

High Melting Lead-Free Mixed BiAgX Solder Paste System

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Abstract

Although lead-free soldering has been main stream in the industry since 2006 with the replacement of the eutectic SnPb system by the SnAgCu system, the development of drop-in lead-free alternatives for high melting high lead solder alloys is still far from mature. The BiAg alloy exhibits acceptable bulk strength, but very poor ductility and wetting. Therefore, it is not acceptable as an option. In this current work, a mixed-powder BiAgX solder paste system has been developed as a viable alternative high temperature lead-free solder. The metal powder in the paste is composed of a high-melting first alloy powder as a majority and the additive powder as a minority. The additive contains a reactive element to react with various metallization surface finishes. The additive will melt and react on the parts before or together with the melting of the majority solder. The reactive element in the additive is designed to be converted completely into IMCs during the reflow process, resulting in a high-melting solder joint. In the mixed-powder paste system, a melting temperature above 260°C was verified by both DSC and TMA data. The mixed-powder solders show significantly improved wetting compared to Bi/11Ag. The voiding and TCT performance are comparable with high-lead solders. The IMC layer thickness of the mixed-powder system is insensitive toward thermal aging at 175°C while the high-lead solders show a considerable increase. The fine and well-dispersed Ag particles in the joint, together with the controlled IMC thickness, are attributed for the reliability improvement.

Introduction

Lead generated by the disposal of electronics assemblies is considered hazardous to the environment and the health of humans. The use of lead-containing solders is prohibited in most electronics interconnection and packaging industries. The lead-free solders to replace the eutectic PbSn have been widely and well-studied, and SnAg, SnCu and SnAgCu solders

are becoming mainstream in the electronics industry. However, the development of high-temperature lead-free (HTLF) solders to replace the conventional high-lead solders, i.e., Pb/5Sn and Pb/5Sn/2.5Ag, is still in its infancy. Semiconductor or power die-attachment requires the use of high temperature solders in order to maintain the integrity of the joint between the die and the lead frame at board level

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assembly. The major requirements for the die attachment are a softening temperature no lower than 260°C; a drop-in compatible with the current process for high-lead solders; good thermal fatigue resistance; and low cost.

Currently, there are no drop-in lead-free alternatives for the high lead-containing solders. However, some possible alternative lead-free solders and innovative potential solutions for the die-attachment applications have been studied and reported. The possible alternative solders include SnSb, BiAg, ZnSn, ZnAl, and AuSn, etc. [1-4].

SnSb alloys, with less than 10wt% Sb, maintain good mechanical properties without forming the massive intermetallic compounds, but their solidus temperature is no higher than 250°C and, therefore, is not acceptable [1].

Zn-based alloys, including the eutectic ZnAl, ZnAlMg, and ZnAlCu [2], have a melting temperature above 330°C. However, the high affinity of Zn, Al, and Mg toward oxygen causes very poor wetting. Zn (20-40wt%) Sn solder alloys, proposed to be one of the high-temperature lead-free substitute solders [3], have a liquidus temperature above 300°C while the solidus temperature is around 200°C. The pasty state of the ZnSn solder around 260°C may maintain the joint between the parts. However, solder extrusion may occur at the encapsulation process and cause failure. Also, Zn-based solder alloys will form massive IMC layers between the metallization surface and the solder. The existence of the IMC layer and its intensive growth during the subsequent reflow and operation will cause reliability concerns.

Eutectic AuSn, composed of the two intermetallic compounds, has been proven to be a reliable high-temperature solder based on the melting temperature of 280°C, the high electrical and thermal conductivities, the excellent corrosion resistance, and the high strength, although low ductility. However, the extremely high cost restricts its application within the fields where the cost is outbid by reliability consideration.

BiAg alloys have a solidus temperature of 262°C, which satisfies the softening temperature requirement for the high-temperature die-attach solders [4]. However, there are two major concerns: (1) poor wetting on many surface finishes, including the most commonly used Cu, and (2) the low ductility.

On the basis of the softening temperature requirement for the high-melting lead-free solder, SnSb and ZnSn solders are not suitable. The extremely high cost of Au-rich solders limited

their acceptance by the industry. ZnAl and BiAg meet the melting temperature requirement and have a reasonably low cost. However, the high affinity to oxygen in the ZnAl solder system, or the poor reaction chemistry between BiAg solder and the substrate metallization, makes them hard to be used by industry because of poor wetting. Despite the poor wetting, the desired high-melting temperature of BiAg and ZnAl still makes them attractive as the candidates for the high-temperature lead-free solders.

The Ge-doped BiAg alloy (EP705258) is aiming at preventing the excessive formation of dross on the alloy's surface during soldering. However, this does not change the reaction chemistry between Bi and the metallization surface finish of the substrate.

Modifying the reaction chemistry between the solder alloy and the metallization surface finish can be achieved by alloying the additional elements in the solder. However, alloying is often associated with some loss of properties. For example, Sn shows a better reaction chemistry comparing to Bi.

