

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 eutectic SnPb system by the Sn/Ag/Cu system, the development of drop-in lead-free alternatives for high melting high lead solder alloys is still far from mature. The Bi/Ag 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 Bi/Ag/X 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 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 solders do 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 electronic 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 Pb-Sn have been widely and well-studied and Sn/Ag, Sn/Cu and Sn/Ag/Cu solders are becoming the mainstream for 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 assembly. The major requirements for the die attachment are (i) a softening temperature no lower than 260°C, (ii) a drop-in compatible with the current process for high-lead solders, (iii) good thermal fatigue resistance, and (iv) low cost.

Currently, there are no drop-in lead-free alternatives for the high lead-containing solders. Although some possible alternative lead-free solders and some innovative potential solutions for the die-attachment applications have been studied and reported. The possible alternative solders include Sn/Sb, Bi/Ag, Zn/Sn, Zn/Al and Au/Sn etc. [1-4].

Sn/Sb 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, is not acceptable [1].

Zn-based alloys, including the eutectic Zn/Al, Zn/Al/Mg and Zn/Al/Cu [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 only around 200°C. The pasty state of the Zn/Sn solder at 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 Au/Sn, 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.

Bi/Ag 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 a couple major concerns: (1) poor wetting on many surface finishes, including the most commonly used Cu, and (2) the low ductility.

On basis of the softening temperature requirement for the high-melting lead-free solder, Sn/Sb and Zn/Sn solders are not suitable. The extremely high cost of Au-rich solders limited their acceptance by the industry. Zn/Al and Bi/Ag meet the melting temperature requirement and have a reasonably low cost. However, the high affinity to oxygen in Zn/Al solder system, or the poor reaction chemistry between Bi/Ag 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 Bi/Ag and Zn/Al still make them attractive as the candidates for the high-temperature lead-free solders.

The Ge-doped Bi/Ag 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 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.

However, directly alloying Sn into Bi/Ag could cause (1) a low melting phase (Bi/Sn) if Sn is excessive and/or (2) the complete conversion of Sn into Ag_3Sn 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 Bi/Ag alloys, as shown in Fig.1.



Figure 1 - Wetting of Bi/11Ag (left) and Bi/10Ag/4Sn (right) on Ag/Pd thick film pad Al_2O_3 substrate

Alternatively, a novel technology to improve the interface reaction chemistry efficiently has been invented to provide a

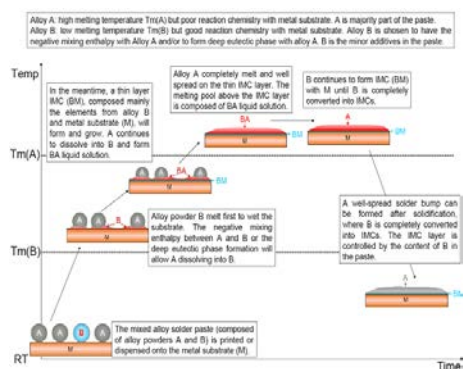


Figure 2 - Design idea of the mixed solder paste system

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. 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, Bi/Ag 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 Ag/Pd (left) and Ag/Pt (right) thick-film pad Al_2O_3 substrate, shown in Fig.3. Wetting of Pb/5Sn/2.5Ag on a Ag/Pt thick-film pad Al_2O_3 substrate has also been exhibited in Fig.3. A comparable spreading from both the 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 Bi/Ag system 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.

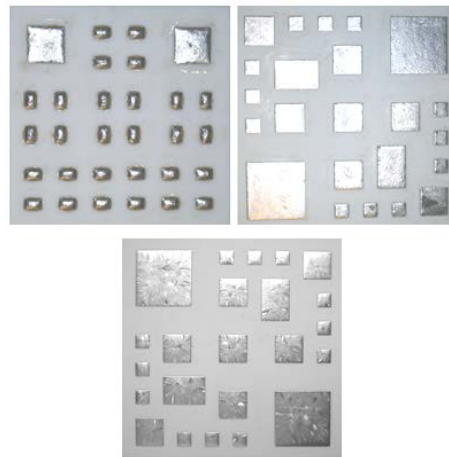


Figure 3 - Wetting of the mixed-powder solder on Ag/Pd (left) and Ag/Pt (right) thick-film pad Al_2O_3 substrate. Wetting of Pb/5Sn/2.5Ag on Ag/Pt (bottom) thick film pad Al_2O_3 substrate.

