Intermetallic Growth on PWBs Soldered with Sn3.8Ag0.7Cu

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Abstract

This paper describes the nature of the intermetallic phases observed at the interface and in the bulk of Sn3.8Ag0.7Cu solder immediately after reflow on PWBs coated with a variety of commercial plating systems. It also discusses the growth of these intermetallic phases after aging at homologous temperatures of 0.8Tm, 0.85Tm, and 0.9Tm for 10, 100 and 1000 hours. The following board plating systems were investigated: organic solderability preservative (OSP) over bare copper, immersion tin, immersion silver, and immersion gold over electroless nickel. This study revealed that the composition, microstructure, and thickness of intermetallics at the interface were strongly dependent on the plating system. The effect of the bulk and interface microstructure on the shear strength of the joints was also investigated. For all plating systems, the shear strength of the solder joints did not degrade with aging, and the failure mechanism continued to be cohesive failure through the bulk of the solder.

Introduction

Most of the lead-free solder candidates being considered for moderate temperature applications consist of tin with small additions of alloying elements. Lead-free solders recommended as the most promising candidates for replacing eutectic tin-lead by the National Center for the Manufacturing Sciences (NCMS) and the National Electronics Manufacturing Initiative (NEMI) are based on additions of silver and/or copper to tin. These solders have a combination of a moderate melting point, good shear strength, good fatigue resistance, and good surface wetting to copper leads and pads. The good surface wetting properties come from the abundance of tin, which easily adheres to pad surfaces plated with copper, silver, tin or gold/nickel by forming a thin layer of M-Sn (Cu-Sn, Ag-Sn, Ni-Sn) intermetallic. Other binary systems in the solder-substrate system do not form intermetallics.

It is this same tendency of tin to form intermetallics that raises reliability concerns with high tin solders. Frear[1] has found that compared to Sn37Pb solder, SnAgCu solder will produce a thicker interfacial intermetallic on copper and Ni-P under bump metallurgy immediately after reflow and after subsequent aging, due to its higher tin content and higher reflow temperature. The formation over time of a thick layer of brittle intermetallic can lead to adhesive fracture of the solder joint, especially in the presence of voids created by asymmetric interdiffusion.

A number of studies have examined intermetallic growth when solders, including Sn37Pb and Sn0.7Cu, are reflowed over bare copper or gold over electroless nickel (Ni/Au) [2-10]. It is commonly accepted that for bare copper, copper from the pad will interact with tin from the solder and form Cu6Sn5 at the interface. If the joint is aged for a long period of time at a high enough temperature, a Cu3Sn layer will form between Cu6Sn5 and the bare copper pad. For gold over nickel plating, gold will dissolve into the bulk solder during the soldering process, possibly forming AuSn4 in the bulk, and permitting a layer of Ni3Sn4 to form at the interfaces. Some AuSn4[17] has been observed to form at the interface, however, after high temperature aging. Cu6Sn5 has also been observed to be the dominant intermetallic at the interface of SnAgCu solder on bare copper. For Ni/Au plating, a ternary intermetallic, Cu-Ni-Sn[11-14] or quaternary intermetallic, Cu-Sn-Ni-Au[9] was detected at the interface with SnAgCu solder. Zribi and Zeng[13,14] found the intermetallic to be (CuNi)xSn5y, which can grow significantly faster than Ni3Sn4.

Even if the intermetallic is distributed throughout the bulk of the solder, however, it could have an effect on lead-free solder joint strength and reliability. Intermetallics in solder microstructures can make the solder stronger and less compliant during thermal cycling [1]. One study of the
microstructure of Sn4.0Ag0.5Cu found a distribution of Ag3Sn and Cu6Sn5 particles in a matrix of tin [16]. Ka Yau Lee[9] and Frear[1] have also detected Ag3Sn in an elongated form in the SnAgCu solder, and Lee[9] found Cu-Sn-Au particles present along the Sn-rich phase boundary on Cu/Ni/Au.

Growth of intermetallic at the interface or in the bulk is strongly dependent on the plating system used as well as the type of solder used. As discussed above, there have been some studies on bare copper and gold over nickel [5,9-15], but not of other widely used plating systems. It is important to address intermetallic growth on other commercially available plating systems along with the influence of these different platings on the bulk microstructure of SnAgCu solder after long-term temperature aging.

