Microstructure Evolution at the Solder Joint during Isothermal Aging

A.M. Zetty Akhtar¹, K. Hardinna Wirda², J. Siti Rabiatull Aisha³ and I. Mahadzir⁴
¹Faculty of Mechanical Engineering, University Malaysia Pahang, 26600, Pekan, Pahang.
² zetty_9371@yahoo.com
³ wirda_rose@yahoo.com
⁴ rabiatull@ump.edu.my *
⁵ mahadzir@ump.edu.my

Abstract

The intermetallic compound formation and growth between Sn-3.0Ag-0.5Cu solder and surface finish, mainly immersion Au-plated Cu and immersion Sn-plated Cu were investigated in this study. This study aimed to examine the effect of different immersion types of surface finish towards the intermetallic compound formation in terms of its thickness and activation energy. In this works, evolution of microstructure at the interfacial region was studied for after reflow and isothermal aging at 150°C, up to 1000 hours. The thickness of the intermetallic was measured using ImageJ software and activation energy was calculated using measured data. The compositions of intermetallic compound were confirmed using Scanning Electron Microscopy-Energy-dispersive X-ray spectroscopy (SEM-EDX) and its microstructure were observed using optical microscope. The cross sectional microstructure of Sn-3.0Ag-0.5Cu/ImAu joint shows that Au layer disappears completely, suggesting that it was entirely dissolved into the molten solder. The same result obtained from reflowed Sn-3.0Ag-0.5Cu/immersion Sn. The thickness of IMC layer at Sn-3.0Ag-0.5Cu /ImAu interface is similar to that at at Sn-3.0Ag-0.5Cu /ImSn interface, especially for Cu₃Sn₅ layer. The intermetallic growths of the intermetallic structure during isothermal aging were discussed.

Keywords: Intermetallic compound formation, Surface finish, Isothermal aging, Activation energy.

1.0 Introduction

The increasing awareness of health risk associated with lead (Pb) containing solder alloys has pushed the electronics industry toward lead-free solder [1-6]. Among many developed lead-free solder alloys, the Sn-Ag-Cu (SAC) lead-free solder alloy is considered the best alternative to replace eutectic tin-lead solder [7, 8]. Besides concern on solder, it is also important issue for development of Pb-free packaging system to find an appropriate Pb-free surface finish on printed circuit board (PCB) due to its effect on intermetallic growth. Immersion surface finish is another promising option for the Pb-free surface finish since it has the advantages of lower cost and simpler operation [9]. The solder joint strength is controlled by good metallurgical bond between the component and the board. A reliable solder connection must have solderable surface to form good solder joint since interfacial reaction at solder joint are key factors in the fabrication of electronic products [10].

Generally, the thickness of the IMC layer at the interface between the solder and substrate is very important in determining the reliability of the whole package [11]. Besides that, activation energies of IMCs layer also contributed to the coarsening of IMC grains and nucleation kinetics. Therefore, as the growth of the IMC layer could degrade the reliability of the solder joint and influence its grain structure it is essential to study the formation and growth of the IMC layer [12-15].

Many studies have been performed on the interfacial reaction between Sn-Ag-Cu solders and various surface finishes, such as Cu, Au/Ni/Cu and electroless nickel-immersion gold (ENIG), during reflow or aging. However, insufficient comparative studies have been done on the interfacial reactions of Sn-Ag-Cu/ImAu solder joints. Therefore, in this study, the effect of using different immersion types of surface finish towards the intermetallic compound formation in terms of its thickness and activation energy was investigated.

2.0 Experimental Procedure

The solder ball used in this study was Sn-3.0Ag-0.5Cu (in wt%) with diameter of 500µm. The substrate used in this study are Immersion Gold (ImAu) and Immersion Tin (Sn)-plated Cu. The coating process of ImAu and ImSn on Cu substrate were done starting from pre-treatment process, soaking the substrate in ImAu and ImSn solution respectively in plating bath and ended in solder masking process. Then, reflow process was conducted in a furnace under peak temperature 250°C for 25 minutes. To evaluate the interfacial reactions between solder alloys substrates during the solid-state reaction, isothermal aging treatment was performed. The samples were then aged up to 1000 hours in an aging oven. After the reflow and aging treatment, the samples were prepared for the observation of the interface cross-section. The common metallographic practices, grinding and polishing, were used to prepare the samples. The compositions of intermetallic compound were confirmed using Scanning Electron Microscopy-Energy-dispersive X-ray spectroscopy (SEM-EDX) and its microstructure were observed using optical microscope. The thickness of the intermetallic was measured using ImageJ software and activation energy was calculated using measured data.

