Microstructure and Intermetallic Formation in SnAgCu BGA Components Attached With SnPb Solder Under Isothermal Aging

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***Abstract*—The global transition to lead-free (Pb-free) electronics has led component and equipment manufacturers to transform their tin–lead (SnPb) processes to Pb-free. At the same time, Pb-free legislation has granted exemptions for some products whose applications require high long-term reliability. However, due to a reduction in the availability of SnPb components, compatibility concerns can arise if Pb-free components have to be utilized in a SnPb assembly. This compatibility situation of attaching a Pb-free component in a SnPb assembly is generally termed "backward compatibility." This paper presents the results of microstructural analysis of mixed solder joints which are formed by attaching Pb-free solder balls (SnAgCu) of a ball-grid-array component using SnPb paste. The experiment evaluates the Pb phase coarsening in bulk solder microstructure and the study of intermetallic compounds formed at the interface between the solder and the copper pad.**

***Index Terms*—Backward compatibility, BGA components, ENIG, exemption, ImAg, ImSn, intermetallics, isothermal aging, microstructure, mixed solder joint, SnAgCu, SnPb, solder.**

I. INTRODUCTION

MOST ELECTRONICS companies have transitioned to lead-free (Pb-free) processes, both to comply with government legislation and to avoid issues related to mixing of tin–lead (SnPb) and Pb-free metallurgies [1]–[8]. However, exemptions from Pb-free legislation have been granted for certain products, particularly those intended for high-reliability applications. An overview of the exemptions from Pb-free legislation can be found in [1] and [2]. One major concern with these exempt products is that, during assembly or rework, Pb-free components will have to be used due to the unavailability of SnPb components. This will result in the mixing of SnPb and Pb-free metallurgies.

A solder joint formed due to the mixing of SnPb and Pb-free materials is termed a "mixed solder joint." The mixing of metallurgies can induce new reliability concerns because solder-joint reliability depends on loading conditions, material properties, and microstructure of the solder joint. Furthermore, the microstructure of the solder joint continues to evolve over time depending on temperature and mechanical loading conditions. One of the microstructural features known to influence the reliability of conventional SnPb solder is the Pb phase, which coarsens with time, temperature and mechanical loading, causing reliability concerns [9], [10].

Another microstructural feature, which influences the reliability of solder joints, is associated with intermetallic compounds (IMCs) [11], [12]. IMCs are formed due to the interdiffusion of two dissimilar materials, which are governed by a thermally activated diffusion process. The initial formation of IMC during soldering can ensure a good metallurgical bond, but the growth of IMCs can also result in a weak interface that can lead to early failures.

Several studies [7], [8], [13]–[18] have been conducted to investigate the reliability of the mixed solder joints subjected to various loading conditions and metallurgical combinations. For Pb-free ball-grid-array (BGA) components assembled with Pb-based solder, the reliability has been shown to be equivalent to completely Pb-free assemblies, provided that the Pb is distributed evenly throughout the joint. However, significantly, earlier failures can occur if the Pb is not distributed in the mixed solder joint [13].

From a manufacturing perspective, mixed solder assemblies have a narrow window for the reflow temperature because of the different melting temperatures of SnPb and Pb-free solders and the changes in solder volume depending on application. Due to the sensitivity to the mixing of Pb in the solder joints, process development should be conducted to develop a reflow process which would result in a homogeneous distribution of Pb over each solder ball. From a microstructural perspective, studies [19]–[22] have reported that a percentage of Pb greater than 3% in a Pb-free solder will reduce the solidification temperature of the Pb-free solder from 217 °C to 176 °C. However, the significance of this solidification behavior on reliability has not been established.

Several studies have already focused on the effect of reflow on the microstructure of mixed solder joint [15]–[20], but a fundamental understanding on the changes in microstructure is missing in the literature. This paper presents our study on the microstructural changes in mixed solder joints and the degradation mechanisms in mixed solder joints. This paper discusses

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TABLE I
CIRCUIT-BOARD SOLDER AND PAD-FINISH ASSEMBLY MATRIX

Identifier	BGA Solder ball	Solder paste	Reflow condition	Pad finish
Mixed	Sn3.0Ag0.5Cu	Sn37Pb	Peak temperature: 220°C, time above liquidus: 67-70 sec, cooling rate: 2°C/sec	ImSn, ImAg, ENIG, HASL (SnPb)
Pb-free	Sn3.0Ag0.5Cu	Sn3.0Ag0.5Cu	Peak temperature: 245°C, time above liquidus: 77-81 sec, cooling rate: 2.1°C/sec	ImSn, ImAg, ENIG
SnPb	Sn37Pb	Sn37Pb	Peak temperature: 215°C, time above liquidus: 67-70 sec, cooling rate: 1.8°C/sec	HASL (SnPb)