Experimental

1. Pastes

In 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.

2. 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. Then, a quarter 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 1000 hrs. The evolution of the IMC layers was studied at different aging times, namely, 0, 100, 500, and 1000 hrs.

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

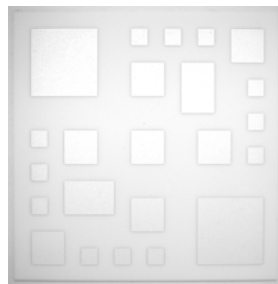


Figure 4 - Customized Ag/Pt thick-film pad Al_2O_3 substrate.

reflowed. The mismatch in coefficient of thermal expansion (CTE) between alumina (6-7 ppm/ $^\circ\text{C}$) and Cu (16.7 ppm/ $^\circ\text{C}$) 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

1. DSC

With appropriate design of the mixed solder paste system, the additives should not influence the melting behavior of the first alloy. Fig. 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 at 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 Bi/Sn phases left after the first run.

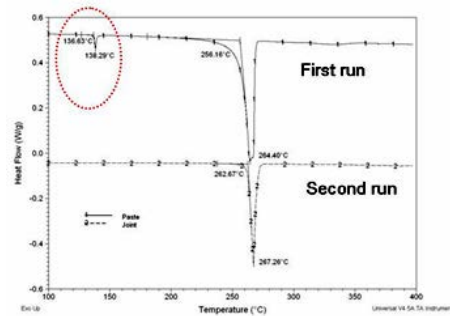


Figure 5 - First and second runs of DSC for a mixed solder paste

2. 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.

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

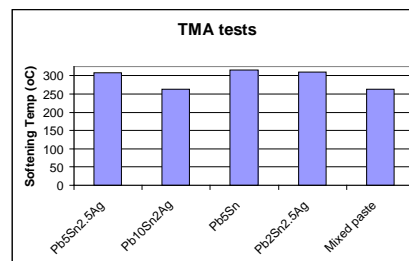


Figure 6 - TMA test results for the high lead-containing solder and the mixed solder paste

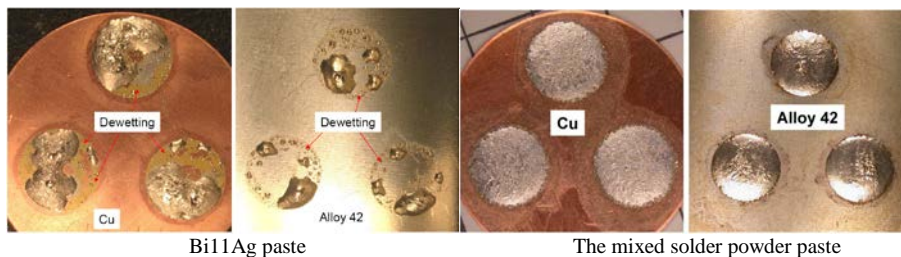


Figure 7 - Improved wetting of the mixed solder paste comparing Bi/11Ag paste on Cu to Alloy 42 coupons.

3. Wetting

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

The left image of Fig. 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 Fig. 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 20 μ m 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 Bi/Ag joint, the fine Ag particles and the associated network band have not been observed.

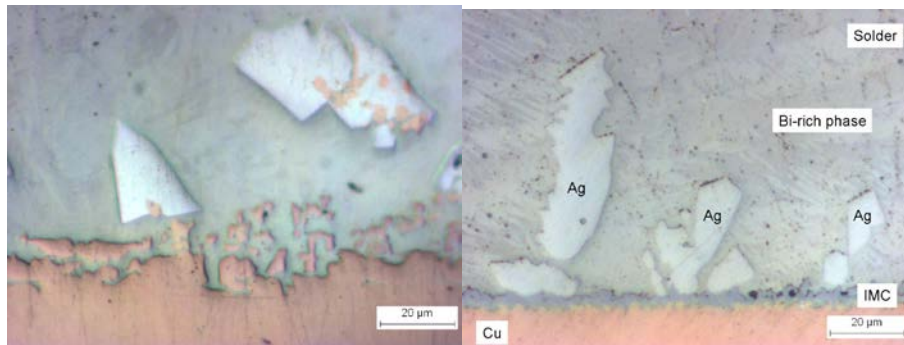


Figure 8 - Cross-section images of joints: left, Bi/11Ag on Cu and right, the mixed solder (Bi/11Ag+Bi/42Sn) on Cu.

