Microstructures Variations of Sn-9Zn-1Al and Sn-8Zn-3Bi Solder Pastes with Sn-3.8Ag-0.7Cu Solder Balls on OSP PCBs after Thermal Cycling Test

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Using an organic solderability preservative (OSP), the morphology and microstructure of Sn-9Zn-1Al (SZA) and Sn-8Zn-3Bi (SZB) lead-free solder pastes used to assemble BGA packages with Sn-3.8Ag-0.7Cu (SAC) solder balls on a printed circuit board (PCB) were investigated. The scallop-shaped (Cu,Ag)₅Zn₈ intermetallic compound (IMC) is formed in both SZA and SZB solder joints, and the belt-shaped (Cu,Ag)₅Zn₈ IMC is also formed at the interfaces of both SZA/Cu and SZB/Cu. At 125°C, the Zn atoms in the IMC layer have sufficient energy to diffuse towards the Cu pad and react with it. The IMC belt composed of island-shaped compounds formed in the SZA and SZB solder joints and the size of island-shaped compounds and amount of microvoids increased after 1,000 times thermal cycling.
[\[doi:10.2320/matertrans.M2012136\]](https://doi.org/10.2320/matertrans.M2012136)

(Received April 10, 2012; Accepted December 13, 2012; Published February 25, 2013)

Keywords: lead-free solder, microstructure, thermal cycling test

1. Introduction

Eutectic Sn-37Pb solder has been used as a standard material for the joints of electronic components because of its suitable physical properties and low cost. Due to the toxicity of Pb, various kinds of lead-free solder, such as Sn-3.5Ag,¹⁾ Sn-9Zn²⁾ and Sn-3.5Ag-0.9Cu,³⁾ have been developed to substitute for Sn-37Pb solder alloy. However, problems arising from the use of lead-free solders, such as the high melting point of Sn-3.5Ag and Sn-3.5Ag-0.9Cu, oxidation of Sn-9Zn, and Kirkendall voids formation at the solder joints, must be resolved before these alloys can be implemented.

Zinc (Zn) is a relatively low-priced metal, which means that the Sn-Zn solder alloys have the advantage of being more cost-efficient.⁴⁾ However, Zn shows the properties of insufficient oxidation resistance and inferior wettability on Cu, which is detrimental to consistent solder joint formations.⁵⁾ In order to address the weakness of the solder joint, aluminum (Al)⁶⁻⁸⁾ or silver (Ag)⁹⁻¹¹⁾ metal was added into the Sn-9Zn binary alloy. Addition of Bi to the Sn-Zn solder alloys increased the solder joint's strength due to the precipitation of the Zn rich phase, which also decreased the melting point of the solder alloy from 198.4 to 186.1°C.¹²⁾ Although the addition of Al or Bi effectively increased the mechanical properties, wettability and oxidation resistance of the Sn-Zn solder alloy system, it still exhibits insufficient reliability.^{8,12,13)} The interfacial reaction between the solder and the substrate formed the intermetallic compounds (IMCs), which caused the brittle behaviors of the solder joint, and the dissimilar coefficients of thermal expansion of

the solder joint degraded the interface integrity between the substrate and solder.^{14,15)} The interactions between Sn-Zn solders and the copper (Cu) pads on the substrates and their influences on the solder joint strengths must be understood before being applied to a manufacturing process. Two commercial Pb-free solder pastes of Sn-8Zn-3Bi (SZB) and Sn-9Zn-1Al (SZA) have been used to assemble 0603 passive components on a printed circuit board (PCB) finished using an organic solderability preservative (OSP)¹⁶⁾ and electroless nickel immersed gold (ENIG, Au/Ni(P)) for short pads.¹⁷⁾ However, the effect of thermal cycling test on the morphology and microstructure of the SZA and SZB lead-free solder joints on OSP PCBs have not been reported.

In the present study, the morphologies and microstructure of SZA and SZB solder joints on OSP PCBs after thermal cycling test have been investigated. After thermal cycling test, the assembled boards were characterized by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The mechanism of the formation of IMC and microvoids were also discussed in detail.