Directly alloying Sn into BiAg could cause a low melting phase (BiSn) if Sn is excessive and/or cause the complete conversion of Sn into Ag₃Sn IMCs in the alloy if the Sn is not excessive. This will not improve the reaction chemistry between Sn with substrate metals if there is not enough time for them to be re-dissolved back into the molten solder during reflow. Thus, it is hard to see the benefits of alloying Sn directly into BiAg alloys, as shown in Figure 1.



Figure 1. Wetting of Bi/11Ag (left) and Bi/10Ag/4Sn (right) on AgPd thick film pad Al₂O₃ substrate.

Alternatively, a novel technology to improve the interface reaction chemistry efficiently has been invented to provide a method of designing the mixed-alloy powder pastes, in which the additive powder is present in the paste to improve the reaction chemistry at a temperature at or below the melting

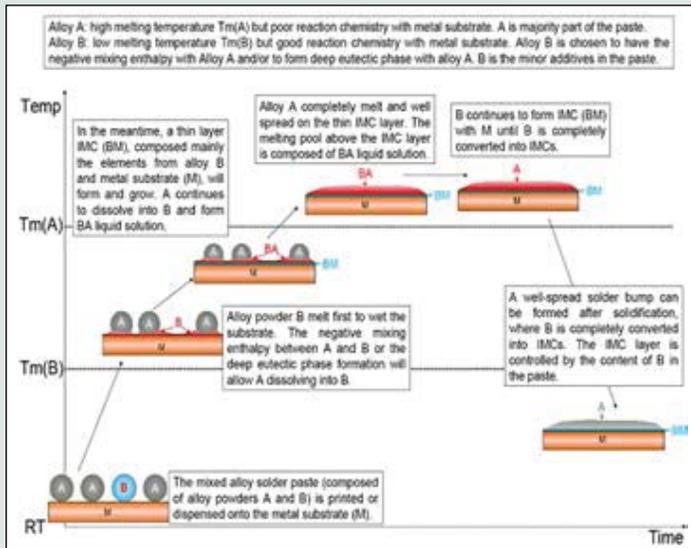


Figure 2. Design idea of the mixed solder paste system.

temperature of the first alloy solder powder. The metal powder in the paste is composed of one solder powder (the first alloy powder) as the majority and the additive powder (the second alloy powder) as the minority. The additive contains a reactive element to react with various metallization surface finishes, namely the commonly used Cu, Ag, and Ni finishes. In this design, the additive will melt before or together with the melting of the majority solder (the first alloy powder). The molten additive will react and wet on the parts before, or together with, the partially or completely molten first alloy. The reactive element in the additive is designed to dominate the formation of IMCs at the metallization surface and, finally, be converted completely into IMCs during the reflow process.

In the design, the selection of the additive is critical. First, the additive should contain a reactive element, which preferentially reacts with commonly used surface finish materials such as Cu, Ag, and Ni. Second, the IMC layer, formed by chemical reaction between the reactive element and the surface finish materials, should be easily wetted by the first alloy (the majority solder body). For instance, BiAg can serve as the first alloy, while Sn, In, and Zn metals or alloys can serve as the potential additives. Sn, In, and Zn show good reactivity with Cu, Ag, Ni (surface finish materials) and have good affinity toward Bi (solder). An improved wetting has been observed after reflowing the mixed powder solder paste on AgPd (left) and AgPt (right) thick-film pad Al_2O_3 substrate, shown in Figure 3. Wetting of Pb/5Sn/2.5Ag on a AgPt (bottom) thick-film pad Al_2O_3 substrate has also been exhibited in Figure 3. A comparable spreading from both the

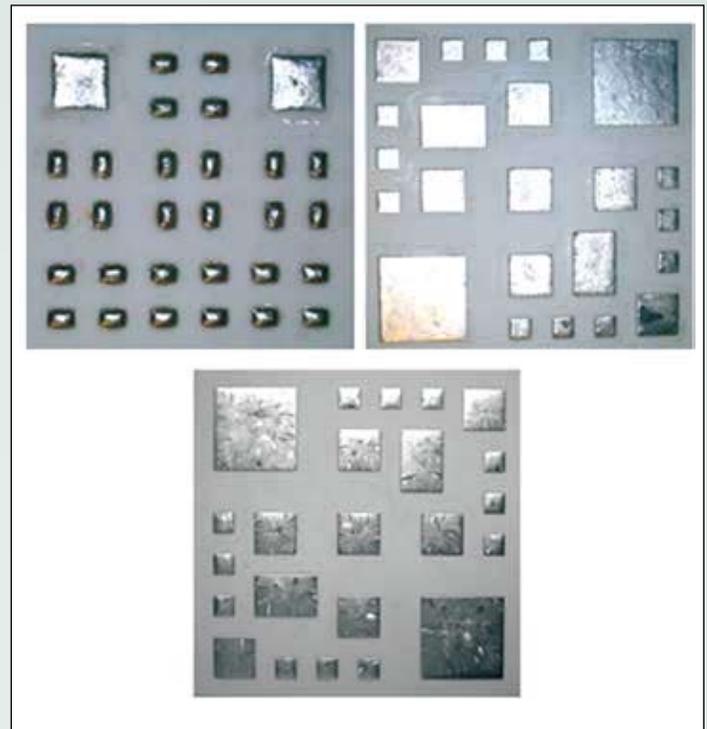


Figure 3 - Wetting of the mixed-powder solder on AgPd (left) and AgPt (right) thick-film pad Al_2O_3 substrate. Wetting of Pb/5Sn/2.5Ag on AgPt (bottom) thick film pad Al_2O_3 substrate.

high lead-containing solder and the mixed-powder solder has been observed.