TABLE II
COMPOSITION OF PHASE AT LAST SOLIDIFICATION TEMPERATURE (181 °C) FOR THE Sn–Cu–Pb SYSTEM

Reaction	Phase	Mass % Cu	Mass % Pb	Mass % Sn
$L \rightarrow (Sn) + (Pb) + Cu_6Sn_5$ [24]	Liquid	0.09	37.27	62.64
	Cu_6Sn_5	39.07	0	60.93
	(Pb)	0	81.23	18.77
	(Sn)	0	3.39	96.61

the reliability of mixed solders as a function of the microstructural changes that can occur during environmental storage and operation, focusing on the microstructural characterization for the mixed solder joints. Two microstructural features, namely, the Pb phase coarsening and the IMCs, were analyzed for mixed solder microstructure under various isothermal aging conditions. A Pb phase study was conducted to evaluate the extent of coarsening in the bulk of mixed solder as compared with the SnPb. An intermetallic study was then conducted to analyze the growth and composition of IMC for the mixed solder joints.

II. EXPERIMENTAL DESIGN

In our studies, BGA components were assembled onto circuit boards, at a high-volume assembly house, using Sn37Pb and Sn3.0Ag0.5Cu solders, and various board pad finishes: immersion tin (ImSn), immersion silver (ImAg), electroless nickel-immersion gold (ENIG), and hot air solder leveled. The assembly matrix is shown in Table I. Board assemblies were aged at 125 °C for durations of 100, 350, and 1000 h after the reflow process. Control assemblies (no aging) were also included for each assembly combination. To simulate a typical solder joint in an industrial surface-mount process, assemblies for this test were prepared in a qualified high-volume contract manufacturing house having a developed and qualified SnPb, Pb-free, and mixed reflow assembly process.

III. Pb PHASE DISTRIBUTION AND COARSENING

To determine the distribution of Pb in the microstructure, first, the behavior of Pb during solidification was analyzed. The maximum solubility of Pb in Sn is 3.4% from the SnPb phase diagram. When the volume of Pb is greater than 3.4%, residual Pb will precipitate in Sn grain boundaries. The diffusion of Pb in solder at 200 °C (below the Pb-free melting temperature 217 °C) was calculated from [23]

$$D = 5.1 \exp\left(\frac{-41\,000}{RT}\right) = 1.5 \times 10^{-4}\ \mathrm{cm}^2/\mathrm{s} \tag{1}$$

$$t = \frac{L^2}{D}. \tag{2}$$

The diffusion time (t) is found to be 6 s, where D is the diffusivity for Pb in Sn [23], R is 8.314 in joules per kelvin per mole, T is the temperature in kelvin, and L is the characteristic length of diffusion (~300 μm solder-joint height for BGA in this paper). Since the diffusion coefficients of solute atoms in liquid are much larger than in solids, the diffusion relation for solid (1) is considered in calculating the diffusion length for Pb in solder for reflow during time above liquidus. Length of diffusion (L) during the time above liquidus (t) of 60 s (typical time above liquidus) can be calculated by (2), which gives a characteristic length of 900 μm. Since the height of solder joint is ~300 μm, Pb will diffuse throughout the solder during reflow.

To understand the location of Pb in the solder, a quaternary phase diagram was considered [20]. The phase diagram suggests that the melting temperature of solder decreases from 217 °C to 176 °C due to the presence of Pb and that the last liquid to solidify contains Pb. This can also be confirmed from ternary phase diagrams of Sn–Cu–Pb which suggest that the last liquid to solidify contains Pb (see Table II).

In this paper, the amount of coarsening in the mixed solder joints was compared with the SnPb solder joints. Phase coarsening is generally referred to as Ostwald ripening. A reduction in the total interfacial energy provides the diving force for coarsening. The process results in an increase in the distance of separation between neighboring particles and in a decrease in the number of particles in the system. The thermodynamic basis

