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 $0.8T_m$, $0.85T_m$ and $0.9T_m$ 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 Cu_6Sn_5 at the interface. If the joint is aged for a long period of time at a high enough temperature, a Cu_3Sn layer will form between Cu_6Sn_5 and the bare copper pad. For gold over nickel plating, gold will dissolve into the bulk solder during the soldering process, possibly forming $AuSn_4$ in the bulk, and permitting a layer of Ni_3Sn_4 to form at the interfaces. Some $AuSn_4$[17] has been observed to form at the interface, however, after high temperature aging.

Cu_6Sn_5 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 $(CuNi)_6Sn_5$, which can grow significantly faster than Ni_3Sn_4.

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 Ag_3Sn and Cu_6Sn_5 particles in a matrix of tin [16]. Ka Yau Lee[9] and Frear[1] have also detected Ag_3Sn 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 themally 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.

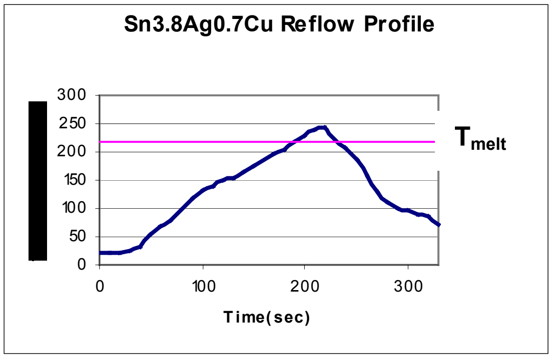


Fig 1. Sn3.8Ag0.7Cu reflow profile (T_{melt}=217 °C)

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

	Recommended by Indium Corp.	Actual Parameter
Heating rate	1~2 °C/sec	1 °C/sec
Peak temp	242-262 °C	244 °C
Time in liquid state	30~90 sec	43 sec
Cooling rate	<4 °C/sec	2 °C/sec

After reflow, a group of three boards from each plating system were aged at 0.8Tm(=119 °C), $0.85T_m$(=143.5 °C) and $0.9T_m$(=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%HNO_3:93%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 Cu_6Sn_5 intermetallic particles (light area) in a dispersed eutectic phase (dark area), which consists of small Ag_3Sn and Cu_6Sn_5 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 Ag_3Sn also appear in Sn3.5Ag and Sn3.8Ag0.7Cu solders [1,6]. However, in this study, no large Ag_3Sn needles were found in the bulk solder. Voids were also observed in the solder at the fracture surface after shear testing.

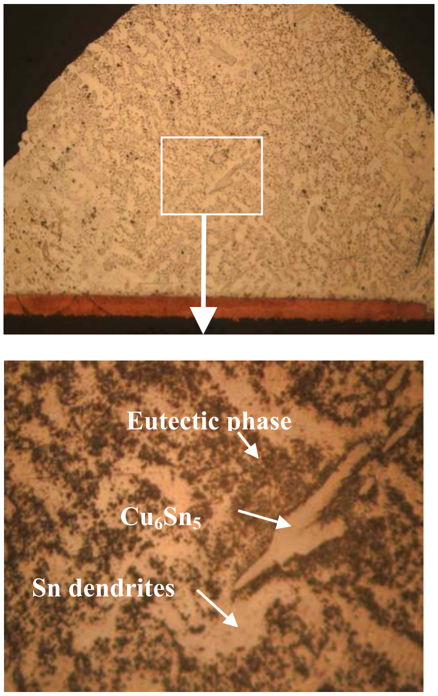


Fig. 2. The microstructure of Sn3.8Ag0.7Cu solder on OSP plating (above) and the enlargement with etching (below).

Interface microstructure

The first intermetallic to form at the interface is Cu_6Sn_5, which is present immediately after reflow. Cu_3Sn appears as a thinner intermediate layer in samples that had been exposed to 100 hours of aging at $0.9T_m$, 1000 hours of aging at $0.85T_m$ and 1000 hours of aging at $0.9T_m$ (see Fig. 3). This is also in agreement with the Cu-Sn phase diagram, which shows Cu_6Sn_5 as the intermetallic phase forming from the liquid solder state, and Cu_3Sn as the phase which forms upon interdiffusion of the copper pad and the Cu_6Sn_5 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].