2. Experimental Procedure

The test vehicles were assembled using a standard surface mount technology (SMT) process. The Sn-9Zn-1Al (SZA) (Type 3, no-clean flux, Marubeni, Japan) and Sn-8Zn-3Bi (SZB) (Type 3, no-clean flux, Nihon Genma, Japan) lead-free pastes were individually deposited on an OSP PCB using a stencil printing process. The stencil thickness was 0.12 mm and the Cu pad size was 670 µm. Ball Grid Array (BGA) packages with Sn-3.8Ag-0.7Cu (SAC) solder balls were placed on the solder pastes deposited OSP PCB. The soldering process was conducted in a reflow oven (Hot

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Fig. 1 The schematic diagram of the BGA225 with Sn-3.8Ag-0.7Cu (SAC) solder ball and Sn-9Zn-1Al (SZA) or Sn-8Zn-3Bi (SZB) solder pastes on an OSP PCB.

flow7, ERS, Germany) with residual oxygen content of less than 500 ppm. The schematic diagram of the reflow profile was shown in the previous paper.¹⁶⁾ In order to maintain structural integrity of the components, the peak temperature of the reflow profile was set at 240°C. The melting time and cooling time in the reflow process were 60 and 40 s. The schematic diagram of the BGA 225 with SAC solder ball and SZA or SZB solder alloys on an OSP PCB is shown in Fig. 1.

After assembly, the test vehicle was under thermal cycling test for 1,000 times. In the thermal cycling test the soldered samples were heated from 20 to 125°C at a heating rate of 15°C/min and held at 125°C for 1 min, then the samples were chilled in a refrigerator at -55°C at a cooling rate 15°C/min and held for 1 min, subsequently heating to 20°C. This procedure was defined as one cycle.

The solder joint was mounted in room-temperature cured epoxy before and after thermal cycling testing, cross-sectioned with a precision diamond saw, polished with 1 μm Al₂O₃ powder paste, and etched by 5% diluted hydrochloric acid. The microstructure was observed using a scanning electron microscope (SEM, JEOL, 6700, Japan) and energy dispersive spectrometer (EDS, Oxford, England).

3. Results and Discussion

Figure 2(a) shows SEM micrographs of the cross-sectional of SZA solder joint of both interface between the SAC solder ball/SZA solder joint reflowed at 240°C. The two solders melted together and showed no visible interfacial boundary. Voids formed in the solders and at interface between the solder and the Cu pad. That was attributed to the melting and interaction of the SAC solder ball and SZA solder alloy during 240°C reflowing due to partially vaporized residual soldering flux in the interior of solder. The volume ratio of the voids is low (<10%), which is considered within the acceptable range. Figure 2(a) also shows the belt-shaped intermetallic compound (IMC) structure in the interior of the solder. It is found that island-shaped IMCs strung together and formed the IMCs belt, as shown in Fig. 2(b). Small white granular particles, as the circled area in Fig. 2(b), locally precipitated in the solder alloy. Figure 2(c) shows the interface morphology between the solder alloy and the Cu pad; a layer of belt-shaped IMC with thickness of 1–2 μm also formed at interface between the solder alloy

and the Cu pad. The enlarged morphology view of the IMCs is shown in Fig. 2(d); the growth direction of scallop-shaped IMC is from the solder alloy toward the Cu pad. This finding differed from the results obtained by the previous investigators,^{18,19)} who indicated that IMC grew toward the solder alloy at the contact of the SAC solder ball and the Cu pad. Micro-voids were found in the island-shaped IMC and IMC belt.

Figure 2(e) shows the EDS analysis results of the belt-shaped IMC, it indicates that the IMC is a Cu-Ag-Zn compound with an atomic ratio of Cu:Ag:Zn = 28:5:63. In the SZB-Ag joint, 2–3 mol% Ag was dissolved into the reaction layer;²⁰⁾ the IMC layer corresponded to be the (Cu,Ag)₅Zn₈ phase.^{20,21)} The EDS analysis results for the IMC layer between the solder alloy and the Cu pad showed ~10 at% Sn, which was caused by Sn diffusing from the solder alloy to the Cu pad which then dissolved into the IMC layer. The scallop-shaped phase was also a Cu-Ag-Zn compound with composition of Cu:Ag:Zn = 27:9:64, which was compatible with the composition of (Cu,Ag)₅Zn₈ phase. In the present study, Cu₆Sn₅ was not found from the solder or interface, this was attributed to the Ag dissolved into the Cu₅Zn₈, which extended the solubility limit of Sn in the IMC and retarded the Cu₆Sn₅ formation at the interface of solder alloy and the Cu pad.²⁰⁾ The size of the white granular particles in Figs. 2(b) and 2(c) were less than 1 μm thus making it difficult to analyze their compositions quantitatively by EDS. A quantitative EDS analysis indicated that the white granular particles area was composed of the Ag-Sn rich phases.