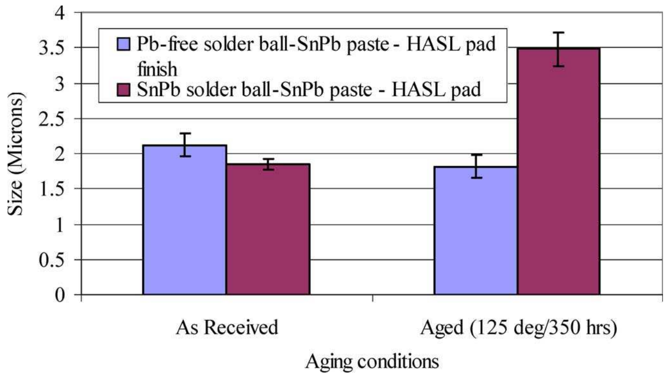


Fig. 1. Comparison of change in Pb phase area for the mixed and SnPb solder joints due to aging.

of coarsening in alloys is the Thompson–Freundlich solubility relationship, according to which, the Pb concentration in a Sn-rich matrix adjacent to a Pb-rich particle is in proportion to its radius of curvature when the phases are in local equilibrium [25]. Upon exposure to thermal aging, Pb-rich particles dissolve in the Sn-rich matrix, causing an increase in the Pb concentration adjacent to the Pb-rich particle. Increase in Pb concentration causes the Pb atoms to diffuse away from the smaller particles; the region of higher concentration towards the larger particle; the region of lower concentration. The diffusion of Pb atoms away from the smaller Pb-rich particle causes a reduction in its radius of curvature. As the flow of atoms proceeds, small Pb-rich particles dissolve to compensate for the decrease in concentration at Pb-rich interface.

Larger distance between the Pb-rich particles will require longer time for the diffusion process, thus influencing the amount of coarsening that is observed after 350 h at 125 °C. In the mixed solder joints, due to the larger average distance between the Pb-rich particles, an equivalent amount of coarsening would require more than 350 h. Thus, in the mixed solder joints, no significant coarsening is visible after 350 h of aging at 125 °C.

Commercial image analysis software was utilized to quantify the Pb in the microstructure before and after aging. The Pb phases were considered as spherical shape, and the diameters of the particles were plotted with respect to aging condition. Analysis was conducted over the entire solder ball, and the total area of Pb in the solder joint was plotted in bars (see Fig. 1). For this analysis, 16 balls were analyzed per BGA component and were found to be the optimal number to get a statistical confidence.

The Pb phase region was found to reduce with aging (350 h at 125 °C) for the mixed solder joint (see Figs. 2 and 3), whereas it increased for the SnPb solder joints (see Figs. 4 and 5). The lack of coarsening in mixed solder can be attributed to an insufficient concentration gradient between the Pb phases due to a larger separation distance between Pb phases in the mixed solder joints (see Fig. 6) compared with the SnPb joints (see Fig. 7). However, a higher quantity of Pb and a smaller separation distance between Pb phases in the SnPb solder produce a sufficient concentration gradient to promote the coarsening process.

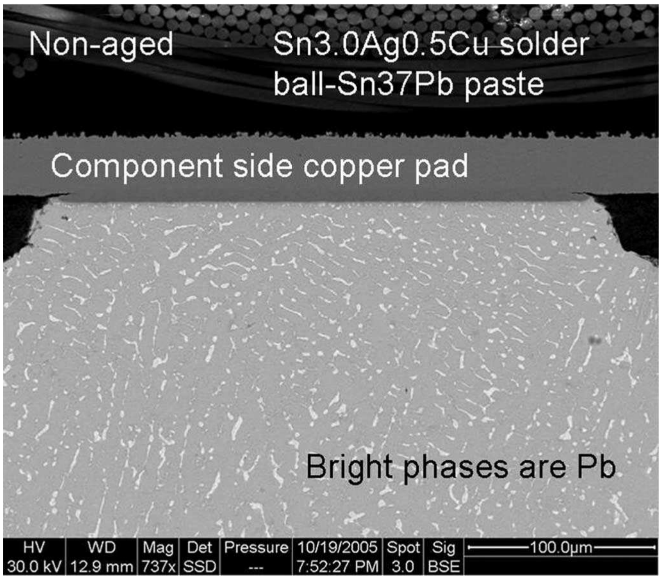


Fig. 2. Distribution of Pb phase in the mixed solder joint (nonaged).

