Reduced temperature soldering of capacitors using Sn-Bi plated Sn-3.5%Ag

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Abstract

Purpose – This paper seeks to decrease the soldering temperature of capacitors using Sn-Bi plated Sn-3.5 wt%Ag solder.

Design/methodology/approach – Sn-Bi layers were electroplated on Sn-3.5 wt%Ag solder. As soldering examples, type 1608 capacitors electroplated with Sn, and printed circuit boards (PCBs) with a surface coating of electroless-plated Ni/Au, were selected. Sn-3.5Ag foil coupons plated with Sn-95.7 wt%Bi were inserted as solder between the capacitors and the lands on the PCBs. The samples were reflowed at 220°C, which is below the normal reflow temperatures of around 240 ~ 250°C used with Pb-free solders. During heating, Bi in the plated layer diffuses into the Sn-3.5Ag core solder resulting in a transient decrease in soldering temperature based on the concept of transient liquid phase bonding.

Findings – The joints made with the Sn-95.7%Bi plated Sn-3.5Ag solder at 220°C showed good appearance, and evidence of significant Bi segregation was absent in the microstructure. The shear strengths of the capacitor joints bonded with Sn-95.7%Bi plated Sn-3.5Ag solder were approximately 5,000-6,000 gf. After 1,000 thermal cycles between −40 and +125°C, the shear strengths of the joints decreased approximately 5-10 percent from the strengths in the as-reflowed state for all plated solders. This confirmed that the soldered joints were stable and not significantly degraded by thermal cycles.

Originality/value – Reduced temperature soldering using Sn-Bi plated Sn-3.5%Ag solder was applied to attach capacitors to PCBs. In a production application, the foil coupons could be replaced by pre-solder on the PCB pads.

Keywords Solder, Bonding, Soldering, Reliability management

Paper type Research paper

1. Introduction

Applications of lead-free solders are increasing in electronics assembly and packaging due to environmental concerns. Sn-Ag-Cu-based solders are especially popular for the replacement of conventional Sn-37 wt%Pb (hereafter, Sn-37%Pb) alloy. Considerable research data have been accumulated on the Sn-Ag-Cu solders, and they are believed to be highly reliable. However, these Sn-Ag-Cu solders have relatively high-melting points, typically around 217-220°C, and this shortcoming can cause thermal damage to electronic parts and printed circuit boards (PCB) during soldering (Harrison *et al.*, 2001).

Meanwhile, Sn-3.5 wt%Ag (hereafter, Sn-3.5%Ag) solder has also been used as a reliable lead-free solder for a long time. The Sn-3.5%Ag alloy has a microstructure strengthened by stable Ag_3Sn and provides good mechanical and thermal properties. Since, the Sn-3.5%Ag has a higher melting temperature of 221°C and good wettability on Cu (Chang *et al.*, 2003), it has been used for automotive electronics and computer motherboards.

In order to decrease the soldering temperature of Sn-3.5%Ag foil, a Sn-Bi layer was electroplated on it in this study. Bi is well known as a melting point depressant for Sn-based solder: the melting point of the Sn-Bi eutectic is at 138.5°C. Several studies of soldering using the concept of transient liquid phase (TLP) have been reported (Lugscheider *et al.*, 2003; Corbin, 2005). In the author's previous study, Sn-Bi was plated on Sn-3.5%Ag solder balls (Lee *et al.*, 2004). During the bonding process, the plated layer melted at lower temperature than that of the core metal, and the melting point depressant in the plated layer then diffused into the core metal according to the TLP concept (Tuah-Poku *et al.*, 1988).

In the present work, Bi was expected to diffuse into the core solder of Sn-3.5%Ag during reflow along the gradient of Bi concentration, which would decrease the soldering temperature. In this study, the Sn-Bi plated Sn-3.5%Ag solder foil coupons have been used to carry out low-temperature soldering of capacitors to PCBs. In a production application, the foil coupons could be replaced by pre-solder on the PCB pads.

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2. Experimental

Sn-3.5%Ag bulk solder was rolled into a sheet of 100 μm thickness, and was cleaned with acetone and 10%HCl solution. The rolled solder (core solder) was then electroplated with Sn-Bi solder. The cathode was Sn-3.5%Ag sheet, and the anode was Sn plate in order to compensate for consumption of Sn^{2+} ions as SnO_2 in the electrolyte.