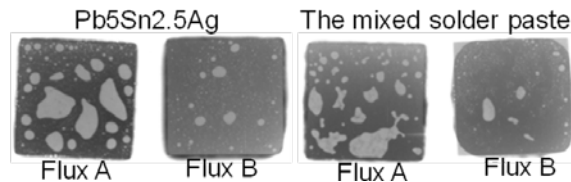


Figure 9 - Voiding performance of Pb/5Sn/2.5Ag (left) and the mixed solder paste (right). Flux B resulted in a lower voiding than flux A.

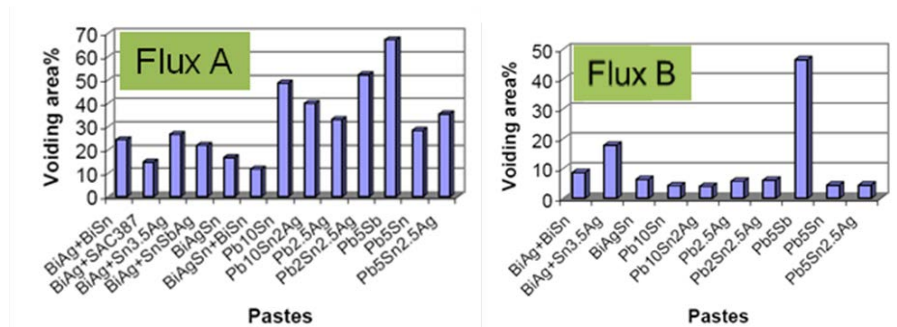


Figure 10 - Voiding performance of both high lead-containing solders and the mixed solders with flux A and flux B.

4. Voiding

Voiding performance of the mixed solder pastes and various high lead-containing solders was studied via X-ray inspection, as shown in Fig. 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 Fig. 9 and Fig. 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.

5. Aging

The cross-section images in Fig. 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 Fig. 12. Here the IMC thickness is expressed as relative IMC thickness, which is defined as the ratio between the measure IMC thickness and the bondline thickness. The proportional relationship between the IMC thickness and the Sn is also illustrated in Fig. 13.

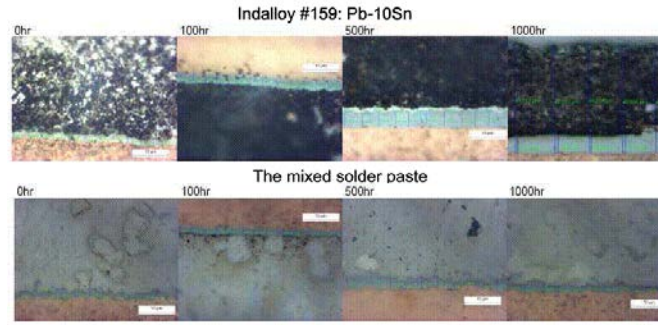


Figure 11 - IMC thickness of the high lead-containing solder and the mixed powder solder upon aging at 175°C for up to

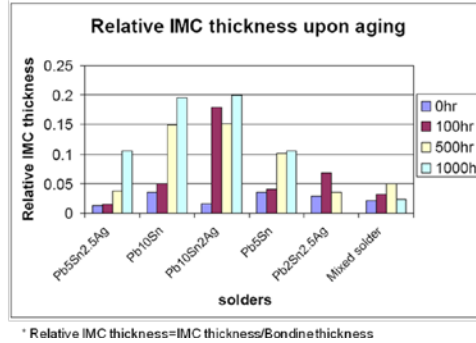


Figure 12 - Relative IMC thickness of high lead-containing solders and the mixed powder solder

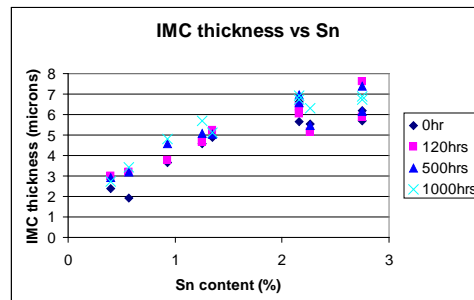


Figure 13- The relationship between IMC thickness and Sn content

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 (1) a low melting phase (i.e. Bi/Sn, Bi/In) and (2) 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, hence a higher reactive element content is not recommended. In this study, the IMC thickness for all the mixed powder solder pastes exhibits insensitivity towards 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.