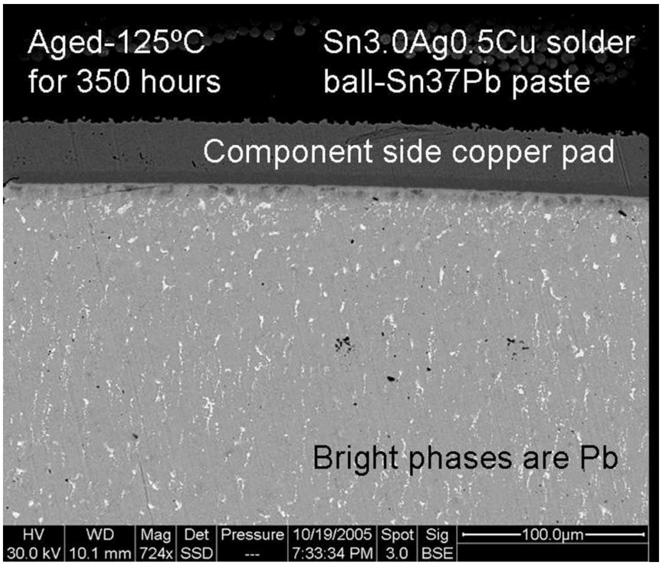


Fig. 3. Distribution of Pb phase in the mixed solder joint (aged at 125 °C for 350 h).

IV. IMC-THICKNESS ANALYSIS

The solder-joint assembly process involves the interaction of metallurgies from the component, the board, and the solder. IMCs are formed due to the interdiffusion of dissimilar materials, which are governed by thermally activated diffusion process. The initial formation of IMCs during soldering ensures a good metallurgical bond. However, the growth of these IMCs results in a brittle interface that can lead to failure under high stress loading such as shock and vibration [31].

To investigate the IMCs, samples were polished and then etched to enhance the contrast of elements under scanning electron microscope (SEM). Etching was conducted using a solution of 2% HCL (30% concentration), 5% HNO_3 (70% concentration), and ethanol. A 5-s etching time was used for each sample. IMC composition was analyzed both at the component

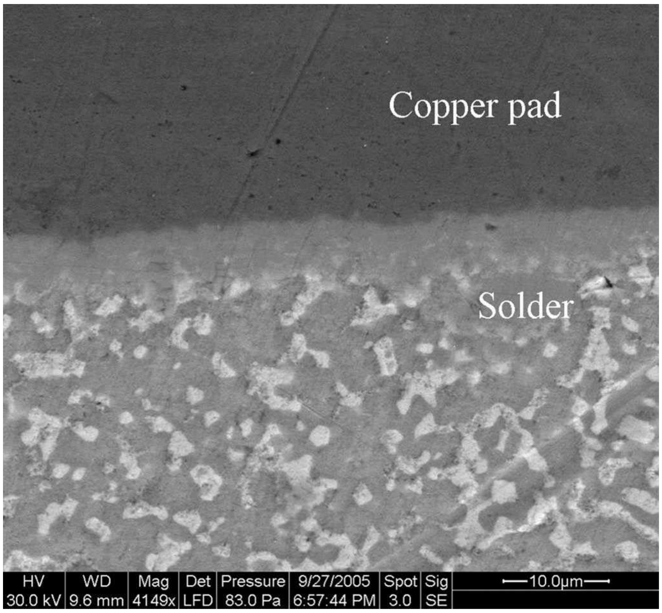


Fig. 4. Distribution of Pb phase in the SnPb solder joint (nonaged).

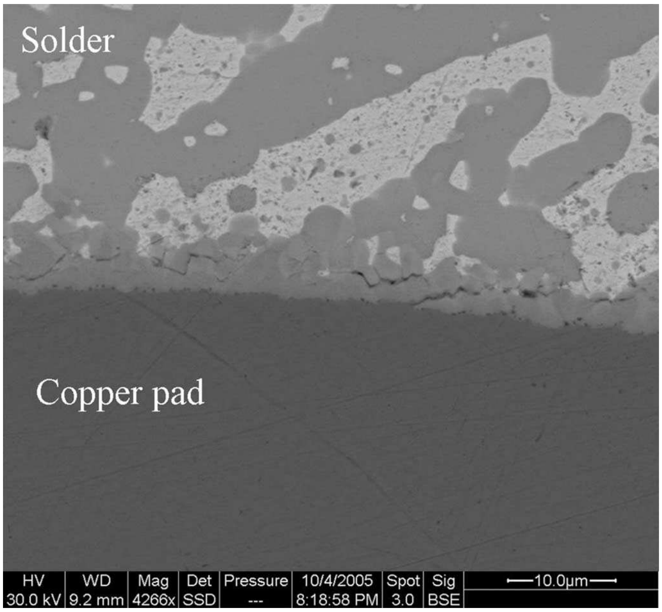


Fig. 5. Distribution of Pb phase in the SnPb solder joint (aged at 125 °C for 350 h).