During electroplating, to get a uniform distribution of Sn^{2+} and Bi^{3+} ions, the electrolyte was stirred with a magnetic stirrer at the rate of 250 rpm (revolutions per minute). The bath temperature was kept at 43°C to avoid deterioration of the electrolyte, and distance between electrodes was set at 30 mm. Electroplating conditions of Sn-Bi on the Sn-3.5%Ag sheet are summarized in Table I.

Since, the composition of the Sn-Bi layer depends upon current density (Lee *et al.*, 2004), experiments were done with current densities of 2 and 4 A/dm^2. Compositions of the electroplated layers were analyzed by electron probe micro analysis (EPMA). The electroplating time affects the thickness of the Sn-Bi layer, and the time was varied in the range from 1 to 10 min. The Sn-Bi plated Sn-3.5%Ag sheets were cut into 0.9 × 0.7 mm coupons which were used as preformed solder coupons to join capacitors to the PCB substrate.

As reference values for comparison, commercial solder pastes of Sn-37%Pb, Sn-3.0 wt%Ag-0.5 wt%Cu (hereafter, Sn-3.0%Ag-0.5%Cu), and Sn-8 wt%Zn-3 wt%Bi (hereafter, Sn-8%Zn-3%Bi) were selected, and for printing of these pastes, a stencil with thickness of 150 μm and hole size of 0.9 × 0.7 mm was prepared.

The electroplated Sn-3.5%Ag solder coupons were coated with RMA-flux and inserted between type 1608 capacitors and a substrate as shown in Figure 1. The substrate was an FR-4 PCB material with contact pads composed of Cu/Ni/Au from bottom to top with the size of 0.9 × 0.7 mm. The capacitor size was 1.6 × 0.8 × 0.8 mm, and its contacts comprised Ni plated with Sn.

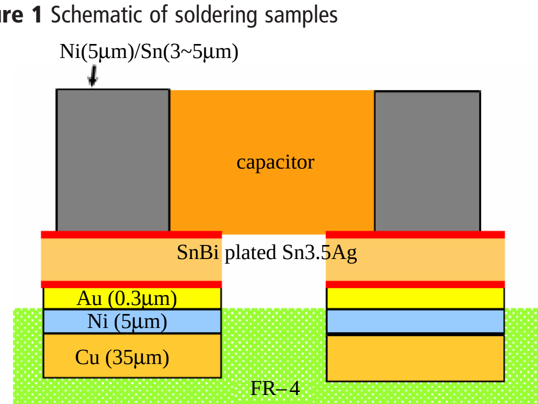
The capacitors on the substrate were soldered using an infrared reflow machine. The preheating temperature for the Sn-Bi plated Sn-3.5%Ag solder was from 130 to 160°C with heating rate of 0.3/s. After preheating, the temperature was increased with 0.5/s, and the peak temperature reached 220°C. The reflow temperature on the surface of the FR-4 substrate was measured by a K-type thermocouple. For the other commercial solders, the peak temperature was 220°C for Sn-37%Pb and Sn-8%Zn-3%Bi, and 250°C for Sn-3.0%Ag-0.5%Cu.

Shear strength and thermal cycle tests were performed to estimate the reliability of the solder joints. The thermal cycle testing employed a temperature range of between -40 and +125°C (Figure 2), and the number of cycles was up to 1,000. After thermal cycling, the samples were shear-tested at ambient temperature. Shearing speed of the shear tip was 200 μm/s, and the gap between the tip and the substrate was 10 μm. The samples were cross sectioned for metallurgical analysis by scanning electron microscopy (SEM), energy dispersive spectroscopy and EPMA.

Table I Conditions for electroplating of Sn-Bi on Sn-3.5%Ag sheet

Electrolyte	Methane sulfonate acid, Bi^{+3}, Sn^{+2} methane sulfonate solution
Anode	Pure Sn plate
Cathode	Sn-3.5%Ag sheet
Stirring rate	250 rpm
Bath temperature	43°C
Distance between electrodes	30 mm

Figure 1 Schematic of soldering samples



3. Results and discussion

3.1 Electroplating and polarization curve

In order to investigate the electroplating behavior of Sn and Bi, polarization curves of these elements were prepared (Figure 3). From the polarization curves of Sn and Bi, Bi^{3+} is preferentially electroplated at lower current densities below approximately 17 A/dm^2, and Sn^{4+} plating rate increases at higher current density. For this study, a Bi-rich layer was required to reduce the soldering temperature of the Sn-3.5Ag alloy. By means of pre-experiments, 2 and 4 A/dm^2 were selected to give a suitable Bi-rich layer. The compositions of the electroplated layers were confirmed to be 4.3 wt%Sn-95.7 wt%Bi and 19.7 wt%Sn-80.3 wt%Bi for 2 and 4 A/dm^2, respectively.

