High Temperature Lead-Free Solder Joints Via Mixed Powder System

Authored by Dr. Ning-Cheng Lee and HongWen Zhang.

Abstract

Although lead-free soldering has been the main stream of industry since 2006, with the replacement of eutectic SnPb system by SnAgCu system, the development of drop-in lead-free alternatives for high melting high lead solder alloys is still far from mature. BiAg alloy exhibits acceptable bulk strength but very poor ductility and wetting, therefore it is not acceptable as an option. In 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 majority and the additive powder as 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, hence 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 a significantly improved wetting comparing to Bi11Ag. 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 ones do show a considerable increase.

Key words: High temperature, lead-free, solder, solder paste, solder joint, mixed, wetting, voiding, BiAg.

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Introduction

Lead generated by disposal of electronic assemblies is considered hazardous to the environment and human health. The use of Pb-bearing solders is prohibited in the electronics interconnection and packaging industries. The Pb-free solders to replace the eutectic Pb-Sn have been widely studied and SnAg, SnCu and SnAgCu solders are becoming the mainstream for electronic industry. However, the development of high temperature lead-free (HTLF) solders to replace the conventional high lead ones (i.e., Pb5Sn and Pb5Sn2.5Ag) is still in its infancy. Semiconductor or power die attachment requires the use of high temperature solders in order to maintain the interconnection integrity between the die and the lead frame at board level assembly. The major requirements for the die attachment are (1) softening temperature no lower than 260°C, (2) a drop-in compatible with the current process for high-lead solders, (3) good thermal fatigue resistance, and (4) low cost.

Currently, there are no drop-in Pb-free alternatives for the high lead solders, although some possible alternative lead-free solders and some innovative potential solutions for the die attachment application 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 hence are not acceptable [1].

Zn-based alloys, including the eutectic ZnAl, ZnAlMg and ZnAlCu [2], have the melting temperature above 330°C. However, the high affinity of Zn, Al, and Mg toward oxygen causes a very poor wetting. Zn(20-40wt%) Sn solder alloys, proposed to be one of the high temperature lead-free substituents [3], have a liquidus temperature above 300°C, while the solidus temperature is only around 200°C. The pasty state of the ZnSn solder at around 260°C may maintain the joint between the parts. However, solder extrusion may occur during 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 the reliability concerns.

Eutectic AuSn, composed of the two intermetallic compounds, has been proven to be a reliable, high temperature solder on basis of 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 the 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 major concerns: poor wetting on many surface finishes, including the most commonly used Cu; and the low ductility.

On 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 limit their acceptance in the industry. ZnAl and BiAg meet the melting temperature requirement and have the reasonable low cost; however, the high affinity to oxygen in ZnAl solder system or the poor reaction chemistry between BiAg solder and the substrate metallization, makes them hard to be used in the industry because of the poor wetting. Despite the poor wetting, the desired high melting temperature of BiAg and ZnAl still make 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 alloy 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 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 property loss. For example, Sn shows the better reaction chemistry compared to Bi. However, directly alloying Sn into BiAg could cause (1) low melting phase (BiSn) if Sn is excessive; and/or (2) the complete conversion of Sn into Ag3Sn IMCs in the alloy if Sn is not excessive, which 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.
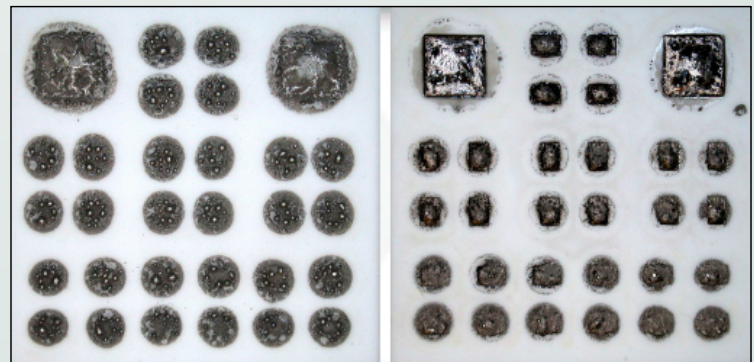
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Figure 1. Wetting of Bi11Ag (left) and Bi10Ag4Sn (right) on Ag-Pd thick film pad Al2O3 substrate.