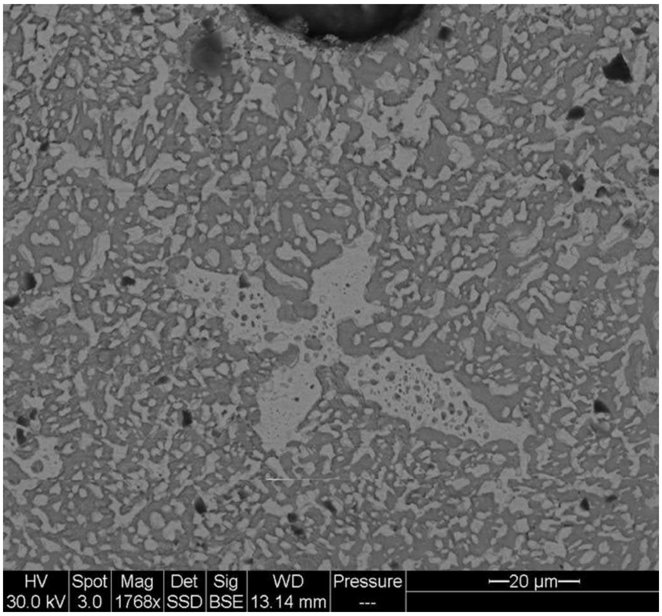


Fig. 6. SnPb solder joint—as reflowed.

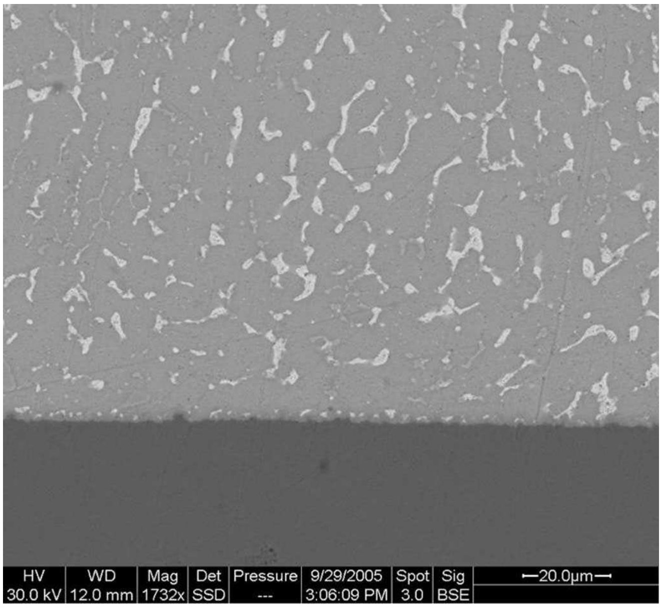
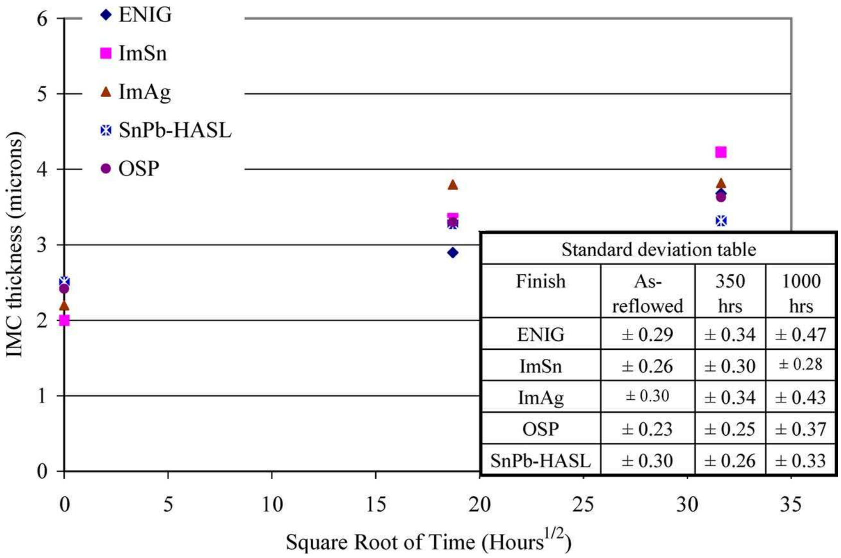


Fig. 7. Mixed (SnAgCu BGA assembled with SnPb paste) solder joint—as reflowed.

and board sides for the BGA component. Pictures of solder-joint cross sections were taken using an optical microscope with a polarized light to clearly demarcate the IMC layer. IMC-thickness measurements taken on optical images were verified using the SEM. Three solder joints per sample were analyzed, and three measurements per solder joint were taken.