The study concentrates on the bulk and interface microstructure of Sn3.8Ag0.7Cu solder reflowed and subsequently thermally aged on four typical plating systems: organic solderability preservative (OSP) over bare copper, immersion tin (ImSn), immersion silver (ImAg) and immersion gold over electroless nickel (ENIG). It also focuses on the effects of different plating systems on solder joint shear strength and reliability. The microstructure and intermetallic growth for each plating system is characterized by optical microscopy and SEM/EDX.

**Experimental Procedure**

Sn3.8Ag0.7Cu solder balls with a ball diameter of 635µm were reflowed onto pads on boards coated with the following four commercial platings: organic solderability preservative (OSP) over bare copper, immersion tin (ImSn), immersion silver (ImAg) and immersion gold over electroless nickel (ENIG). The thickness of plating was 0.5µm for ImAg, 1.0µm for ImSn, and 0.2µm gold and 2.3µm nickel for ENIG.

Sn3.8Ag0.7Cu solder paste was stencil printed (thickness:0.006”) over the pads, and the Sn3.8Ag0.7Cu solder balls were manually placed and reflowed to prepare samples for aging and shear testing. The boards were reflowed using an infrared oven with four heating zones, using the reflow profile shown in figure 1. This profile closely matched the profile recommended for this solder by Indium Corporation. The diameter of the solder ball after reflow was about 730µm.

![Sn3.8Ag0.7Cu Reflow Profile](image)

**Table 1: Sn3.8Ag0.7Cu reflow parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recommended by Indium Corp.</th>
<th>Actual Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate</td>
<td>1~2 °C/sec</td>
<td>1 °C/sec</td>
</tr>
<tr>
<td>Peak temp</td>
<td>242-262 °C</td>
<td>244 °C</td>
</tr>
<tr>
<td>Time in liquid state</td>
<td>30~90 sec</td>
<td>43 sec</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>&lt;4 °C/sec</td>
<td>2 °C/sec</td>
</tr>
</tbody>
</table>

After reflow, a group of three boards from each plating system were aged at 0.8Tm (=119 °C), 0.85Tm (=143.5 °C) and 0.9Tm (=168 °C) in order to accelerate the effects of long term exposure to steady state temperature. One board each was exposed for 10 hours, 100 hours, and 1000 hours. Therefore, each board represented a specific condition of plating type, aging temperature and aging time. Each board contained over 30 sample solder joints for analysis. Samples aged at 0.9Tm for 1000 hours exhibited significant degradation of the laminate boards that included delamination of the plated pads. These boards could therefore not be used for shear testing.

**Microstructure characterization**

Two solder joints from each board were cross-sectioned, polished and etched with an etchant consisting of 5%HCL:2%HNO3:93%methanol to examine the composition, thickness, and uniformity of the intermetallic layers at the interface, and the composition and morphology of the intermetallic in the bulk. Average intermetallic thickness was measured using image analysis software on optical photomicrographs. Microstructures were characterized using optical microscopy and SEM/EDX.
Shear test

A minimum of 25 solder joints from each board were shear tested using a Dage 2400 bond shear testing system. The stylus speed was 100µm/s and the shear force was designated to be the maximum force applied during the test. Three failure modes are expected:

Mode 1: Cohesive failure through the bulk solder.
Mode 2: Adhesive failure at the solder/pad interface. This could be due to poor wetting or to fracture of the intermetallic layer.
Mode 3: Adhesive failure at pad/board interface. This is related to poor adhesion between the pad and the board and is seen when the board is poorly manufactured or damaged in reflow or aging.

Shear strength was calculated as shear force divided by average shear area. It is difficult to measure the exact shear surface area corresponding to each solder ball, so shear area was obtained by randomly choosing ten solder joints and measuring the maximum diameter of each solder joint based on the assumption that the joint is a sphere. Mean shear strength is calculated based on the shear strength of 25 solder joints. Any shear strength values corresponding to failure mode 3 were not considered here. A 3-parameter Weibull distribution is used to calculate the mean shear strength of the solder joint, which corresponds to 50% confidence level.