Figure 3 shows the SEM micrographs of BGA 225 with SZB solder joint and SAC solder ball on an OSP PCB. The belt-shaped IMC and microvoids also existed in the SAC solder ball, as shown in Fig. 3(a), IMCs and voids sizes were less than those shown in Fig. 2(a). Figure 3(b) illustrates the enlarged view of the belt-shaped IMC in Fig. 3(a), the belt-shaped IMC was also constructed by continuous island-shaped IMC with microvoids. It implied that the island-shaped IMC and the microvoids in the IMC of BGA225 with SZB solder joint and SAC solder ball on an OSP PCB were smaller than those in the IMC of SAC solder ball/SZA solder joint, and the BGA substrate and the Cu pad. That was due to Bi addition to the Sn-8Zn solder alloy which decreased the melting temperature of the alloy and made the trapped voids decreased. Figure 3(c) indicates the morphology of the interface between SZB solder alloy and the Cu pad, and reveals similar microstructure to that shown in Fig. 2(c). Figure 3(d) shows the enlarged view of the contact interface of the SZB solder alloy and the Cu pad, in which the size and amount of the island-shaped IMC and microvoids are smaller than those indicated in Fig. 2(d).

The EDS analysis results for the island-shaped IMC illustrated in Fig. 2(d) (denoted by an arrow) was a Cu-Ag-Zn compound with a composition of 27 at% Cu, 62 at% Ag and 7 at% Zn. It was consistent with the composition of (Cu,Ag)₅Zn₈ phase. The compositions of island-shaped IMC in the solder alloy and in the IMC layer between the solder alloy and the Cu pad in Fig. 3(d) were similar to those of the island-shaped IMC shown in Fig. 2(d), which also corresponded to the phase of (Cu,Ag)₅Zn₈.

Fig. 2 SEM micrographs of both interface between SAC solder ball/SZA solder joints, and the BGA substrate and the Cu pad: (a) the cross-sectional view of solder joint, (b) the enlarged view of the IMC belt in (a), (c) the contact point morphology of solder joint and the Cu pad, (d) the enlarged view morphology of IMC layer in (c), and (e) the EDS analysis of IMC belt.

Figure 4 shows the SEM micrographs of the contact interface of the SAC solder ball with the SZA solder alloy on an OSP PCB after 1,000 times thermal cycling test. After 1,000 times thermal cycling test, the volume ratio of IMC belt constructed by the island-shaped compounds increased. This was due to the stress induced in the solder joint after thermal cycling test, which can be mainly attributed to the thermal expansion coefficient mismatch of the different materials in a joint. As the reaction volume between the SZA solder alloy and the Cu pad increased, the IMC also increased resulting in the stress relaxation.²⁴⁾ Figure 4(b) indicates the morphology of the IMC belt of SZA solder alloy after 1,000 times thermal cycling test; the volume and number of microvoids in the island-shaped IMC increased. The thickness of the IMC layer between the solder alloy and the Cu pad also increased from 1–2 to 2–3 μm. After 1,000 times thermal cycling test, the size of (Cu,Ag)₅Zn₈ IMC increased and more microvoids formed in the IMC. Figure 4(b) reveals

that the precipitation of small white particles of Sn–Ag rich phase increased after 1,000 times thermal cycling test as shown in Fig. 2(c). The EDS analysis indicated the chemical composition of the IMC remained the same as that before thermal cycling test.