Fig. 8 shows the IMC thickness for various pad finishes for the Sn3.0Ag0.5Cu and Sn37Pb solders. After 350 h of aging at 125 °C, an IMC-thickness range of 2.5–3.5 μm was observed for all pad finishes. After 1000 h of aging at 125 °C, the IMC thickness was approximately 3–3.5 μm for ImAg and ImSn, whereas it was 2.8 μm for ENIG. The lower IMC thickness in ENIG pad finish is due to the presence of the nickel layer on the copper pad, which acts as a barrier layer for the diffusion of copper and tin, restricting the formation of IMC. Comparing the IMC thickness for the SnPb and Pb-free solder joints with that of the mixed solder joints, it was found that the IMC thickness for mixed solder joints was 30%–40% lower (see Fig. 9).

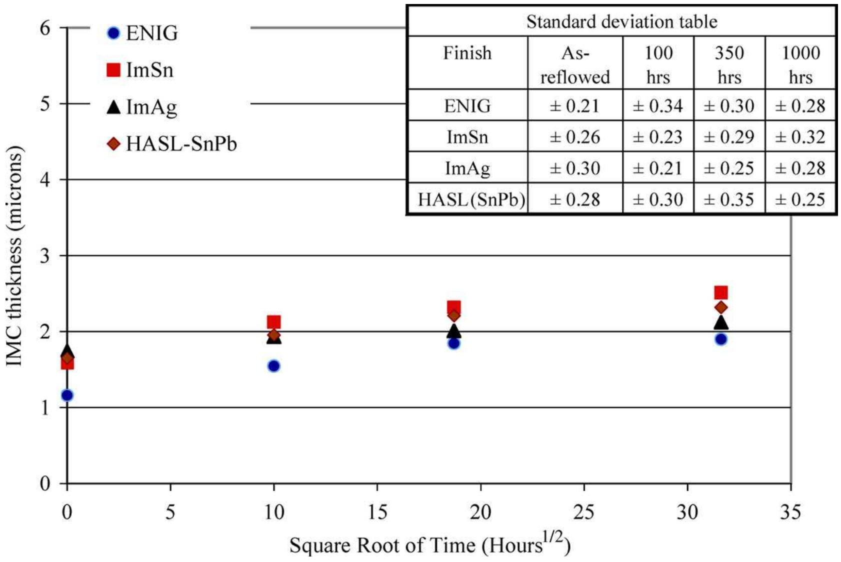
The lower growth of IMCs in the case of mixed solder joints is attributed to the segregation of Pb at the interface of the solder and the copper pad (see Figs. 10 and 11). The presence of Pb retards the formation of IMCs by influencing the diffusion of Sn and Cu at the interface. As it can be observed from the SnPbCu phase diagram, any dissolution of Cu into the solid solder brings the solder into the $\mathrm{Sn} + \mathrm{Pb} + \mathrm{Cu_6Sn_5}$ three-phase field. At the interface, Cu reacts with Sn to form $\mathrm{Cu_6Sn_5}$ IMC by consuming the Sn from the solder. Due to the slower diffusivity of Pb in the solid solder (the diffusivity of Pb in solder is about $10^{-8}\ \mathrm{cm^2/s}$,



Standard deviation table

Finish	As-reflowed	350 hrs	1000 hrs
ENIG	± 0.29	± 0.34	± 0.47
ImSn	± 0.26	± 0.30	± 0.28
ImAg	± 0.30	± 0.34	± 0.43
OSP	± 0.23	± 0.25	± 0.37
SnPb-HASL	± 0.30	± 0.26	± 0.33

Fig. 8. Intermetallic growth for the Pb-free and SnPb solder joints due to aging at 125 °C.



Standard deviation table

Finish	As-reflowed	100 hrs	350 hrs	1000 hrs
ENIG	± 0.21	± 0.34	± 0.30	± 0.28
ImSn	± 0.26	± 0.23	± 0.29	± 0.32
ImAg	± 0.30	± 0.21	± 0.25	± 0.28
HASL(SnPb)	± 0.28	± 0.30	± 0.35	± 0.25

Fig. 9. Intermetallic growth for the mixed solder joints (Sn3.0Ag0.5Cu solder balls attached with Sn37Pb solder) due to aging at 125 °C.

and for Cu, it is 10^{-6} cm^2/s), the depletion of Sn in the solder can lead to a higher concentration of Pb in the solder next to Cu_6Sn_5. This phenomenon leads to the deposition of a thin layer of Pb between the solder and the Cu_6Sn_5 IMC layer [29]. The deposition of Pb retards the diffusion between Sn and Cu. Segregation of Pb on the component side was also observed in this paper, with the presence of Ni. The Pb segregation at the interface with the presence of Ni in the pad finish has been previously reported [30] for the SnPb solders. The deposition of Pb, due to aging in the mixed solder joint (see Figs. 10 and 11), would restrict the IMC formation, whereas in the Pb-free solders, the IMC can be formed without any restriction of Pb.