With this technology, additional benefits can be provided. The thickness of the IMC layer is expected to be insensitive to aging because the reactive elements, which dominate the IMC formation, are controllable in species and quantity. Furthermore, the reaction between the additive elements and Ag in BiAg systems also refines the Ag particles precipitations.

The refined Ag particles and the controlled IMC thickness, together enhance the mechanical properties, including both strength and ductility, and the associated reliability.

Experimental

Pastes

In the current study, Bi/11Ag alloy powder was used as the first alloy. A few different alloys were selected as the additives, including Bi/42Sn, Bi/42Sn/1Ag, SAC387, Sn3.5Ag, and Sn/10Sb/25Ag. At the same time, six high lead-containing solders were chosen as the control, including Pb/5Sn/2.5Ag, Pb/10Sn, Pb/10Sn/2Ag, Pb/5Sn,

Pb/2Sn/2.5Ag, and Pb/2.5Ag. Flux A and B were used to mix with the alloy powders (Type 3) to make the pastes.

Tests

The melting behavior of all the pastes was studied by using DSC (TA Q2000). Also, TMA tests were done on the solder bumps to see the softening temperature for each alloy system.

To study the wetting, the paste was printed on a 1-inch diameter Cu coupon through a three-hole stencil with a stencil thickness of 254 microns, and a hole diameter of 6.35mm. Then the paste was reflowed and the spread of the solder on Cu was examined. After soldering, the joints were cross-sectioned to study the interface structure, which is expected to provide the underlying mechanism of wetting improvement.

For the voiding performance investigation, the paste was printed on a Cu coupon with a three-hole stencil. A 1/4-inch square Cu coupon was placed on each printed paste and followed by reflow. Each of the joints was examined for voiding by X-ray inspection.

Thermal aging tests were done by joining Cu coupons with all the testing pastes, followed by conditioning the sample at 175°C for up to 1,000 hours. The evolution of the IMC layers was studied at different aging times, namely, 0, 100, 500, and 1,000 hours.

Alumina coupons with AgPt thick-film pad was designed for the TCT test, as shown in Figure 4. The pads on the coupon have three different sizes: two 1/2-inch square pads, seven 1/4-inch square pads, and twelve 1/8-inch square pads. After printing the paste with a 4mil thick stencil, different sized Cu coupons were placed onto the corresponding AgPt thick-film pad and reflowed.

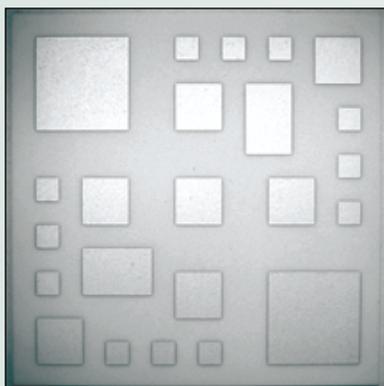


Figure 4. Customized AgPt thick-film pad Al_2O_3 substrate.

The mismatch in coefficient of thermal expansion (CTE) between alumina (6-7 ppm/°C) and Cu (16.7 ppm/°C) is close to that between silicon die (3 ppm/°C) and Cu. Accordingly, the trend of joint reliability observed in the former pair is expected to be similar to that of the latter pair.

Cycling temperature ranged from -55°C to 125°C with a dwelling time at peak temperature for 5 minutes. Assembled coupons were checked at 500, 1000, and 2000 cycles, respectively, with the number of the broken parts counted at each check point. Ranking of pastes is established on the basis of survival rate.

Results

DSC

With appropriate design of the mixed solder paste system, the additives should not influence the melting behavior of the first alloy. Figure 5 shows an example DSC result from a well-designed mixed solder paste system (Bi/42Sn+Bi/11Ag+flux). In the first run, a small melting peak around 140°C corresponding to the additives (Bi/42Sn) is seen, followed by the melting of first alloy (Bi/11Ag) with an onset temperature a few degrees lower than 262°C, the solidus temperature of Bi/11Ag. However, in the second run, no endotherm can be seen below 260°C. The single melting peak around 262°C comes from Bi/11Ag. This observation indicates that the reactive element Sn in Bi/42Sn is completely converted into IMCs and there is no more eutectic BiSn phases left after the first run.