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 temperature of the first alloy solder powder. The metal powder in the paste is composed of one solder powder (the first alloy powder) as majority and the additive powder (the second alloy powder) as minority. The additive contains a reactive element to react with various metallization surface finishes, namely the commonly used Cu, Ag, and Ni finishes, etc. 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 thus 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. Figure 2 depicts the design idea of this technology.
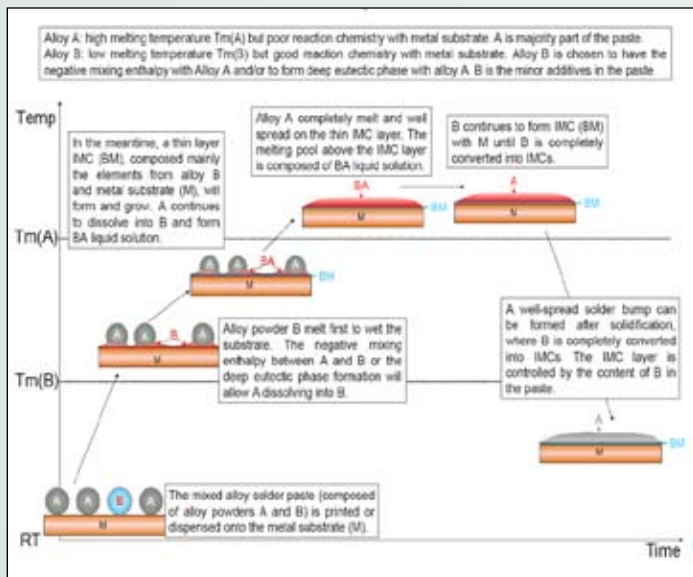

Figure 2. Design idea of the mixed solder paste system.

In the design, the selection of the additive is critical. First, the additive should contain reactive element which preferentially react 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 reflow of the mixed powder solder paste on AgPd (top left) and
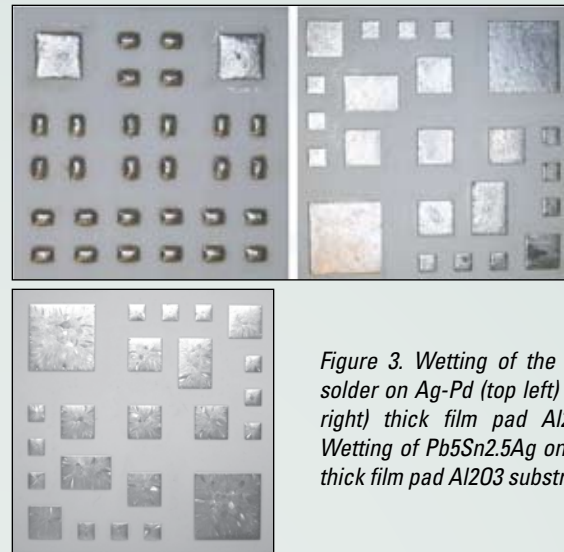

Figure 3. Wetting of the mixed powder solder on Ag-Pd (top left) and Ag-Pt (top right) thick film pad Al2O3 substrate. Wetting of Pb5Sn2.5Ag on AgPt (bottom) thick film pad Al2O3 substrate.

AgPt (top right) thick film pad Al2O3 substrate, shown in Figure 3. Wetting of Pb5Sn2.5Ag on Ag-Pt thick film pad Al2O3 substrate has also been exhibited in Figure 3. A comparable spreading from both the high lead solder and the mixed powder solders 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.

Experimental

Pastes

In current study, Bi11Ag alloy powder was used as the first alloy. A few different alloys were selected as the additives, including Bi42Sn, Bi42Sn1Ag, SAC387, Sn3.5Ag, and Sn10Sb25Ag. At the same time, six high lead solders were chosen as control, including Pb5Sn2.5Ag, Pb10Sn, Pb10Sn2Ag, Pb5Sn, Pb2Sn2.5Ag, and Pb2.5Ag. Flux A and B were used to mix with the alloy powders (Type 3) to make the pastes.

Tests

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 was expected to provide the underlying mechanism of wetting improvement.