OSP Results

Bulk microstructure

As shown in figure 2, the bulk Sn3.8Ag0.7Cu solder microstructure immediately after reflow is composed of large Cu₆Sn₅ intermetallic particles (light area) in a dispersed eutectic phase (dark area), which consists of small Ag₃Sn and Cu₆Sn₅ particles in a tin matrix. This is in accordance with the Cu-Sn and Ag-Sn phase diagrams. The weight ratio of copper in the bulk solder in some cases reached 4.5% based on quantitative analysis of the photomicrographs. Since copper in the bulk solder only occupies 0.7% by weight, copper from the pad must have dissolved into the bulk solder during reflow to form these large intermetallic phases together with copper from the bulk solder. Other studies have reported that large needles of Ag₃Sn also appear in Sn3.5Ag and Sn3.8Ag0.7Cu solders [1,6]. However, in this study, no large Ag₃Sn needles were found in the bulk solder. Voids were also observed in the solder at the fracture surface after shear testing.

![Fig. 2. The microstructure of Sn3.8Ag0.7Cu solder on OSP plating (above) and the enlargement with etching (below).](image)

Interface microstructure

The first intermetallic to form at the interface is Cu₆Sn₅, which is present immediately after reflow. Cu₃Sn appears as a thinner intermediate layer in samples that had been exposed to 100 hours of aging at 0.9Tₘ, 1000 hours of aging at 0.85Tₘ and 1000 hours of aging at 0.9Tₘ (see Fig. 3). This is also in agreement with the Cu-Sn phase diagram, which shows Cu₆Sn₅ as the intermetallic phase forming from the liquid solder state, and Cu₃Sn as the phase which forms upon interdiffusion of the copper pad and the Cu₆Sn₅ intermetallic. The initial morphology of the intermetallic is scalloped, but it becomes thicker and more uniform after aging. This might be attributed to the fact that a smooth grain structure is preferred in order to decrease the surface energy. The growth behavior is similar to Sn37Pb and Sn3.5Ag growth on bare copper [3,4].
The growth of the copper-tin intermetallic layer at the interface with OSP coated copper appeared to follow a square-root dependence with time as is expected for diffusion controlled growth. The initial thickness, \(d_0\), for determining the growth rate was chosen to be the thickness after 10 hours aging. The growth rate at each temperature was calculated by taking square of the slope obtained from the least-squares linear regression (Fig. 4a) of average thickness, \((d - d_0)\), against the square root of aging time, \(t\). An Arrhenius relationship was then used to calculate the effect of temperature on the growth rate. The activation energy calculated from the slope of \(\ln D\) versus \(1/T\) is \(E = 0.93eV\) and the linearity of the data is \(R^2 = 0.85\) (see Fig 4b). The thickness of the layer is thus characterized by the formulae:

\[
d = d_0 + \sqrt{Dt}
\]

\[
D = D_0 \exp\left(-\frac{E}{kT}\right)
\]

**ImSn**

As was the case for OSP coated boards, a layer of \(\text{Cu}_6\text{Sn}_5\) intermetallic formed at the interface between the Sn3.8Ag0.7Cu solder and the immersion tin plating on ImSn boards. However, unlike the OSP coated boards, the \(\text{Cu}_3\text{Sn}\) layer was not formed except for samples aged 1000 hours at 0.9Tm. Also unlike OSP coated boards, no scalloping was observed. Instead, the interfacial intermetallic layer was smooth and uniform in thickness after reflow. This may have been due to the formation of \(\text{Cu}_6\text{Sn}_5\) intermetallic between the tin-plating and the underlying copper trace in storage before reflow, which was not removed during the reflow soldering. This layered structure remained after aging (see Fig. 5), with a relatively constant average intermetallic thickness of around 4-5\(\mu\)m, again indicating that sufficient intermetallic had formed before reflow and aging to limit additional growth. Large \(\text{Cu}_6\text{Sn}_5\) intermetallic particles and voids were also detected in the bulk solder for all conditions as was the case for OSP.
**ImAg**

Intermetallic growth on immersion silver plated boards is more complex than growth on either OSP or ImSn coated boards. Again, the interfacial intermetallic layer formed during reflow is Cu₆Sn₅. However, as with OSP, there is an intermediate layer of Cu₃Sn layer between the Cu₆Sn₅ and the Cu pad that forms after long-term high temperature aging (100 hours at 0.9ₜₚ, 1000 hours at 0.85ₜₚ, and 1000 hours at 0.8ₜₚ). Because of the presence of silver in the plating, however, large Ag₃Sn needles or platelets were also detected just above the Cu₆Sn₅ layer (See Fig. 6) in the as-reflowed samples. This is similar to the findings in Frear’s study[1]. After high temperature aging, however, the Ag₃Sn needles disappeared from the interface. The presence of the silver above but near the interface after reflow and its disappearance upon aging would seem to indicate that the silver is diffusing away from the interface and into the bulk.