Figure 5(a) shows the morphology of the contact interface of the SZB solder alloy with the SAC solder ball and the Cu pad after thermal cycling 1,000 times. The island-shaped IMCs of the sample were smaller than those formed in the SAC solder ball with SZA solder joint on an OSP PCB. Addition of Bi to the Sn–8Zn solder alloy (SZB) decreased the melting temperature and reduced the voids trapped in the solder joint. Thickness of the IMC layer formed at the interface of the solder alloy and the Cu pad grew to 2–3 μm, with some microvoids in the IMC layer after 1,000 times thermal cycling test, as shown in Fig. 5(b). The chemical compositions of IMCs after thermal cycling were consistent with the IMCs in the samples before thermal cycling.

Fig. 3 SEM micrographs of BGA225 with SZB solder joint and SAC solder ball on an OSP PCB: (a) the cross-sectional view of SAC solder ball and SZB solder joint, (b) the enlarged view of IMC belt in (a), (c) the morphology of contact point of SZB solder joint with the Cu pad, and (d) the enlarged view of contact point of SZB solder joint with the Cu pad.

Fig. 4 SEM micrographs of the contact point of SAC solder ball with SZA solder joint on an OSP PCB after thermal cycling 1,000 times: (a) the morphology of the cross-sectional of the SZA solder joint and the Cu pad and (b) the morphology of IMC belt of SZA solder joint after thermal cycling 1,000 times.

Fig. 5 SEM micrographs of the contact point of the SAC solder ball with SZB solder joint on an OSP PCB after thermal cycling 1,000 times: (a) the morphology of the cross-sectional of the SZB solder joint and the Cu pad, and (b) the morphology of the IMC belt of the SZB solder joint after thermal cycling 1,000 times.

Figures 4 and 5 indicate that after 1,000 times thermal cycling test, the thickness of the IMC layer increased, it formed toward the Cu pad and the continuous microvoids formed in the IMC layer as shown in Fig. 3(a). During thermal cycling test, Al, Zn-rich area was formed and adjacent to the Cu pad owing to the atomic diffusion followed the heat flow, its higher Al–Zn content resulted in the size of $(\text{Cu},\text{Ag})_5\text{Zn}_8$ increased. Microvoids formed in the SZA solder joint was due to Zn is consuming and forming of the $(\text{Cu},\text{Ag})_5\text{Zn}_8$ phase with Cu and Ag.^{2,9)} The Zn atoms in the IMC layer had sufficient energy to diffuse toward the Cu pad and react with it; this diffusion created the microvoids in the Cu–Zn–Sn layer. After 1,000 times thermal cycling test, the size of $(\text{Cu},\text{Ag})_5\text{Zn}_8$ increased and the structure became more loosely arranged; this created microvoids in the interior. The Al and Zn diffused faster than Cu and the Zn atoms, which had sufficient energy to diffuse toward the Cu pad and react with it. The free energies of the Cu_5Zn_8 and Cu_6Sn_5 formation at 150°C are -12.10 and -6.26 kJ/mole, respectively. This indicates that the Cu_5Zn_8 is more stable than Cu_6Sn_5 ,²⁵⁾ which explains the formation of $(\text{Cu},\text{Ag})_5\text{Zn}_8$ IMC in SZA solder joint. Different diffusion rate of elements made Kirkendall voids form in the IMC phase.

4. Conclusions

The morphology and microstructure of the Sn–9Zn–1Al (SZA) and Sn–8Zn–3Bi (SZB) lead-free solder joints on OSP printed circuit boards after thermal cycling test have been studied using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The Sn–3.8Ag–0.7Cu (SAC) solder ball with SZA and SZB solder pastes were reflowed at 240°C. The $(\text{Cu},\text{Ag})_5\text{Zn}_8$ belt-shaped intermetallic compound (IMC) is formed in SZA and SZB solder joint, and scallop-shaped $(\text{Cu},\text{Ag})_5\text{Zn}_8$ IMC is also formed at the interface in SZA and SZB solder joints. In addition, the white granular particles of the Ag–Sn rich phase were precipitated in the SZA and SZB solder joints. Microvoids formed in the interior of island-shaped IMC. After 1,000 times thermal cycling test, the IMC belt composed of the island-shaped IMC remained in the solder joint. The size of the island-shaped IMC and the amount of microvoids in the interior of island-shaped IMC increased after thermal cycling test for SAC solder ball with both SZA and SZB solder joints; the thickness of the IMC layer also increased.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan for financial support under contract NSC 101-2221-E-239-009-MY2.

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