The thickness of the Sn-Bi electroplated layer is regarded as another important factor to determine the final composition of the solder joint. As determined by Faraday's law (Tan, 1993), the thickness of the electroplated layer

Figure 2 Temperature-time profile for thermal cycle test

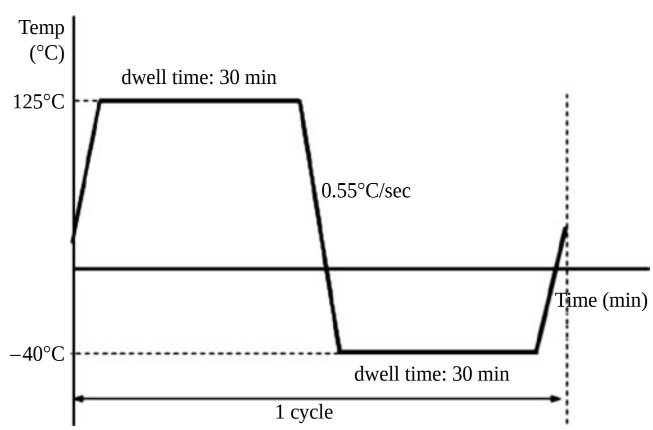
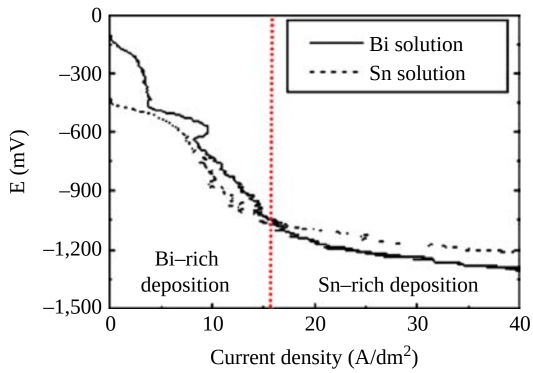


Figure 3 Polarization curve of Sn and Bi deposition on Cu plate with current density

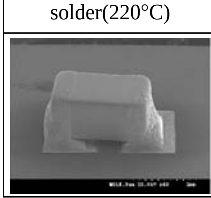
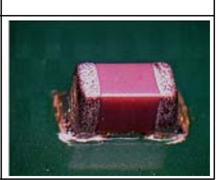


increases with plating time. Results in this study confirmed that the thickness of the electroplated layer of Sn-Bi at 2 mA/dm^2 increased with time, i.e. 1.3, 3.3, 6.9 μm for 1, 5, and 10 min, respectively. The plated Sn-Bi alloy had a needle shape and was relatively weakly bonded to the core solder.

3.2 Reduced temperature soldering and microstructures

The type 1608 capacitors were reflowed at 220°C on the FR-4 PCBs with the Sn-3.5%Ag solder electroplated with Sn-Bi alloy at 2 A/dm^2 for 2 min. Appearances of the soldered capacitors are shown in Figure 4, and results from Sn-37%Pb and Sn-3.0%Ag-0.5%Cu pastes are also illustrated for comparison. The Sn-37%Pb sample was bonded at 220°C, and Sn-3.0%Ag-0.5%Cu at 250°C. The appearance of the 1608 capacitor joints with Sn-Bi plated Sn-3.5%Ag solder did not show any significant problem at 220°C. However, the fillet shape of the Sn-Bi plated solder joint became a little convex compared to the Sn-37%Pb and Sn-3.0%Ag-0.5%Cu. The reason was determined to be different amounts of solder between foil and paste applications. In effect, in the case of the electroplated solder, the entire coupon was metal. On the other hand, in the case of Sn-37%Pb and Sn-3.0%Ag-0.5%Cu pastes, since the pastes were mixtures of metal powder and organics, they contained only 50%metal. Thus, the quantity of electroplated solder alloy was approximately 15 percent larger than that of the solder pastes calculated from the hole size in the stencil. This larger amount of the electroplated solder resulted in the relatively convex shape of the fillet.