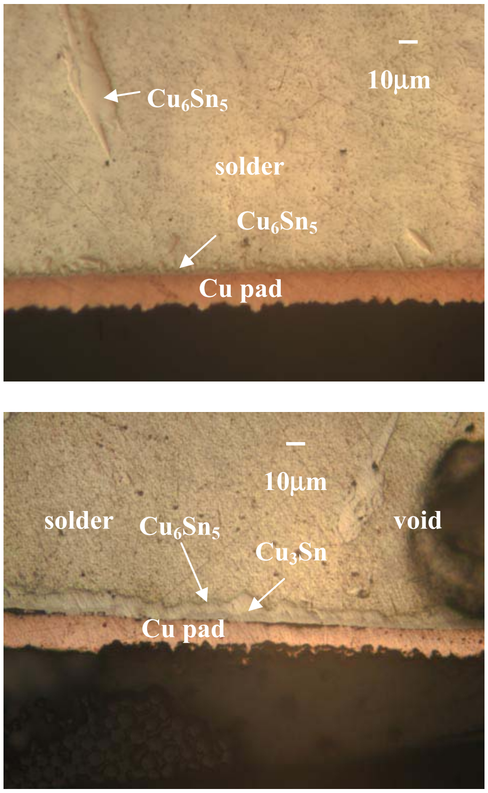


Fig. 3 Optical photomicrograph of Sn3.8Ag0.7Cu solder joint (without etching) on OSP coated boards. Above:just after reflow; Below:after 1000 hours aging at $0.9T_m$(168°C)

The growth of the copper-tin intermetalliclayer 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 $E = 0.93 eV$ 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:

$$d = d_0 + \sqrt{Dt} \quad \text{where}$$

$$D = D_0 \exp(-E/kT)$$

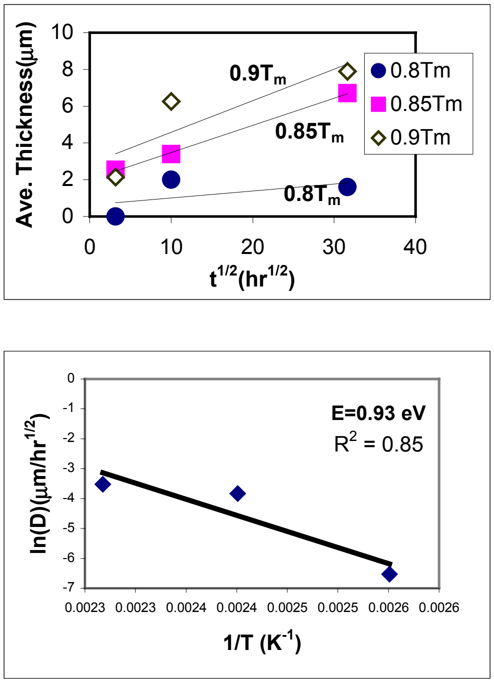


Fig 4 (a).Avg. intermetallic thickness as a function of (time)$^{0.5}$ for Sn3.8Ag0.7Cu/OSP interface
(b). Arrhenius plot for the intermetallic growth rate

ImSn

As was the case for OSP coated boards, a layer of Cu_6Sn_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 Cu_3Sn layer was not formed except for samples aged 1000 hours at $0.9T_m$. 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 Cu_6Sn_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 4~5µm, again indicating that sufficient intermetallic had formed before reflow and aging to limit additional growth. Large Cu_6Sn_5 intermetallic particles and voids were also detected in the bulk solder for all conditions as was the case for OSP.

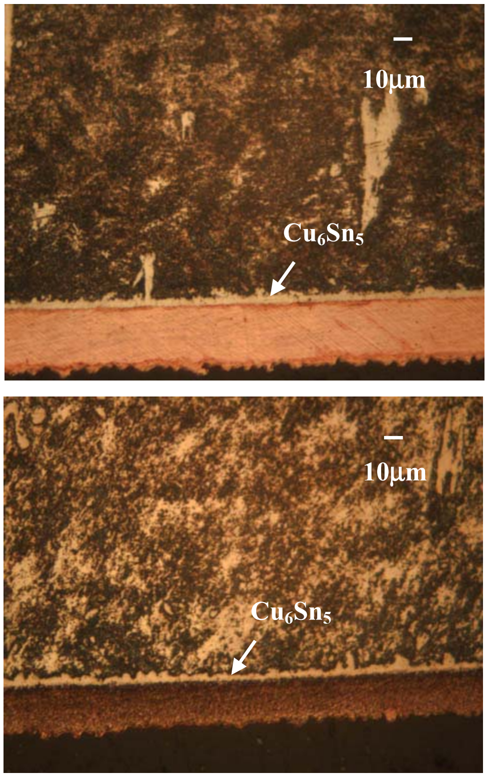


Fig. 5 Optical photomicrograph of Sn3.8Ag0.7Cu solder joint (after etching) on ImSn plating boards Above: just after reflow; Below: after 1000 hours aging at 0.8T$_m$(119°C)

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 Cu_6Sn_5. However, as with OSP, there is an intermediate layer of Cu_3Sn layer between the Cu_6Sn_5 and the Cu pad that forms after long-term high temperature aging (100 hours at 0.9T$_m$, 1000hours at 0.85T$_m$ and 1000 hours at 0.8T$_m$). Because of the presence of silver in the plating, however, large Ag_3Sn needles or platelets were also detected just above the Cu_6Sn_5 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 Ag_3Sn 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.