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

Thermal aging tests were done by joining Cu coupons with all the testing pastes, then followed by conditioning the sample at 175°C for up to 1000 hrs. The evolution of the IMC layers was studied at different aging times, namely, 0, 100, 500 and 1000 hrs.

Alumina coupons with AgPt thick-film pad were designed for a TCT test, as shown in Figure 4. The pads on the coupon had 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, Cu coupons with different sizes were placed onto the corresponding AgPt thick film pad and reflowed. The mismatch in coefficient of thermal expansion (CTE) between alumina (6-7 ppm/°C) and Cu (16.7 ppm/°C) was close to that between silicon die (3 ppm/°C) and Cu. Accordingly, the trend of joint reliability observed in the former pair was 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 min. Assembled coupons were checked at 500, 1000 and 2000 cycles, respectively, with the number of the broken parts counted at each checkpoint. Ranking of pastes was established on 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 (Bi42Sn+Bi11Ag+Flux). In the first run, a small melting peak at around 140°C corresponding to the additives (Bi42Sn) is seen, followed by the melting of first alloy (Bi11Ag) with an onset temperature a few degrees lower than 262°C, the solidus temperature of Bi11Ag. However, in the second run after the joint formed from paste, no endotherm could be seen below 260°C. The single melting peak around 262°C came from Bi11Ag. This observation indicates that the reactive element Sn in Bi42Sn
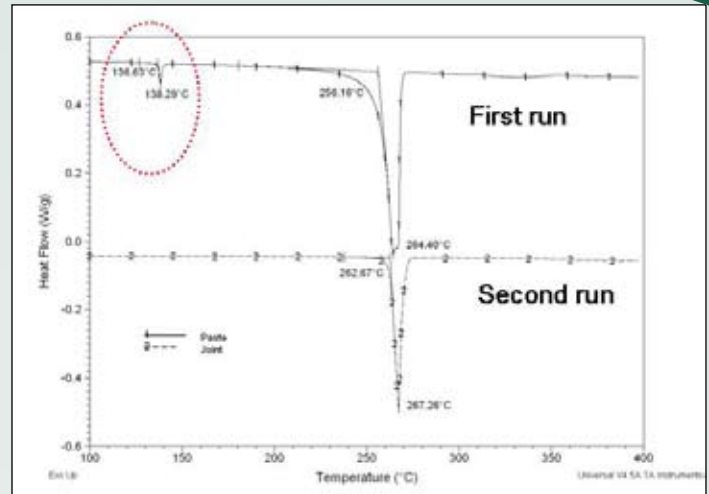

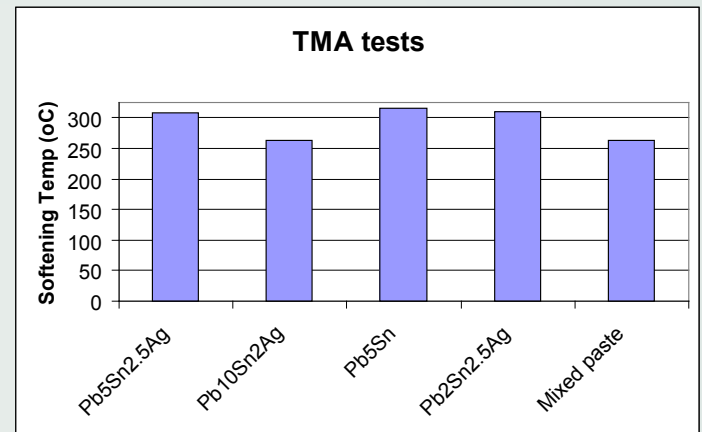Figure 5. First and second runs of DSC for a mixed solder paste.

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

is completely converted into IMCs and there are no more eutectic BiSn phases left after the first run.

TMA
TMA tests were performed on the solder bumps on Cu coupon. The softening temperature was closely associated with the melting temperature of the solder alloys. Figure 6 reveals the softening temperature of a few high lead solders and the mixed powder solder. The softening temperature of the mixed solder was around 262°C, which agreed well with the melting temperature of Bi11Ag measured in DSC. The softening temperature of the mixed powder was comparable with Pb10Sn2Ag, and lower than other high lead solders.