Figure 4 Appearances of capacitor solder joints with different solders

Solder		
Sn–95.7Bi plated Sn–3.5Ag solder(220°C)	Sn–37Pb (220°C)	Sn–3Ag–0.5Cu (250°C)
		

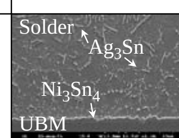
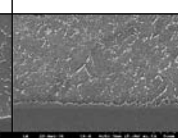
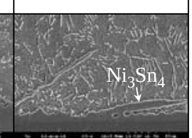
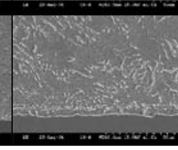
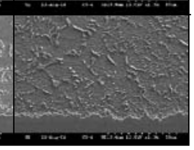
Microstructures and bonded interfaces between the plated solder and the substrate of Au/Ni UBM were examined after reflow at a temperature of 220°C. As shown in Figure 5, the microstructure of the plated solder after reflow consisted of Sn matrix and Ag_3Sn phases with round and rod shapes. In the bonded interface between the solder and Ni/Au pads, Ni_3Sn_4, a typical intermetallic formed on a Ni pad (Shiau *et al.*, 2002), was observed. Thus, the microstructure composed of Sn matrix, Ag_3Sn and Ni_3Sn_4 is similar to that of the core solder, and significant new phases or other effects of the Sn-Bi layer were not found.

Microstructures around the interface between the plated solder and the contacts on the 1608 capacitors are shown in Figure 6. The structure comprised a Sn matrix and Ag_3Sn, which were found to be similar to those of Figure 5.

In some Sn-Bi alloys, nearly pure (99.9 wt%) Bi precipitates exist in Sn because Sn is almost insoluble in Bi (Massalski, 1986). Shin and Yu confirmed the observation of Bi particles by XRD in alloys of compositions, Sn-3.5 wt%Ag-7.5 wt%Bi and Sn-3.5 wt%Ag-10.0 wt%Bi (Shin and Yu, 2003). According to Kariya and Otsuka (1998), in the case of 5 and 10 wt%Bi, the addition of Bi into Sn-3.5%Ag resulted in the crystallization of fine Bi. Especially, in 10 wt%Bi alloy, fine Bi particles formed a network around β-Sn. The precipitated Bi particles caused brittleness which deteriorated reliability factors such as ductility, thermal fatigue, creep and aging properties (Yoshiharu and Masahisa, 1998; Yoshiharu *et al.*, 1999).

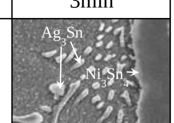
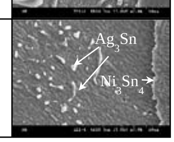
Because of the importance of the Bi particle effects on solder properties, more detailed analysis of elemental Bi was

Figure 5 Microstructures and interfaces between the Au/Ni UBM and the Sn-Bi plated Sn-3.5%Ag solder

Plating Condi.	Plating time		
	1min	2min	3min
2A/dm^2			
4A/dm^2			

Note: Soldering temperature; 220°C

Figure 6 Microstructures and interfaces between the contact of 1608 capacitor (right side) and the Sn-Bi plated Sn-3.5%Ag solder (left side)

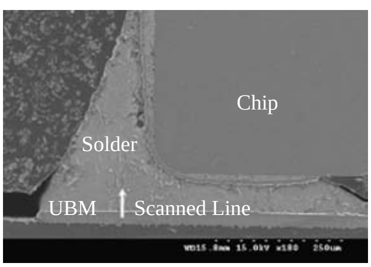
Current density	Plating time 3min
2A/dm^2	
4A/dm^2	

carried out for the Sn-Bi plated Sn-3.5%Ag joints. In Figure 7, Bi distribution with reflow time was analyzed by line scanning using an EPMA. At 40 s a Bi peak was observed at the Sn-Bi layer; the peak was decreased at 60 s due to Bi diffusion into the core solder along the gradient of Bi concentration. After reflow for 120 s at 220°C, Bi was homogeneously distributed in the Sn-3.5%Ag solder. In this study, the total Bi content in the solder joint was calculated as 2-4 wt% depending upon the thickness of the plated layer and upon the current density. Meanwhile, according to the Sn-Bi binary phase diagram (Massalski, 1986), Bi is soluble in Sn up to 21 wt% at eutectic temperature and to 4.8 wt% at room temperature. Thus, in the present work since the net Bi content was less than the solubility limit in Sn at room temperature, Bi particles were not expected nor observed in the solder microstructure after homogenization.