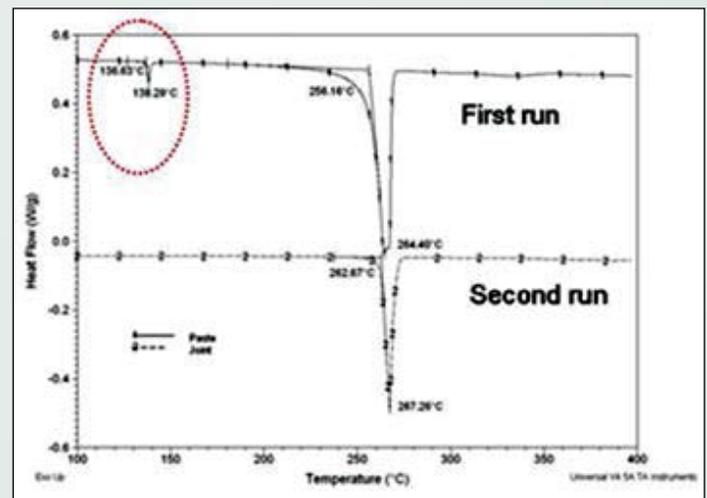


Figure 5. First and second runs of DSC for a mixed solder paste.

TMA

TMA tests were performed on the solder bumps on the Cu coupon. The softening temperature is closely associated with the melting temperature of the solder alloys.

Figure 6 reveals the softening temperature of a few high lead-containing solders and the mixed-powder solder. The

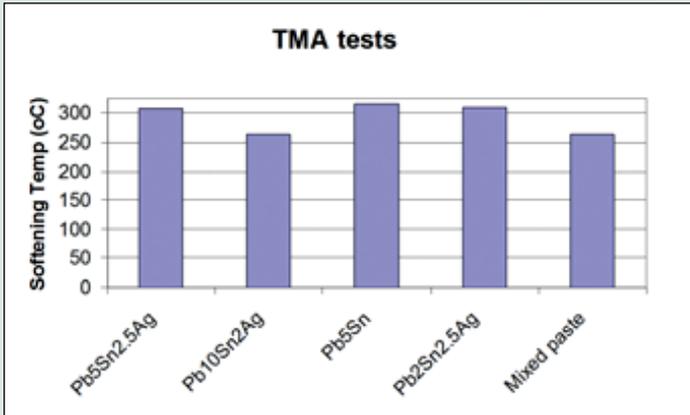


Figure 6. TMA test results for the high lead-containing solder and the mixed solder paste.

softening temperature of the mixed solder is around 262°C, which agrees well with the melting temperature of Bi/11Ag measured in DSC. The softening temperature of the mixed powder is comparable with Pb/10Sn/2Ag, and is lower than other high lead-containing solders.

Wetting

The wetting of the mixed solder pastes was studied. Bi/11Ag shows obvious dewetting on both the Cu and Alloy42 coupons shown in Figure 7. The mixed solder paste with additives shows no obvious trace of dewetting, also shown in Figure 7. Recall the comparable wetting of the high lead-containing solder and the mixed-powder solder on AgPt thick-film pad in Figure 3. This clearly indicates that the additives effectively improve the wetting.

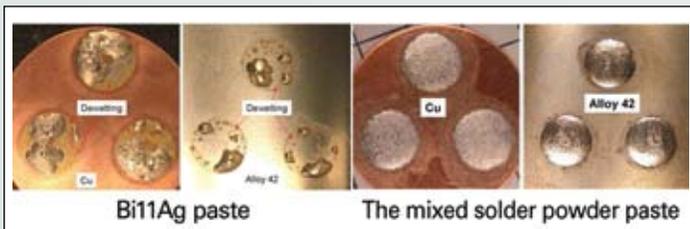


Figure 7. Improved wetting of the mixed solder paste comparing Bi/11Ag paste on Cu to Alloy 42 coupons.

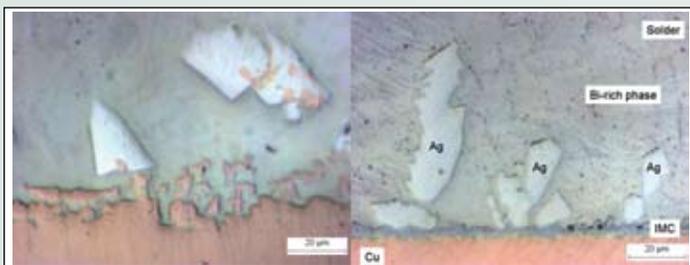


Figure 8. Cross-section images of joints: left, Bi/11Ag on Cu and right, the mixed solder (Bi/11Ag+Bi/42Sn) on Cu.

The left image of Figure 8 shows no IMC layer being formed between the Cu and the Bi/11Ag solder. The dissolution of Cu into the solder matrix has been observed along the interface. With the mixed solder paste where Bi/42Sn was mixed with Bi/11Ag, an IMC layer is observed at the interface between the solder and Cu substrate, as shown in the right image of Figure 8. This IMC layer is composed mainly of Sn and Cu, indicating that the Sn in Bi/42Sn is responsible for this IMC formation and the improved wetting. Additionally, two types of Ag particles have been observed in the joint formed by the mixed solder pastes. The relatively coarse Ag particles around 20µm are primarily concentrated along the bonding interface and the fine Ag particles in submicron size constituted the network band surrounding the small Bi-rich colonies inside the solder joint. In the BiAg joint, the fine Ag particles and the associated network band have not been observed.