Wetting
The wetting of the mixed solder pastes was studied. Bi11Ag shows obvious dewetting on both Cu and Alloy42 coupons shown in
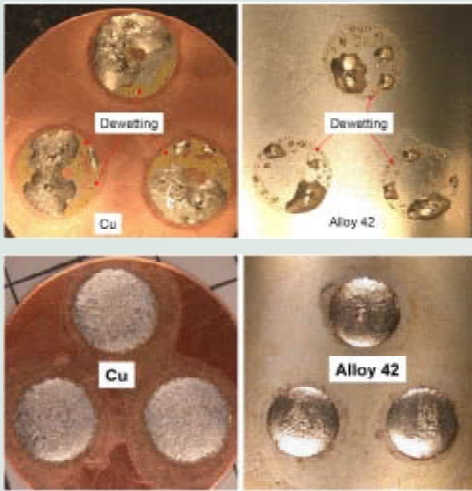
Figure 7. The mixed solder paste with additives showed no obvious trace of dewetting also shown in Figure 7. Recall the comparable wetting of the high lead solder and the mixed powder solder on AgPt thick film pad in Figure 3. This clearly indicates that the additives effectively improve the wetting.
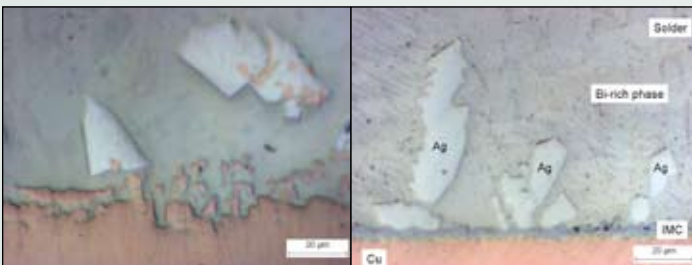

Figure 8. Cross-section images of joints: left, Bi11Ag on Cu and right, the mixed solder (Bi11Ag+Bi42Sn) on Cu.

The left image of Figure 8 shows no IMC layer being formed between Cu and Bi11Ag solder. The dissolution of Cu into the solder matrix has been observed along the interface. With mixed solder paste where Bi42Sn was mixed with Bi11Ag, an IMC layer was observed at the interface between the solder and Cu substrate, shown the right image of Figure 8. This IMC layer was composed mainly of Sn and Cu, indicating that Sn in Bi42Sn is responsible for this IMC formation, and the resultant better wetting.

Voiding

Voiding performance of the mixed solder pastes and various high lead 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 Pb5Sn2.5Ag and mixed solder paste, as shown in Figure 9 and Figure 10. No significant difference in voiding performance can be
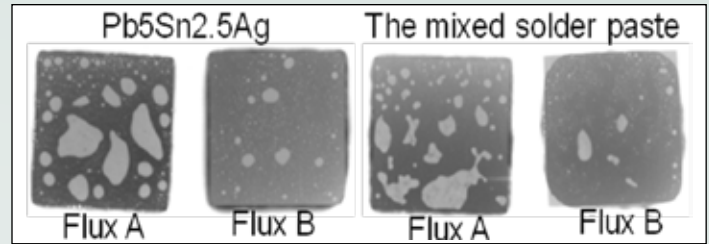

