5Ag, Sn-3.2Ag-0.8Cu, Sn-0.7Cu and Sn-9Zn, being Sn-3.5Ag the system that exhibited the least IMC growth. The Sn-3.5Ag system also reported the highest activation energy to promote combined IMC formation, 0.85 eV/atom.

5. ACKNOWLEDGEMENTS

The authors would like to thank the National Institute of Standards and Technology (NIST) for their support.

6. REFERENCES

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APPENDIX – A

Copper–Tin equilibrium phase diagram

\[ \varepsilon = \text{Cu}_3\text{Sn} \]

\[ \eta' = \text{Cu}_6\text{Sn}_5 \]

APPENDIX – B

Tin–Silver equilibrium phase diagram

\[ \gamma = \text{Ag}_3\text{Sn} \]

APPENDIX – C

Copper–Zinc equilibrium phase diagram

\[ \gamma = \text{Cu}_5\text{Zn}_8 \]