Voiding

Voiding performance of the mixed solder pastes and various high lead-containing solders was studied via X-ray inspection, as shown in Figure 9. Two fluxes were used to see the influence on the voiding performance. Flux A resulted in a higher voiding than flux B for both Pb/5Sn/2.5Ag and the mixed solder paste, as shown in Figures 9 and 10. No significant difference in voiding performance can be discerned between Pb/5Sn/2.5Ag and the mixed solder paste when the same flux is employed.

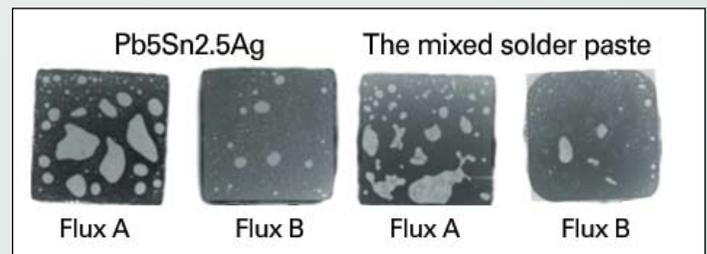


Figure 9. Voiding performance of Pb/5Sn/2.5Ag (left) and the mixed solder paste (right), Flux B resulted in a lower voiding than flux A.

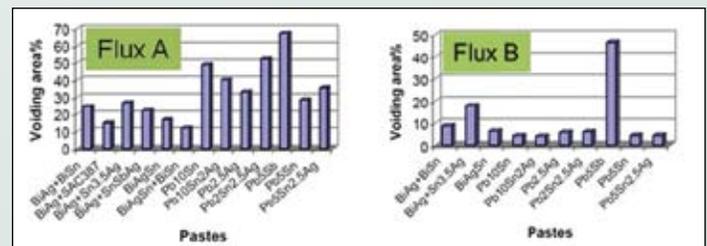


Figure 10. Voiding performance of both high lead-containing solders and the mixed solders with flux A and flux B.

Aging

The cross-section images in Figure 11 show the evolution of the IMC layer for a high lead-containing solder and a mixed powder solder upon aging. With increased aging time, the IMC layer thickness for high lead-containing solder increases, while there is no significant change in the IMC layer thickness for the mixed powder solder. The IMC thickness of various high lead-containing solders and the mixed powder solder is summarized in Figure 12. Here the IMC thickness is expressed as relative IMC thickness, which is defined as the ratio between the measured IMC thickness and the bondline thickness. The proportional relationship between the IMC thickness and the Sn is also illustrated in Figure 13.

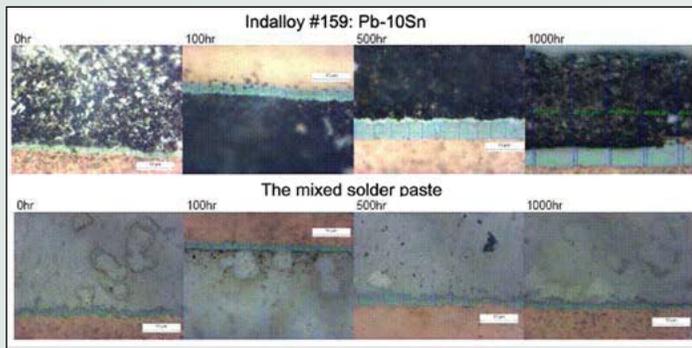


Figure 11. IMC thickness of the high lead-containing solder and the mixed powder solder upon aging at 175°C for up to 1,000 hrs.

In the design, the IMC layer formation is known to be closely related to the reactive elements from the additives. Although the reactive elements play a dominant role in wetting improvement, the side effects still exist if the reactive elements are excessive. The excessive reactive elements may lead to a low melting phase (i.e., BiSn, BiIn) and a thicker IMC layer. With the increasing reactive element (Sn) content from ~0.5wt% to ~2.8wt%, the IMC layer thickness increases from ~2μm to ~7μm. The thicker IMC may lead to the poor reliability, therefore a higher reactive element content is not

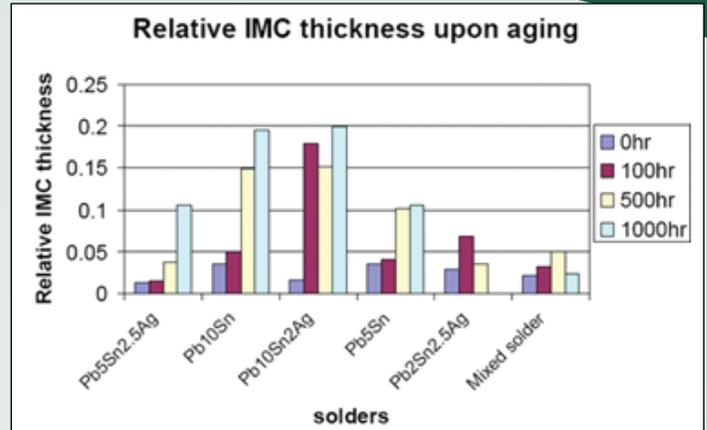


Figure 12. Relative IMC thickness of high lead-containing solders and the mixed powder solder.