**ENIG**

The last plating system studied was electroless nickel overplated with immersion gold (ENIG). The gold plating was very thin (0.2µm) and it rapidly dissolved in the bulk solder during reflow, leaving the fresh nickel underplate to form intermetallics with the Sn3.8Ag0.7Cu solder. Nickel from the pad, together with tin and copper from the solder participate in the reaction to form a ternary intermetallic (Cu₆Ni₅)₅Sn₅ at the interface. The intermetallic layer is very thin after reflow, and it grows more slowly with aging than the copper-tin intermetallic.
intermetallic. However, the thickness reached 4–5µm after 1000 hours aging for all the temperature conditions. Unlike the other plating systems, there were no large Cu₆Sn₅ intermetallic particles detected in the bulk solder (See Fig. 7b). Very small Cu-Sn needles were found just above the interface (See Fig. 7a). The fact that large Cu₆Sn₅ intermetallics could not be found in the bulk solder on ENIG plating lends further evidence to the presumption that the source of the Cu for the formation of these intermetallics was dissolution of the pad. ENIG plating alone had a Ni₃Sn intermetallic layer that would serve to constrain the underlying copper from dissolving into the bulk solder during reflow and aging. Instead, with ENIG, copper from the solder will have the tendency to migrate toward the interface and contribute to the formation of (CuNi)₆Sn₅. Undoubtedly, the limited availability of copper from the solder influences the growth of (CuNi)₆Sn₅ and is a reason the thickness of the intermetallic for ENIG after aging for 1000 hours at different temperatures is relatively constant. Some bulk voids were detected, but there were fewer voids than with other plating systems.

**Shear test**

After reflow and aging, the solder joints were shear tested. Most of the solder joints failed cohesively through the bulk solder, indicating the failure was not related to the thickness or composition of the interfacial intermetallic. In addition, the shear strength remained relatively constant during aging for all platings, indicating little influence of the bulk intermetallics as well. Both the mean and the distribution remain relatively constant as a function of time, temperature and plating system (see Fig. 8).

**Fig 8:** Mean shear strength of solder joint vs. thermal aging. a) OSP, b) ImAg, c) ImSn, d) ENIG

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Fig. 7(a). SEM image of interface of Sn3.8Ag0.7Cu solder joint on ENIG plated boards after 10 hours aging at 0.9Tₘ (168°C) (b). Optical photomicrograph after 10 hours aging at 0.9Tₘ (168°C)(after etching)
The solder joint shear strength on ENIG plating was slightly higher and more stable with time than other plating systems, perhaps attributable to the presence of fewer voids. After 1000 hours of aging at 0.9Tm, failure was often observed between the copper pad and the underlying laminate because of degradation of the epoxy resin laminate after long-term, high temperature aging. The shear test data corresponding to this failure mode was not included. No failure through the intermetallic at the interface was detected for any of the samples.

Summary and Conclusions:
The bulk microstructure of Sn3.8Ag0.7Cu consisted of a eutectic matrix of Sn, Cu6Sn5 and Ag3Sn. Large Cu6Sn5 dendrites were also observed in the bulk for all platings except ENIG, where the nickel layer limited the diffusion of copper from the pad into the solder. Interfacial layers consisted mostly of Cu6Sn5 with some Ag3Sn in the case of ImAg plating, and some Cu6Sn in the case of OSP coating, ImAg and ImSn plating. It should also be noted that the thickness of gold in the ENIG plating was insufficient to form brittle Au-Sn intermetallics in the bulk solder [17].

The failure mode in shear testing was not affected by the growth of the intermetallic at the interface but remained as mode 1 (failure through the bulk solder) for all plating and aging conditions. Furthermore, there was no significant degradation in solder ball shear strength after long-term exposure (1000 hours) to high temperatures (143°C), indicating that the bulk microstructure did not degrade during long-term high temperature aging. This may be because the small, distributed Ag3Sn intermetallic particles, makes the microstructure more resistant to grain coarsening with long-term high temperature aging[16].

References
16. S.Wiese et al, “Constitutive behavior of lead-free solders vs. lead-containing solders-experiments on bulk specimens and flip-chip joints”, 2001 ECTC, pp890-902

Acknowledgments
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