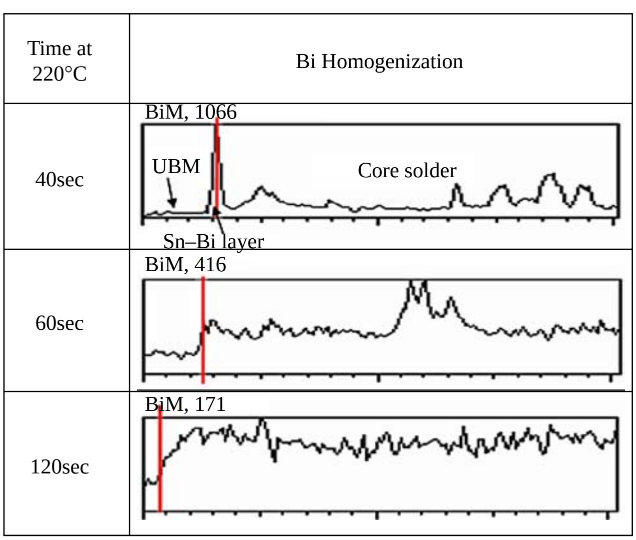
3.3 Shear strength

Figure 8 shows the shear strength of 1608 capacitor joints bonded with Sn-Bi plated Sn-3.5%Ag solder. The thermal cycling exposure was – 40/+125°C, and the electroplated layer was Sn-95.7%Bi which was plated at 2 A/dm^2 for between 1 and 3 min. The shear strength in the as – soldered state of the 1608 capacitor was approximately 5,000-6,000 gf. After 1,000 thermal cycles the average shear strengths decreased slightly, approximately 5-11 percent, compared to the as-reflowed state for all plated solders. This confirmed

Figure 7 Homogenization of Bi at 220°C for the sample of Sn-80.3%Bi plated Sn-3.5%Ag

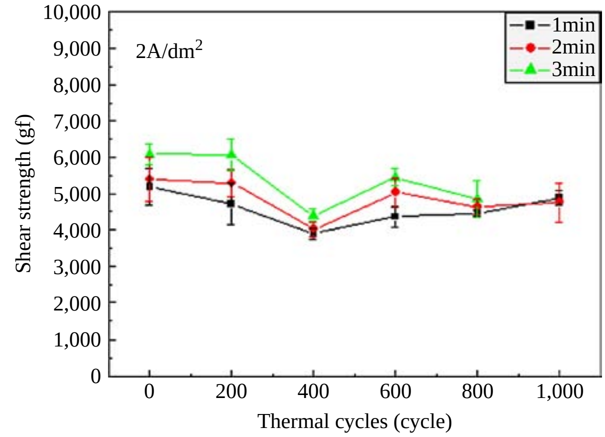


(a)



(b)

Figure 8 Shear strengths of Sn-Bi plated solders with thermal cycles



Notes: –40°C/+125°C, plated at 2A/dm^2 for 1, 2, 3 min

that the soldered joints were not significantly damaged by thermal cycles.