The composition of IMC for the Pb-free and mixed solder joints was determined using energy dispersive X-ray facility in SEM. A list of IMCs found at the interface is listed in Table III. On the board side, for the mixed solder joints, the IMC layer was composed of Cu_6Sn_5 and Ag_3Sn IMCs (see Figs. 12 and 13).

V. DISCUSSION AND SUMMARY

The global transition to Pb-free electronics has raised concerns among manufacturers with the mixing of SnPb and Pb-free metallurgies, as well as the effect of complex microstructures on the reliability of solder joints. This paper examines two aspects that are related to mixed solder-joint microstructure: the Pb phase coarsening in bulk solder and the IMC formed at the interface of solder–copper pad finish.

The assessment of isothermal aging indicated a negligible coarsening of Pb in the mixed solder joints. The lack of coarsening in the mixed solder is attributed to a larger average distance between the Pb-rich particles compared with the SnPb solder joint. Larger average distance between the Pb-rich particles will require longer time for the diffusion process, thus influencing the amount of coarsening that is observed after 350 h at 125 °C.

Thermal cycling fatigue failures occur in the region of high stress concentration in the bulk solder. The presence of Pb

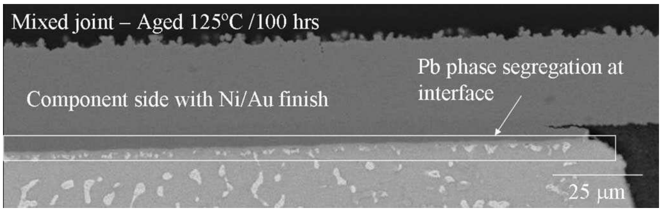


Fig. 10. Segregation of Pb at the component side for the mixed solder joint (Pb_free solder balls–SnPb solder paste).

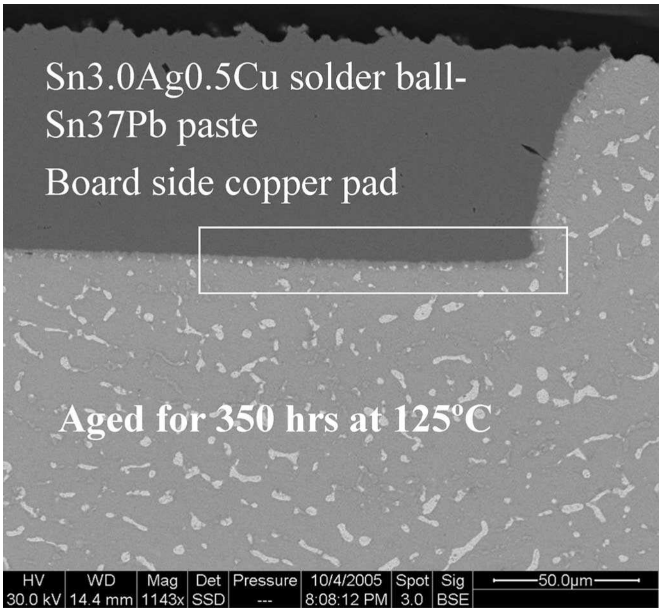


Fig. 11. Segregation of Pb at the board side for the mixed solder joint (Pb_free solder balls–SnPb solder paste).

TABLE III
TYPE OF IMCS FOR SEVERAL PAD FINISHES

Finish	Type of IMC
ENIG	$(Cu,Ni)_6Sn_5$, $(Ni,Cu)_3Sn_5$, $(Au,Ni)Sn_4$
ImSn	Cu_6Sn_5, Cu_3Sn
ImAg	Cu_6Sn_5, Cu_3Sn, Ag_3Sn
OSP	Cu_6Sn_5, Cu_3Sn

in the solder causes a reduction in thermal cycling durability due to coarsening [9], [10], [26]–[28]. Due to the coarsening behavior of Pb, the SnPb solder joints are less durable than the Pb-free solder joints which are subject to thermal fatigue loading. Mixed solder joints are more resistant to the coarsening phenomena and, hence, result in joints with a better thermal fatigue resistance compared with the eutectic SnPb joints. Thermal fatigue performance of the mixed solder joints has been reported to be better than the SnPb and comparable to the Pb-free in several studies [8], [18], [32].