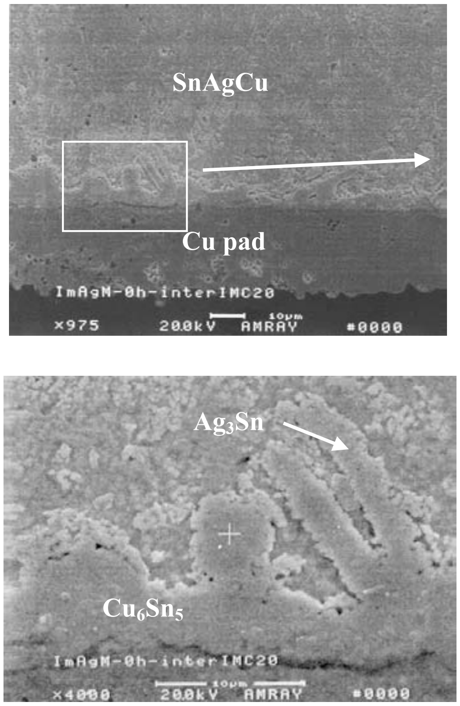
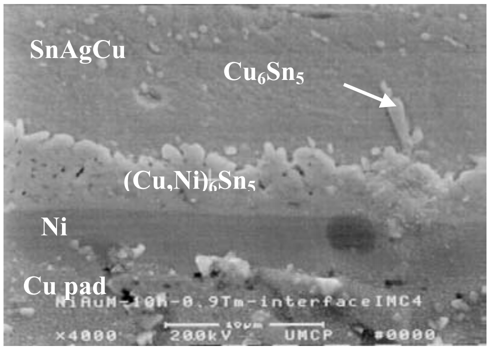


Fig. 6 SEM image of Sn3.8Ag0.7Cu solder joint on ImAg plated boards just after reflow.

Also intermetallic growth at the interface was more irregular than with the other plating systems. This may be due to the influence of Ag from the plating. The initial intermetallic reached 7µm in some cases, but as aging continued, intermetallics could increase or decrease. The average thickness is normally between 5µm and 8µm, but it could reach as high as 12µm or as low as 3.4µm. As with the other plating systems, large Cu_6Sn_5 intermetallics and voids were also found in the bulk solder for all the conditions here.

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 $(Cu,Ni)_6Sn_5$ at the interface. The intermetallic layer is very thin after reflow, and it grows more slowly with aging than the copper-tin 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 Cu_6Sn_5 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 Cu_6Sn_5 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 Ni_3Sn 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 $(CuNi)_6Sn_5$. Undoubtedly, the limited availability of copper from the solder influences the growth of $(CuNi)_6Sn_5$ 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.



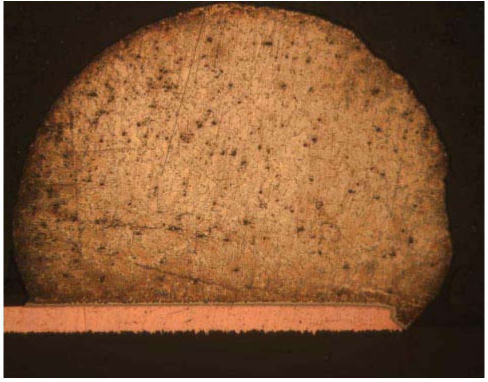


Fig. 7(a). SEM image of interface of Sn3.8Ag0.7Cu solder joint on ENIG plated boards after 10 hours aging at 0.9T_m (168°C) (b). Optical photomicrograph after 10 hours aging at 0.9T_m (168°C)(after etching)

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)