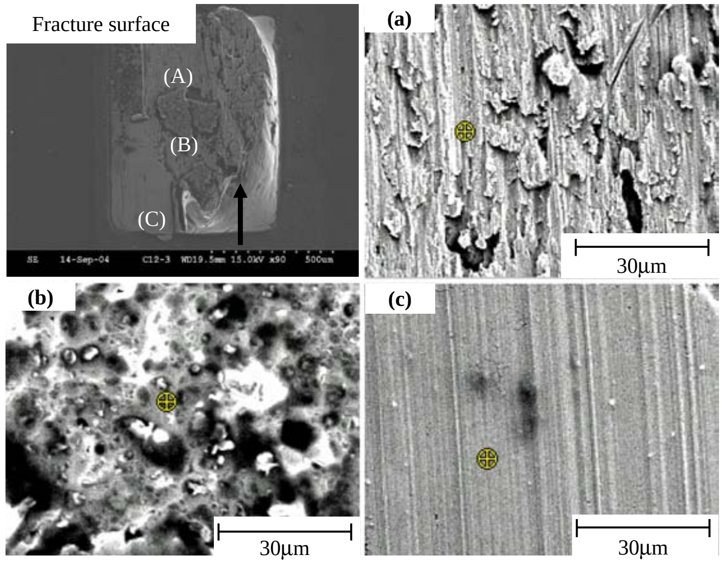
The shear strength of the Sn-Bi plated Sn-3.5%Ag solder was compared to those of commercial solder pastes of Sn-37%Pb, Sn-3.0%Ag-0.5%Cu, Sn-8%Zn-3%Bi. In the as-soldered state, the Sn-Bi plated Sn-3.5%Ag solder showed the highest shear strength of 6,000 gf, and Sn-37%Pb, Sn-3.0%Ag-0.5%Cu, and Sn-8%Zn-3%Bi showed 3,796, 3,204, and 4,102 gf, respectively. After 1,000 thermal cycles between -40 and 125°C, the Sn-Bi plated Sn-3.5%Ag solder had still the highest shear strength of 5,796 gf. Meanwhile, Sn-37%Pb, Sn-3.0%Ag-0.5%Cu, and Sn-8%Zn-3%Bi showed 3,296, 3,500, and 4,602 gf, respectively. These results tend to confirm that the Sn-Bi plated Sn-3.5%Ag solder has relatively high strength compared to the commercial solders.

Figure 9 shows the fracture surface of the UBM side of a Sn-Bi plated solder joint. The sample was taken from a 1,000 cycled joint. From the composition analysis of the fracture surface, fracture propagated both along the solder and along the capacitor contact of Ni. Specifically, the compositions were confirmed as 98.42 wt%Sn-1.21 wt%Bi-0.3 wt% Ni-0.04 wt%Cu-0.03 wt%Ag for point A, 87.81 wt% Ni-11.44 wt%Sn-0.55 wt%Ag-0.20 wt%Cu for point B, and 97.29 t%Sn-1.20 wt%Bi-0.8 wt%Cu-0.71 wt%Ni for point C. Thus, points A and C showed 97-98%Sn which indicated solder fracture, but the B point approximately 88%Ni which indicated contact fracture. From these composition and fracture analyses, the joints made with electroplated solder were evaluated as reliable after 1,000 thermal cycles. During the analysis of fracture surfaces, no significant areas of brittle fracture were observed.

4. Conclusions

Using the concept of TLP bonding, type 1608 capacitors were reflow soldered on FR4 substrate at reduced soldering temperature of 220°C using Sn-Bi plated Sn-3.5 wt%Ag solder. The Sn-3.5%Ag sheet was electroplated with Sn-(80.3 ~ 97.5) wt%Bi, and the thickness of Sn-Bi layer ranged from 1.3 to 6.9 μm with plating times of 1-10 min at 2 A/dm^2. The microstructure of the Sn-Bi plated Sn-3.5%Ag joints after reflow consisted of Sn matrix and Ag_3Sn, similar

Figure 9 SEM images of fracture surface after shear test



Notes: Sn-80.3Bi, Plating time: 3min, 1,000 cycle between −40°C and +125°C; →: shear direction

to typical Sn-3.5%Ag solder. Bi distribution in the solder was homogenized by holding 120 s at 220°C. The shear strength of the soldered joints in the as-soldered state was approximately 5,000-6,000 gf. The shear strength was not significantly degraded by thermal cycling, that is 5 ~ 10 percent decrease after 1,000 cycles. The fracture occurred mostly along solder and UBM, and no significant areas of brittle fracture were observed.

References

Chang, H.Y., Chen, S.W., Wong, D.S.H. and Hsu, H.F. (2003), "Determination of reactive wetting properties of Sn, Sn-Cu, Sn-Ag, and Sn-Pb alloys using a wetting balance technique", *Journal of Materials Research*, Vol. 18 No. 6, pp. 1420-8.