3.0 Results and Discussion

3.1 Interfacial microstructure

After solder reflow, interfacial reaction occurred. As the SAC 305/ immersion Au-plated Cu interface was reflowed for 25 minute, the topmost Au layer was dissolved completely into the molten Sn-Ag-Cu solder, leaving the Cu layer exposed to the molten solder.
SEM micrographs of cross section between Sn-Ag-Cu/ImAu and Sn-Ag-Cu/ImSn; both after isothermal aging are presented in Fig. 1 and 2 respectively. The cross sectional microstructure of Fig.1 shows that Au layer disappears completely, suggesting that it was entirely dissolved into the molten solder. The same result obtained from refloved SAC305/ immersion Sn. Such complete consumption of the immersion layer after reflow process was also observed in other studies as it explains rapid dissolution of Ag layer in liquid solder [9, 16].

Former researchers also concluded that Cu$_6$Sn$_5$ layer was formed as reflow condition and Cu$_3$Sn formed during solid state aging between Cu$_6$Sn$_5$ and Cu substrate. The morphology of Cu$_6$Sn$_5$ also changed from scallop-type to layer-type after isothermal aging process, thus supporting the studies by Zhang et.al and Yoon et.al [9, 20, 21].

The EDX analysis also indicates that there is no Au composition on the IMC layer, whether as reflow condition or after solid state aging. Zhang et.al [20] in his studies has mentioned that existence of such thin Au layer did not influence the morphology of the interfacial IMCs significantly. Zhang et.al in his studies has also stated that, if Au layer is thick enough, it is believed that the close proximity of the crystal structure and chemistry between Au and Cu may make Au present in the Cu$_6$Sn$_5$ type compound as a form of (Cu, Au)$_6$Sn$_5$ phase. As in this studies, the thickness of the Au layer after electroplated range from 0.4 to 0.5 µm, thus explained the phenomenon where no Au detected in IMC layer. As for Sn-Ag-Cu/ImSn, the IMC that formed after reflow process is Cu$_6$Sn$_5$, which is common IMC type that has been found by previous researcher due to reaction between Cu in substrate and Sn in solder. However the differences found between ImSn and ImAu was that their IMC thickness, which are going to be discussed in the next section.

\[ \text{Cu}_6\text{Sn}_5 + 9\text{Cu} \rightarrow 5\text{Cu}_3\text{Sn} \] (1)

Figure 1: SEM micrographs of Sn-Ag-Cu/ImAu joints after aging time; (a) as reflow, (b) 500 hour and (c) 1000 hour.

Based on close examination of the cross sectional image discloses using EDX, it is found that the Sn and Cu were precipitated as Cu$_6$Sn$_5$ IMCs in the solder matrix as seen in Fig. 1 and 2. Soon, as the solder joint exposed to the solid-state aging at 150˚C, thin layer of Cu$_3$Sn start to appear on the interface as can been on both Fig 1 (b) and 2 (b).

In a Cu-Sn system, the Cu$_6$Sn$_5$ phase formed during the early stages of solder/substrate interactions, which correspond to a higher driving force for precipitation than that of the Cu$_3$Sn phase [17, 18]. After the formation of Cu$_6$Sn$_5$ phase, the formation of Cu$_3$Sn phase becomes thermodynamically possible. However, the thickness of Cu$_3$Sn is expected to be much smaller than that of Cu$_6$Sn$_5$, because Cu$_3$Sn was grown by solid state diffusion [10]. The formation of Cu$_3$Sn is governed by the phase stability according to the following reaction [19]:

Figure 2 : Microstructure of Sn-Ag-Cu/ImSn joints after aging time; (a) as reflow, (b) 500 hour and (c) 1000 hour.
3.2 IMC thickness and Activation Energy

The average thickness of total $\text{Cu}_3\text{Sn} + \text{Cu}_5\text{Sn}_3$ layer and are plotted in Fig. 3. The thickness of IMC layers ($d_1$ and $d_2$) are respectively measured at multiple selected areas and divided by the numbers of selected points to obtain average value as been illustrated in Fig 4.

Based on the result obtained, the value of thickness of SAC/ImAu joint are closely similar to that SAC/ImSn joint. The highest measured thickness for both joint are 13.38μm and 12.35μm respectively. The difference on thickness measured for Cu$_3$Sn phase between after reflow and isothermal aging for both joints are approximately 5μm.

For Sn–Cu reaction couple after a few seconds, Cu$_3$Sn is either absent or too thin to be resolved by scanning electron microscopy or any optical microscope. The observations show that the formation of interfacial intermetallic compound Cu$_3$Sn may occur through a homogeneous nucleation process within the amorphous [22]. Obviously, the increase of total IMC thickness is mainly due to the growth of Cu$_3$Sn rather than Cu$_5$Sn$_3$.