Figure 9. Voiding performance of Pb5Sn2.5Ag (left) and the mixed solder paste (right). Flux B resulted in a lower voiding than flux A.
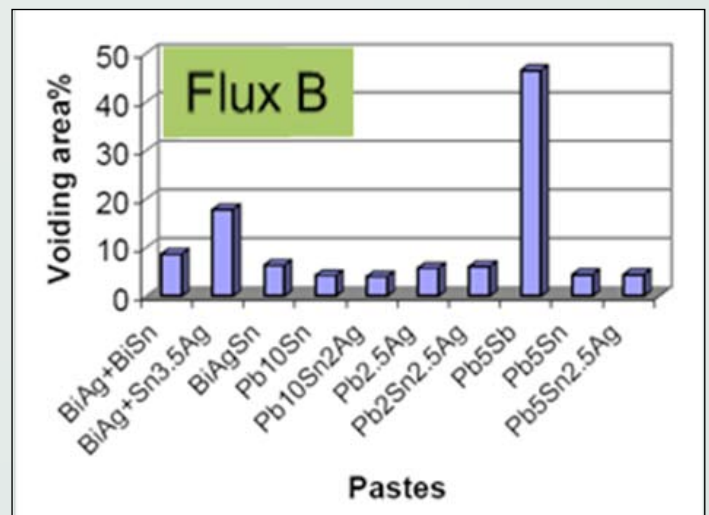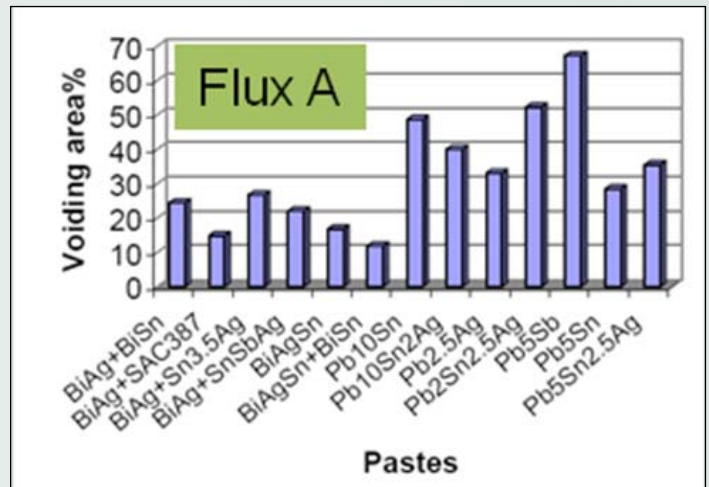

Figure 10. Voiding performance of both high lead solders and the mixed solders with flux A and flux B.

discerned between Pb5Sn2.5Ag and the mixed solder paste when the same flux is employed.

Aging

The cross-section images in Figure 11 show the evolution of IMC layer for a high-lead solder and a mixed powder solder upon aging. With increased aging time, the IMC layer thickness for high-lead

Figure 11. IMC thickness of the high lead solder and the mixed powder solder upon aging at 175oC for up to 1000 hrs.
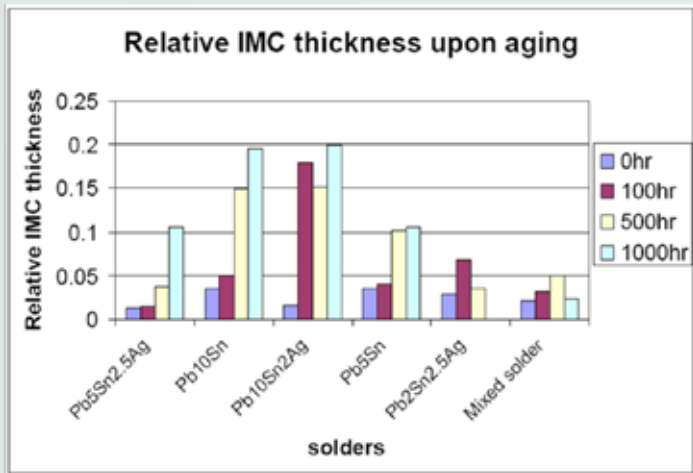
* Relative IMC thickness=IMC thickness/Bondinethickness

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

solder increases, while there is no significant change of IMC layer thickness for the mixed powder solder. The IMC thickness of various high lead 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 IMC thickness and the bondline thickness.

The IMC thickness from the mixed powder solder is found to be insensitive to aging. This is attributable to that most of the reactive element was consumed to form the IMC layer during soldering and no more reactive element was available in the joint for assisting further IMC formation during aging.