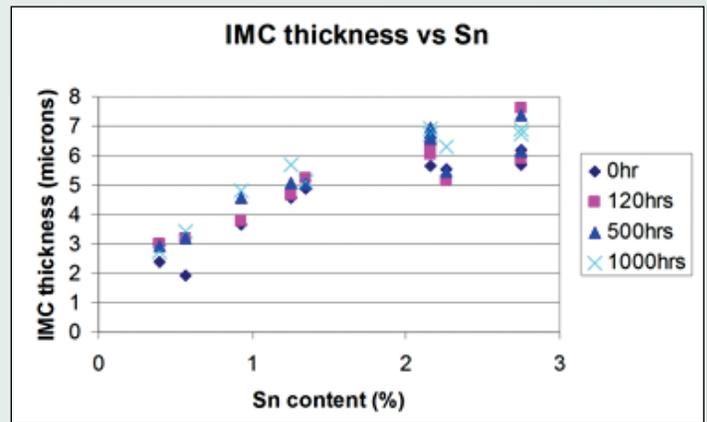


Figure 13. The relationship between IMC thickness and Sn content.

recommended. In this study, the IMC thickness for all the mixed powder solder pastes exhibits insensitivity toward aging. This is attributable to the fact that most of the reactive elements were consumed to form the IMC layer during soldering and no more reactive elements are available in the joint to further assist with IMC formation during aging.

Thermal cycling tests

Figure 14 reveals the failure percentage of all the testing pastes as a function of cycling time for the three different die

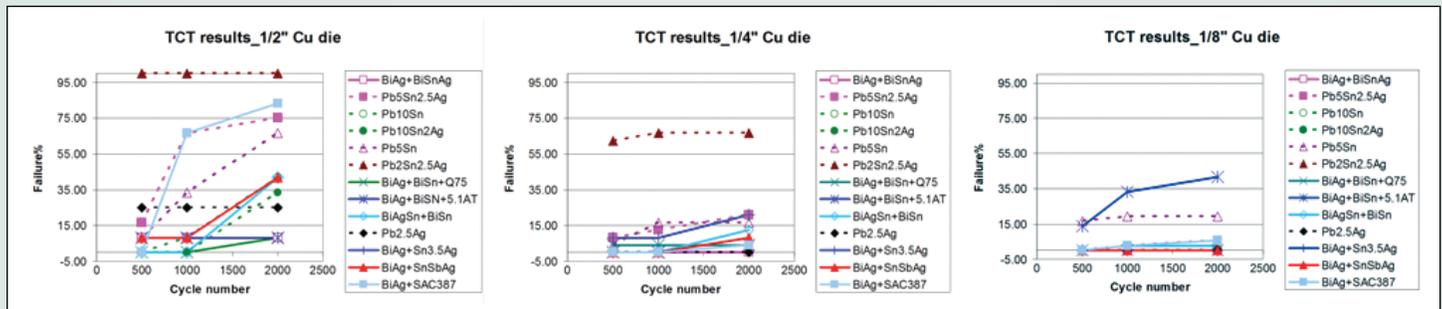


Figure 14. Thermal cycling tests results of high lead-containing solders and the mixed powder solder.

sizes. The failure percentage is the ratio between the number of broken parts and the number of total testing parts. For the large die size (1/2-inch), the performance of all the pastes varies significantly. The failure percentage ranges from less than 10% to 100% after 2,000 cycles for different pastes. For mid-size (1/4-inch) and small size (1/8-inch) die, most of the pastes exhibit comparable performance.

The TCT performance is ranked in Figure 15, with paste type as the X-coordinate. For the large sized die (1/2-inch), the three mixed solders ranked best, followed by the high lead-containing solders. For mid-size and small-size die, no clear difference in ranking can be discerned between the mixed powder group and the high lead-containing group. Overall, the mixed powder system performs equal to or better than high lead-containing solders in TCT tests.

Discussion

The design of the mixed powder solder paste is aimed at finding an HTLF solder solution, which can satisfy the requirements of the die-attach application. In this system, the first alloy is designed to dominate the melting and the mechanical behavior of the joint. The additives in a minor amount melt earlier than, or at the same time as, the first alloy during soldering, and are designed to modify the bonding interface, thus improving the associated bonding strength. A thin layer of IMCs at the interface between the solder and the components will be formed through the chemical reaction between the additives and the surface finish materials of the components.

An endothermic peak, due to the additives in the first run, is seen in Figure

5, but vanishes in the second run. This indicates that the additive phase was consumed in the first reflow, likely forming the IMCs by reacting with the first alloy. This phenomenon clearly indicates that direct alloying, instead of a mixed powder approach, will not be effective in improving the wetting. Direct alloying of Sn in BiAg will deplete the Sn by forming Ag_3Sn IMCs. As a result, no free Sn will be available for assisting with the wetting. The poor wetting of Bi/10Ag/4Sn on an AgPd thick file pad, shown in Figure 1, indeed verifies the concern arising from the direct alloying method. Additionally, DSC data in the second run indicates that the additives have no effect to the melting behavior of the first alloy at post reflow. This is consistent with TMA findings in Figure 6.