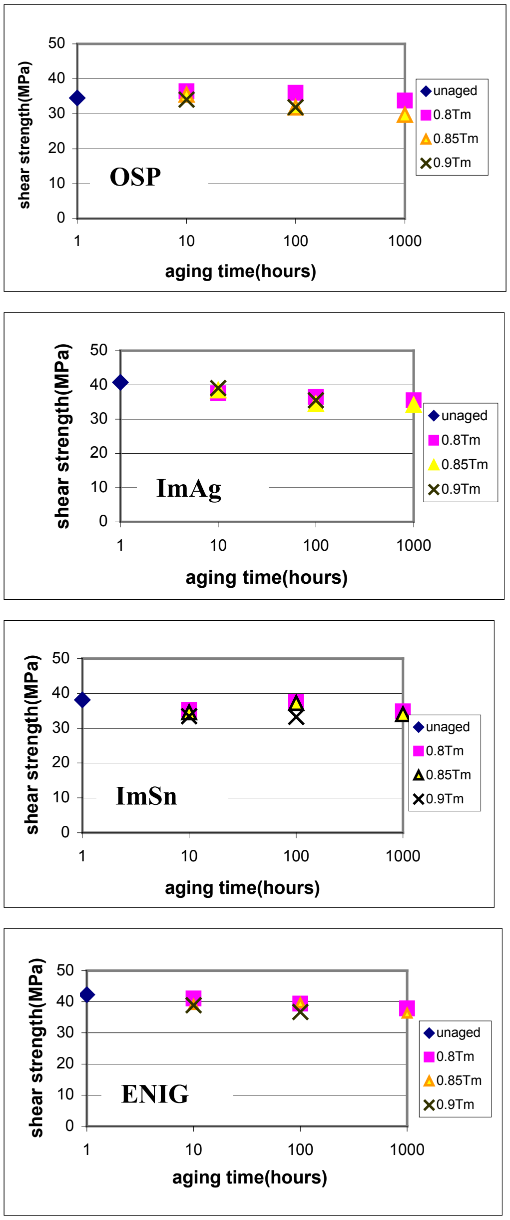


Fig 8: Mean shear strength of solder joint vs. thermal aging. a) OSP, b) ImAg, c) ImSn, d) ENIG

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, Cu_6Sn_5 and Ag_3Sn. Large Cu_6Sn_5 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 Cu_6Sn_5 with some Ag_3Sn in the case of ImAg plating, and some Cu_3Sn 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 Ag_3Sn intermetallic particles, makes the microstructure more resistant to grain coarsening with long–term high temperature aging[16].

References

1. D.R.Frear, et al “Pb-Free Solders for Flip-chip Interconnects”, JOM, 53(6)(2001), pp.28-32
2. K.N.Tu and K.Zeng, “Tin-lead(SnPb) solder reaction in flip chip technology”, Materials Science and Engineering , R 34(2001) pp 1-58
3. K.N.Tu et al “Kinetics of interfacial reaction in bimetallic Cu-Sn system”, Acta Metall., 30(1982), pp947-952
4. S.Choi et al, “Effect of soldering and aging time on interfacial microstructure and growth of intermetallic compounds between Sn-3.5Ag solder alloy and Cu substrates”, J. Electro. Mater., 28(11), 1999,pp1209-1215
5. Katuaki Suganuma et al, “Microstructure and strength of interface between Sn-Ag eutectic solder and Cu”, J. Janpan Inst. Metals, 59(12) 1995, pp.1299-1305
6. Wenge Yang, Robert W. Messler, Jr. “Microstructure Evolution of Eutectic Sn-Ag Solder Joints”, J. of Electron. Mater. , Vol.23, No.8, 1994 pp765-772
7. Peng Su, Tia Korhonen, Matt Korhonen, and Che-Yu Li, “Intermetallic Phase Formation and Growth Kinetics at the Interface Between Molten Solder and Ni-Containing Under Bump Metallization”, 2000 IEEE ECTC.
8. C.E. Ho et al, “Interactions between solder and metallization during long-term aging of advanced microelectronic packages”, J.Electr. Mater. 30(4),2001
9. Ka Yau Lee, Ming Li Dennis R. OLSEN,“Microstructure , Joint Strength and Failure Mechanism of Sn-Ag, Sn-Ag-Cu versus Sn-Pb-Ag Solders in BGA Packages”, 2001 ECTC , P478-485
10. Toshihiko Taguchi, Rikiya Kato, Satoru Akita, “Lead Free Interfacial Structures and Their Relationship to Au Plating”, 2001 ECTC, pp675-680
11. S.K.Kang, et al, “Interfacial reaction studies on lead-free solder alloys”, 51st ECTC 2001, pp448-454
12. Ka Yau Lee, et al, “Microstructure, joint strength and failure mechanism of Sn-Ag, Sn-Ag-Cu versus Sn-Pb-Ag solders in BGA packages”, 51st ECTC 2001, pp478-485
13. K. Zeng, et al, “Intermetallic reactions between lead-free SnAgCu solder and Ni(P)/Au surface finish on PWBs”, 51st ECTC 2001, pp693-698
14. A. Zribi et al, “The kinetics of ternary intermetallic alloys in Pb-Sn and Cu-Ag-Sn Pb free electronic joints”, 2001 ECTC pp687-692
15. P. T. Vianco, et al “Solid-state intermetallic compound growth between copper and high temperature, tin-rich solders-Part 1: experimental analysis”, J. Electr. Mater. 23(8), 1994 pp721-734
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
17. Z. Mei, et al “Brittleness interfacial fracture of PBGA packages soldered on electroless nickel/immersion gold”, 1998 ECTC, pp952-961

Acknowledgments

The authors would like to thank the corporate and industrial sponsors of the CALCE Electronic Products and Systems Center at the University of Maryland for their support of this research and Dr. K. N. Tu of UCLA for his technical assistance.