Thermal cycling tests

Figure 13 reveals the failure percentage of all the testing pastes as a function of cycling time for three different die sizes. The failure percentage is the ratio between the number of broken parts and the number of total testing parts.
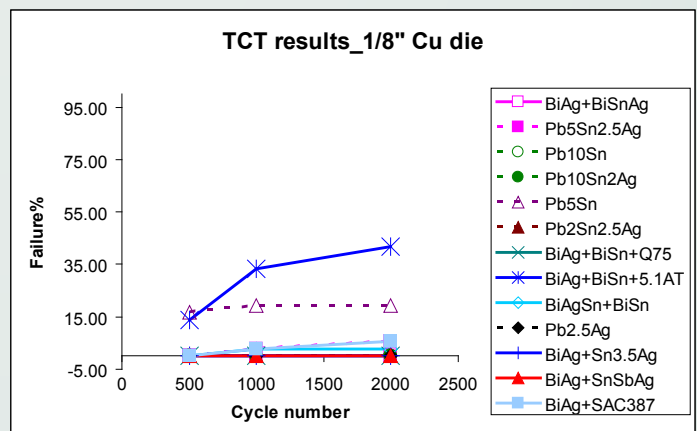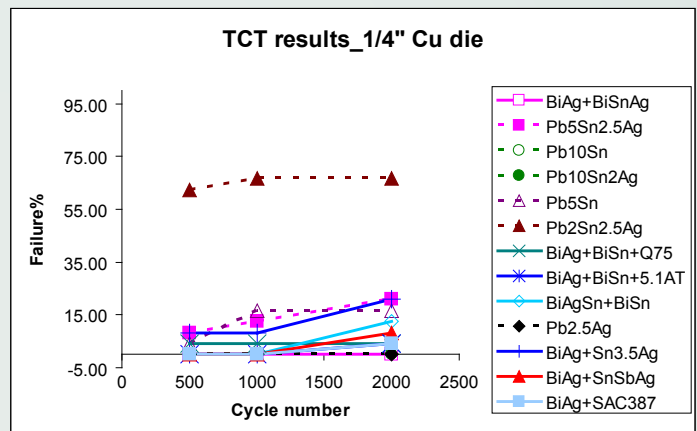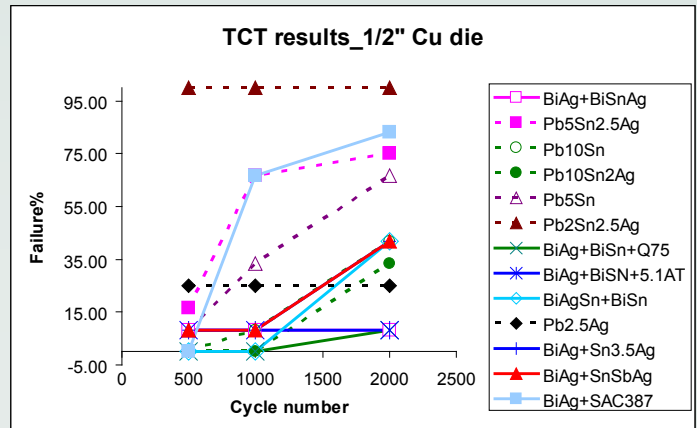

Figure 13. Thermal cycling test results of high lead solders and the mixed powder solder.