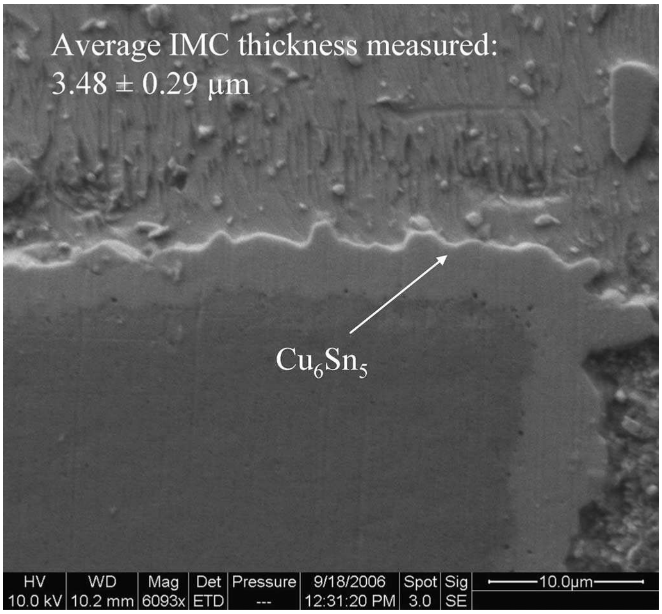


Fig. 12. Sn3.0Ag0.5Cu solder joint on ImSn pad finish (aged at 125 °C for 350 h) showing higher IMC thickness than the mixed solder joint (see Fig. 13).

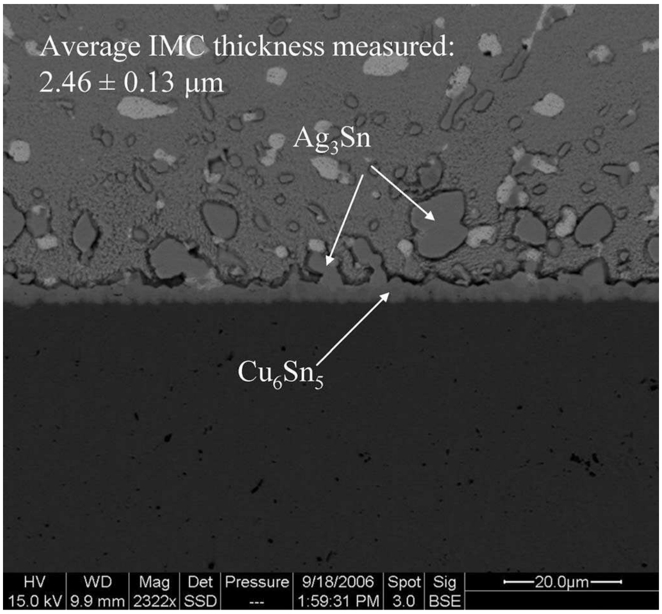


Fig. 13. Mixed solder joint on ImSn pad finish (aged at 125 °C for 350 h) showing lower IMC thickness than the Pb_free joint (see Fig. 12).

The assessment on interfacial intermetallics shows that the mixed solder joints result in 30%–40% lower IMC thickness than the SnPb and the Pb-free. Lower IMC thickness in mixed solder joint is attributed to the presence of a Pb-rich layer found at the interface between the solder and the copper pad, which, in turn, retards the growth of intermetallics in the mixed solder joints. The presence of Pb-rich interface acts as a diffusion barrier between the base metal copper and solder.

Failures in high mechanical loading environments, such as vibration and shock, often occur at interfacial intermetallic layers. Liu *et al.* [31] have reported that under drop tests, failures occur in the IMC layer and that reliability in a drop decreases with the increase in IMC thickness. In this paper, because the thickness of intermetallics layer for the mixed solder joints is smaller than the SnPb and the Pb-free, the mixed solder joints are expected to perform better under vibration and shock conditions.

For the Pb-free BGA components assembled with Pb-based solder, the thermal fatigue reliability has been reported to be equivalent to completely Pb-free assemblies, provided that the Pb is distributed evenly throughout the solder joint. However, significantly, earlier failures can occur if the Pb is not distributed. From a microstructural perspective, changes occurring in the mixed solder joints, such as negligible coarsening of Pb after 350 h of isothermal aging at 125 °C compared with the SnPb and lower IMC thickness compared with the SnPb and the Pb-free, must be accounted for when predicting the reliability of mixed solder joints.

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