This is due to dependability of the growth of Cu$_5$Sn$_3$ on Cu atoms availability on solder side. Since most of the Cu atoms in the solder have been reacted to form Cu$_5$Sn$_3$ particles, the amount of Cu that can diffuse between solder and Cu$_5$Sn$_3$ layer is very small, thus greatly limiting the growth of Cu$_5$Sn$_3$ on solder side. Therefore, during isothermal aging, Cu$_5$Sn$_3$ layer expand and shifting between both Cu/Cu$_3$Sn interface and Cu$_5$Sn$_3$/Cu$_3$Sn$_3$ interface, which explained the phenomenon where Cu$_5$Sn$_3$ grew much slower than Cu$_3$Sn [21].

For the growth of the IMC layers, because of the diffusion of Cu through Cu$_3$Sn is the rate-limiting factor, its thickness as a function of the time can be expressed as the following equation [23]:

$$d = d_0 + \sqrt{k_t}$$  \hspace{1cm} (2)

where $d_0$ is the initial thickness (cm), $t$ is the aging time (s), and $k$ is the growth rate constant which is strongly related to the diffusion coefficient of IMC (cm$^2$/s) and can be obtained from the linear regression line.

![Figure 4: Schematic diagram of IMC thickness measurements where $d_1$ is Cu$_3$Sn$_3$ thickness and $d_2$ is Cu$_5$Sn$_3$ thickness.]

Meanwhile, the activation energies for the intermetallic growth can be calculated using the Arrhenius relationship [24]:

$$k = k_0 \exp \left( \frac{-Q}{RT} \right)$$  \hspace{1cm} (3)

Using Eq. (3), the activation energy $Q$ can be determined from the slope of straight line obtained by plotting ln($k$) against 1/$T$: Eq. (3) could then be expressed as below [25]:

$$\ln(k) = \ln(k_0) - \left( \frac{Q}{RT} \right)$$  \hspace{1cm} (4)

The activation energy of IMC layer for both Sn-Ag-Cu/ImAu and Sn-Ag-Cu/ImSn joint was calculated using Eqs. (2)–(4). The calculated results, activation energies for total IMC layer (Cu$_3$Sn$_3$ + Cu$_5$Sn$_3$), Cu$_5$Sn$_3$ layer and Cu$_3$Sn layer, are displayed in Table 1 below.

<table>
<thead>
<tr>
<th>Solder/Substrate</th>
<th>Aging time (h)</th>
<th>IMCs</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC 305/ImAu</td>
<td>250</td>
<td>Cu$_3$Sn$_3$ + Cu$_5$Sn$_3$</td>
<td>30.44</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>Cu$_3$Sn$_3$ + Cu$_5$Sn$_3$</td>
<td>26.63</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>Cu$_3$Sn$_3$ + Cu$_5$Sn$_3$</td>
<td>27.99</td>
</tr>
<tr>
<td>SAC 305/ImSn</td>
<td>250</td>
<td>Cu$_5$Sn$_3$ + Cu$_3$Sn</td>
<td>26.24</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>Cu$_5$Sn$_3$ + Cu$_3$Sn</td>
<td>27.29</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>Cu$_5$Sn$_3$ + Cu$_3$Sn</td>
<td>28.29</td>
</tr>
</tbody>
</table>

The activation energy for the IMC growth during isothermal aging is estimated to be 30.44 kJ/mol for SAC/ImAu joints and 26.24 kJ/mol for SAC/ImSn joints at 250 hours aging time. Consequently, the IMC growth rate is much higher for the SAC/ImSn system than that SAC/ImAu system according to smaller value in activation energies. The estimated value for activation energies in this work may differ from others work due to differences on materials, diffusion couple methods, and aging conditions (temperature and time) as been stated by Zhang et.al [21] regarding his
work. The elements in the substrates and the solder used should be somekind of controller to the interdiffusion between IMCs layer. This is because, interfacial IMCs layer will continue to grow even at room temperature after solder joints have completed solidification due to its low activation energy [26, 27].

4.0 Conclusion

The analysis of IMCs growth for Sn-Ag-Cu/ImAu and Sn-Ag-Cu/ImSn system was performed during isothermal aging. In this present study, observation of morphology and calculated activation energies were used to measure the IMCs growth over aging time. The results show that interfaces of IMCs for both joints gradually change from scallop to layer type. The Au and Sn particle also dissolve completely into molten solder after reflow process. The thickness value of the IMCs layer are closely similar for both joints and it’s increasing over aging time. The activation energy that calculated from measured thickness data showed that Sn-Ag-Cu/ImSn have smaller activation energies compared to Sn-Ag-Cu/ImAu system. Consequently, the Sn-Ag-Cu/ImSn system have been proven to have higher IMCs growth rate compared to Sn-Ag-Cu/ImAu system.

5.0 References