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 2000cycles for different pastes. For mid-size (1/4 inch) and small size (1/8 inch) dies, most of the pastes exhibit comparable performance.
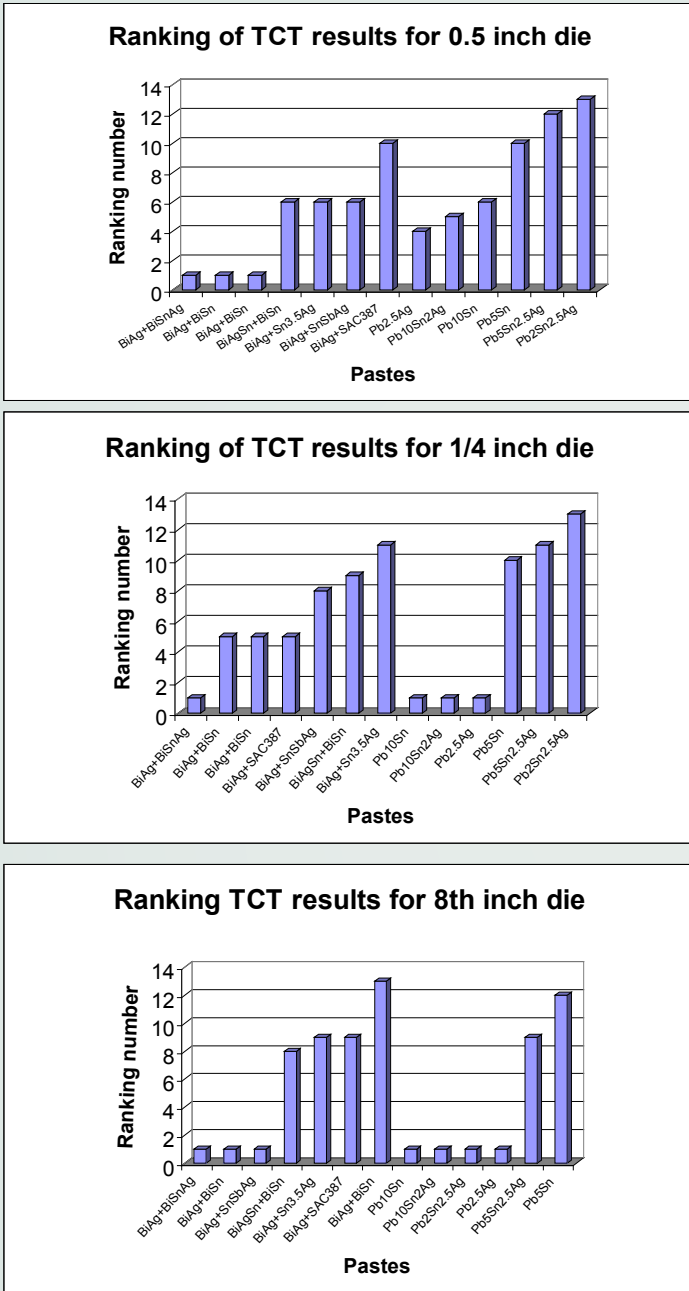
Ranking of TCT results for 0.5 inch die

Ranking of TCT results for 1/4 inch die

Ranking TCT results for 8th inch die

Figure 14. Ranking of all tested pastes under thermal cycling tests for three different die sizes.

The TCT performance is ranked in Figure 14 with paste type as X-coordinate. For the large die size (1/2 inch), three mixed solders rank best, followed by the high lead ones. For mid-size and small size dies, no clear difference in ranking can be discerned between mixed powder group and high lead group. Overall, mixed powder system performs equal to or better than high lead solders in TCT tests.
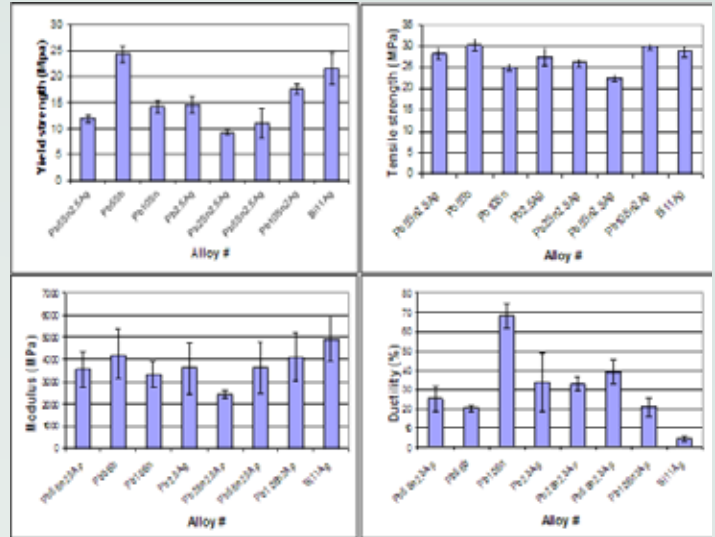

Figure 15. Mechanical behavior of the high lead solder alloys and Bi11Ag alloy from tensile tests on quarter inch bars.