Corbin, S.F. (2005), "High-temperature variable melting point Sn-Sb lead-free solder pastes using transient liquid-phase powder processing", *Journal of Electronic Materials*, Vol. 34 No. 7, pp. 1016-25.

Harrison, M.R., Vincent, J.H. and Steen, H.A.H. (2001), "Lead-free reflow soldering for electronics assembly", *Soldering & Surface Mount Technology*, Vol. 13 No. 3, pp. 21-38.

Kariya, Y. and Otsuka, M. (1998), "Effect of bismuth on the isothermal fatigue properties of Sn-3.5mass%Ag solder alloy", *Journal of Electronic Materials*, Vol. 27, pp. 866-70.

Lee, J.S., Bang, W.H., Jung, J.P. and Oh, K.H. (2004), "Microstructure and strength of Sn-Bi coated Sn-3.5 mass%Ag solder alloy", *Materials Transactions*, Vol. 45, pp. 783-9.

Lugscheider, E., Bobzin, K. and Erdle, A. (2003), "Solder deposition for transient liquid phase (TLP)-bonding by MSIP-PVD-process", *Surface Coating Technology*, Vol. 174-175, pp. 704-7.

Massalski, T. (1986), *Binary Alloy Phase Diagrams*, American Society for Metals, Metals Park, OH, p. 540.

Shiau, L.C., Ho, C.E. and Kao, C.R. (2002), "Reactions between Sn-Ag-Cu lead-free solders and the Au/Ni surface finish in advanced electronic packages", *Soldering & Surface Mount Technology*, Vol. 14 No. 3, pp. 25-9.

Shin, S.W. and Yu, J. (2003), "Creep deformation of lead-free Sn-3.5Ag-Bi solders, Japanese", *Journal of Applied Physics*, Vol. 42, pp. 1368-74.

Tan, A.C. (1993), *Tin and Solder Plating in the Semiconductor Industry*, Chapman & Hall, London, p. 23.

Tuah-Poku, I., Dollar, M. and Massalski, T.B. (1988), "A study of the transient liquid phase bonding process applied to a Ag/Cu/Ag sandwich joint", *Metallurgical Transactions A*, Vol. 19A, pp. 675-86.

Yoshiharu, K. and Masahisa, O. (1998), "Effect of bismuth on the isothermal fatigue properties of Sn-3.5mass%Ag solder alloy", *Journal of Electronic Materials*, Vol. 27 No. 7, pp. 866-70.

Yoshiharu, K., Yasunori, H. and Masahisa, O. (1999), "Effect of thermal cycles on the mechanical strength of quad flat pack leads/Sn-3.5Ag-X (X = Bi and Cu) solder joints", *Journal of Electronic Materials*, Vol. 28 No. 11, pp. 1263-9.

Further reading

Glazer, J. (1994), "Microstructure and mechanical properties of Pb-free solder alloys for low-cost electronic assembly: a review", *Journal of Electronic Materials*, Vol. 23 No. 8, pp. 693-707.

Korhohen, T.M., Vuorinen, V. and Kivilahti, J.K. (2001), "Interconnections based on Bi-coated SnAg solder balls", *IEEE Transactions on Advanced Packaging*, Vol. 24 No. 4, pp. 515-20.

Plumbridge, W.J., Gagg, C.R. and Peters, S. (2001), "The creep of lead-free solders at elevated temperatures", *Journal of Electronic Materials*, Vol. 30, pp. 1178-83.

Qiao, X. and Corbin, S.F. (2000), "Development of transient liquid phase sintered (TLPS) Sn–Bi solder pastes", *Materials Science & Engineering A*, Vol. 283, pp. 38-45.

Reader, C.H., Messler, R.W. Jr and Coffin, L.F. Jr (1999), "Partially-constrained thermomechanical fatigue of eutectic Tin-bismuth/copper solder joints", *Journal of Electronic Materials*, Vol. 28, pp. 1045-54.
Reinikainen, T. and Kivilahti, J. (1999), "Deformation behavior of dilute Sn-Bi (0.5 to 6 at%) solid solutions", *Metall. Trans. A*, Vol. 30A, pp. 123-32.
Tomlinson, W.J. and Collier, I. (1987), "The mechanical properties and microstructures of copper and brass joints soldered with eutectic tin-bismuth solder", *Journal of Material Science*, Vol. 22, pp. 1835-9.

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