With the mixed powder solder, an improved wetting was observed, comparing to BiAg and BiAgSn as shown in Figures 1, 3, and 7. The improved wetting is attributed to the formation of an IMC layer at the interface because of the existence of the additives. At the same time, the controllable additives in species and quantity lead to the insensitivity of the IMC layer thickness toward aging. The constant IMC layer thickness is expected to stabilize the joints.

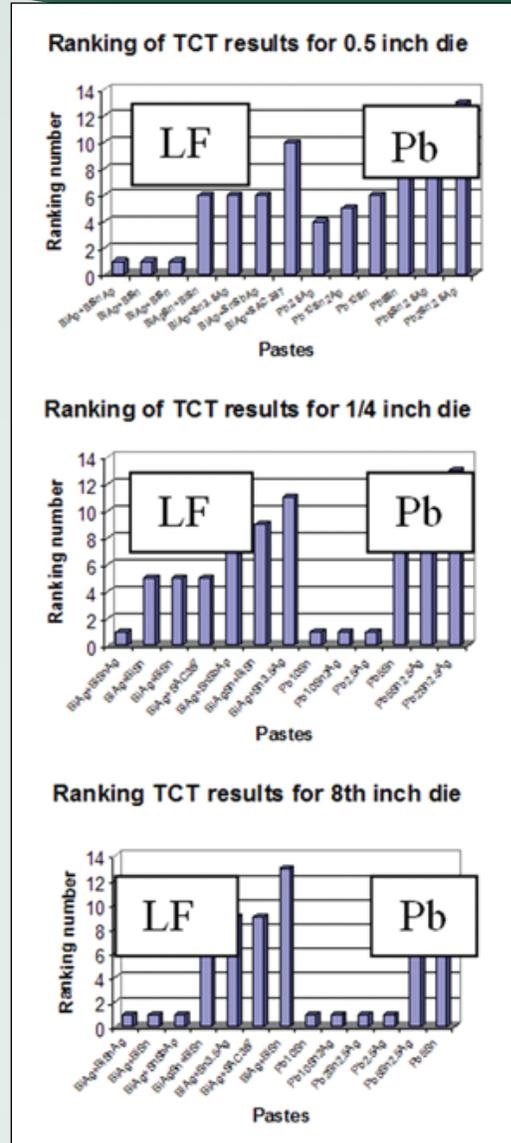


Figure 15. Ranking of all tested pastes under thermal cycling tests for three different sized die.

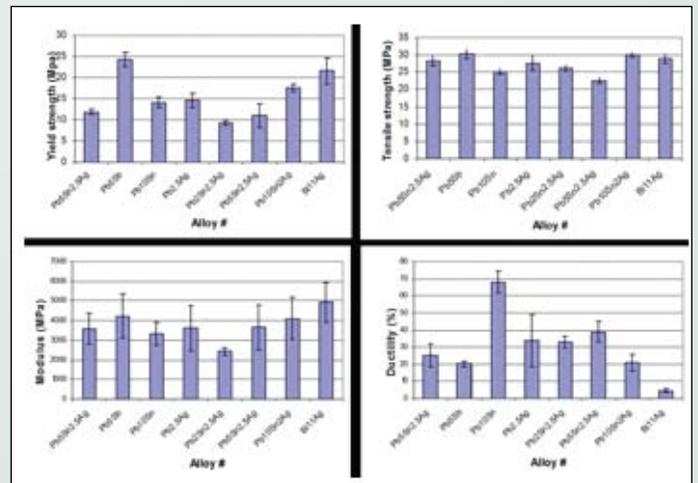


Figure 16. Mechanical behavior of the high lead-containing solder alloys and Bi/11Ag alloy from tensile tests on quarter inch bars.

TCT results show mixed ranking results on the mixed powder solders versus the high lead-containing solders. Generally speaking, Bi-rich solder is strong, but brittle. In Figure 17, the bulk Bi/11Ag alloys have a comparable or higher strength and higher modulus than the bulk high lead-containing alloys in tensile tests using cast 1/4-inch bar. However, the ductility of Bi/11Ag alloy is lower than all the high lead-containing solders tested. Thus, it was not expected that comparable TCT results can be obtained for both mixed powder and high lead-containing solders.

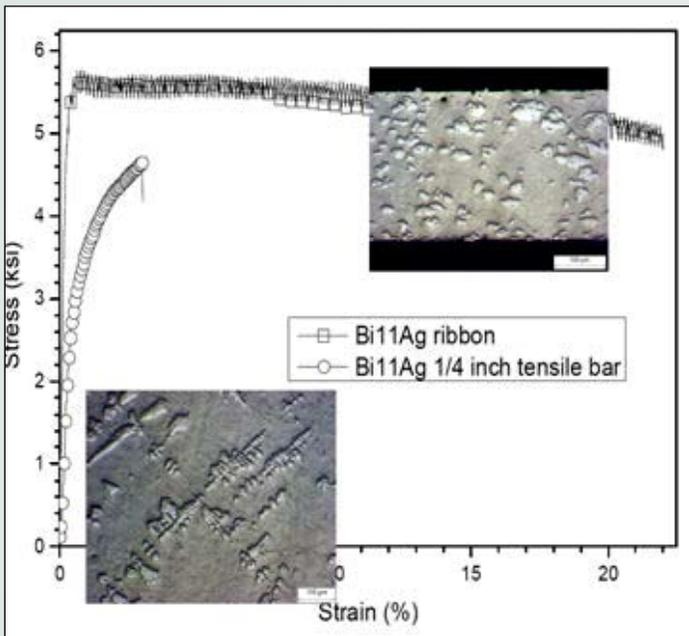


Figure 17. Bi/11Ag microstructure and mechanical behavior of the quarter inch tensile bar and the 10 mil thick ribbon.