Discussion

The design of the mixed powder solder pastes is aimed at finding a HTLF solder solution, which can satisfy the requirements of the die attach application. In the system, the first alloy is designed to dominate the melting behavior and the mechanical behavior of the joint. The additives in a minor amount, melting earlier than or at the same time as the first alloy during soldering, are designed to modify the bonding interface and thus improve the associated bonding strength. A thin layer of IMCs at the interface between solder and 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 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 the mixed powder approach, will not be effective in improving the wetting. Direct alloying Sn in BiAg will deplete Sn by the formation of Ag3Sn IMCs. As a result, no free Sn will be available for assisting the wetting. The poor wetting of Bi10Ag4Sn on AgPd thick file pad, shown in Figure 1, indeed verifies the concern arising from the direct alloying method. Additionally, DSC data of the second run indicates that the additives have no harmful influence on the melting behavior of the first alloy at post reflow. This is consistent with TMA findings in Figure 6.

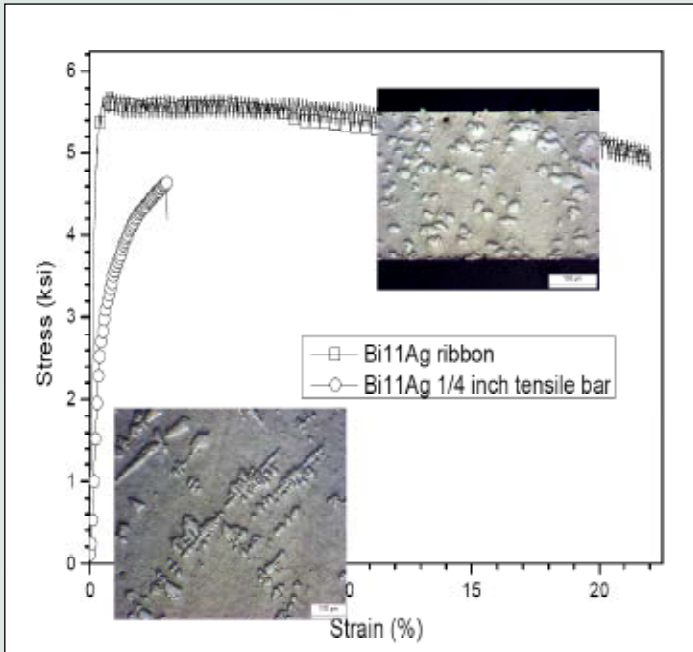With the mixed powder solder, an improved wetting was observed

Figure 16. Bi11Ag microstructure and mechanical behavior of the quarter inch tensile bar and the 10 mil thick ribbon.

comparing BiAg to BiAgSn, as shown in Figures 1, 3 and 7. The improved wetting is attributed to the formation of the 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 insensitiveness of the IMC layer thickness towards aging. The constant IMC layer thickness is expected to stabilize the joints.

TCT results show mixed ranking results on the mixed powder solders versus the high-lead ones. Generally speaking, Bi-rich solder is strong but brittle. In Figure 15, the bulk Bi11Ag alloys have a comparable or higher strength and higher modulus than the bulk high lead alloys in tensile tests using cast 1/4-inch bar. However, the ductility of Bi11Ag alloy is lower than all high lead solders tested. Thus, it was not expected that a comparable TCT results could be obtained for both mixed powder solders and the high lead ones.

There are two rationales for the TCT results for the mixed powder system. First, the microstructure of joint from mixed powder is significantly finer than that of the 1/4-inch tensile bars. For the quarter inch Bi11Ag tensile bar, Ag dendrites of several hundred microns are observed, as shown in Figure 16. On the other hand, the Ag particle sizes in the Bi11Ag ribbon range from 20-50 microns, and the ribbon shows higher yield strength, higher modulus and much higher ductility (20%) than tensile bar. The Ag particle size in joint from mixed powder (Figure 8) ranges from 20-40 microns,

thus is fairly close to that of ribbon. Consequently, the joint is expected to exhibit mechanical properties similar to that of ribbon, which explains the comparable TCT results as the high lead ones. Second, the IMC layer of the mixed powder system is thin and stable, while that of high lead ones thickened significantly with time (Figure 12).

Conclusions

A mixed powder solder paste technology has been invented to design the alternative HTLF solder pastes. The paste is designed to be composed of the high melting first alloy powder as majority, the additive powder as 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, hence resulting in a high melting solder joint. In the example, mixed powder paste system studied here, a melting temperature above 260°C was verified by DSC and TMA data. The mixed powder solders show a significantly improved wetting compared to Bi11Ag. 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 ones do show a considerable increase.

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