There are two rationales for the TCT results for the mixed powder system. First, the microstructure of joint formed by the mixed powder paste could be significantly different from that of the 1/4-inch tensile bars. In the 1/4-inch Bi/11Ag tensile bar, Ag dendrites of several hundred microns are observed, as shown in Figure 17. In Bi/11Ag ribbon, the refinement of the Ag particle down to 20-50 microns renders higher yield strength, higher modulus, and a much higher ductility (20%) than the tensile bar. In the solder joint, there are two types of Ag particles: the coarse particles along the bonding interface, ranging from 20 μ m to 40 μ m, and the fine particles (submicrons), forming the network band to isolate the Bi colonies (Figures 8 and 18). These network bands formed by the fine particles, together with the coarse particles, serve as the obstacles and restrict the movement of dislocation and the propagation of dislocation

from one Bi colony to another. Therefore, it is expected that the joint would exhibit a higher strength and a higher ductility comparing to the BiAg tensile bars. After TCT tests, although the fine Ag-rich particles become coarser and the spacing between the particles is enlarged, they are still well dispersed in the joint and in submicron size, as shown in Figure 18. The relatively well-maintained microstructure indicates that the mechanical properties may be well preserved during TCT test. Secondly, the well-controlled IMC thickness (Figure 12) may also contribute to the improved reliability. More studies on the joint microstructure and the microstructural evolution are in progress.

Conclusions

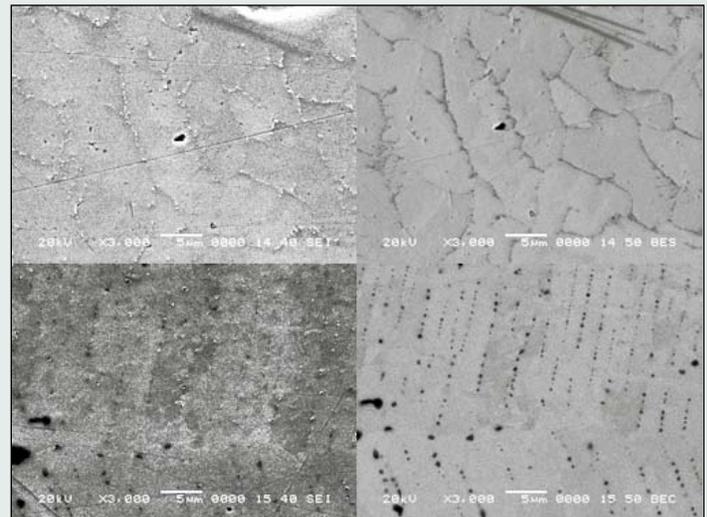


Figure 18. The microstructure of the BiAgX solder joint before TCT tests (top left: SE image and top right: BS image) and after TCT tests (bottom left: SE image and bottom right: BS image).

A mixed powder solder paste technology has been invented to design the alternative HTLF solder pastes. The paste is designed to be composed of a high melting first alloy powder as a majority, the additive powder as a minority, and the flux. The reactive element(s) contained in the additives react aggressively with various metallization surface finishes. The additive will melt and react before or together with the melting of the majority solder. The reactive element in the additive is designed to be completely converted into IMCs during the reflow process. This results in a high melting solder joint. For example, in the mixed powder paste system studied here, a melting temperature above 260 $^{\circ}$ C was verified

by DSC and TMA data. The mixed powder solders show significantly improved wetting compared to Bi/11Ag. The voiding and TCT performance are comparable with high lead-containing solders. The IMC layer thickness of the mixed powder system is insensitive toward thermal aging at 175°C, while the high lead-containing solders show a considerable increase. The underlying mechanism of the enhanced reliability for the BiAgX system has been investigated based on observation of the joint microstructure and the microstructural evolution.

References

1. Chen S.W. et al, "Phase equilibria of the Sn-Sb Binary System," *Journal of Electronic Materials*, Vol.37, No.7 (2008), pp.992-1002.
2. Takaku, Y. et al, " Interfacial Reaction between Cu substrate and Zn-Al base High-Temperature Pb-Free Solders," *Journal of Electronic Materials*, Vol.37, No.3 (2008), pp.314-323.
3. Kim, S. et al, "Interfacial Reaction and Die Attach Properties of Zn-Sn High-Temperature Solders," *Journal of Electronic Materials*, Vol. 38, No.2 (2009), pp.266-272.
4. Lalena, J. et al, " Experimental Investigation of Ge-doped Bi11Ag as a New Pb-Free Solder alloys for Powder Die Attachment," *Journal of Electronic Materials*, Vol.31, No.11 (2002), pp.1244-1249.

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