6. Thermal cycling tests

Fig. 14 reveals the failure percentage of all the testing pastes as a function of cycling time for the three different die 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 2000 cycles for different pastes. For mid-size (1/4 inch) and small size (1/8 inch) die, most of the pastes exhibit comparable performance.

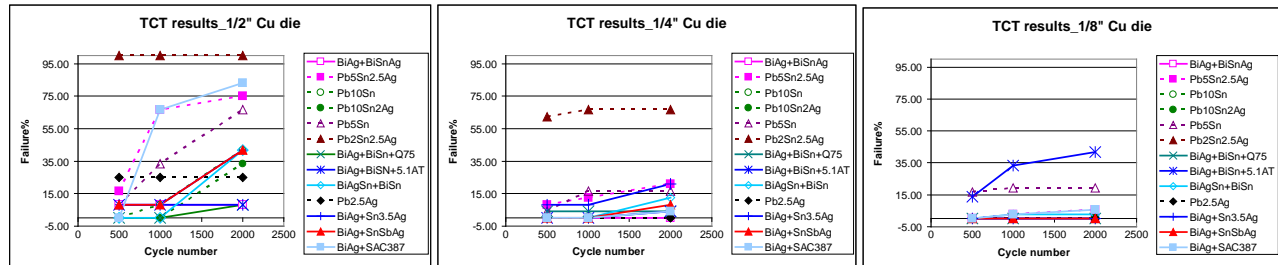


Figure 14 - Thermal cycling tests results of high lead-containing solders and the mixed powder solder.

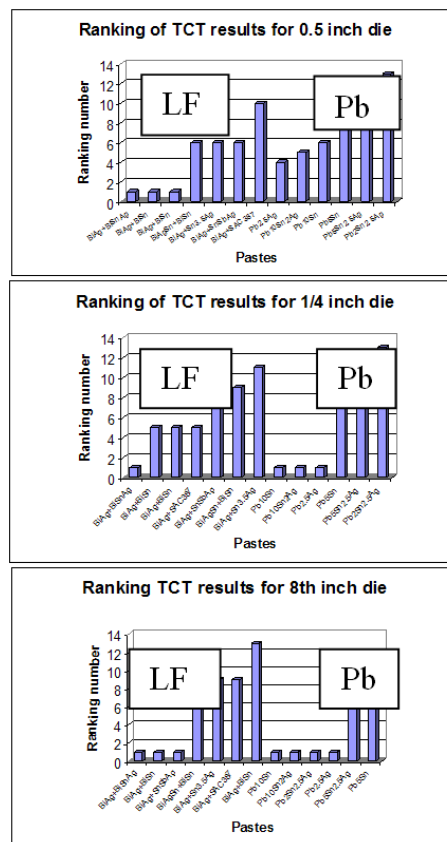


Figure 15 - Ranking of all tested pastes under thermal cycling tests for three different sized die

The TCT performance is ranked in Fig. 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 pastes is aimed at finding a 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.

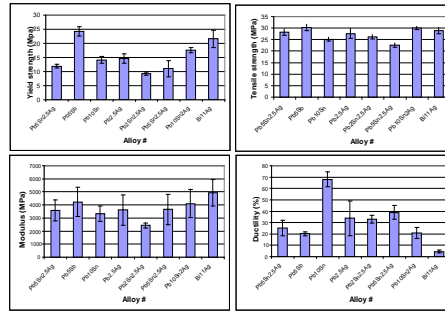


Figure 16 - Mechanical behavior of the high lead-containing solder alloys and Bi/11Ag alloy from tensile tests on quarter inch bars.

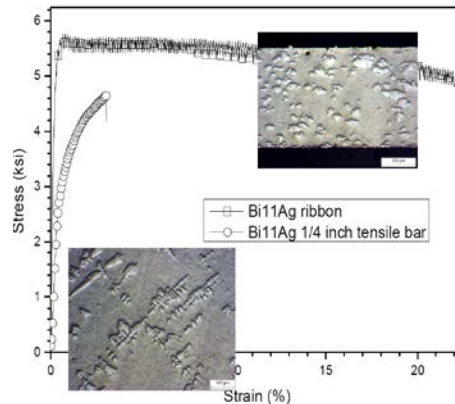


Figure 17 - Bi/11Ag microstructure and mechanical behavior of the quarter inch tensile bar and the 10 mil thick ribbon.

An endothermic peak, due to the additives in the first run, is seen in Fig.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 Bi/Ag 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 Ag/Pd thick file pad, shown in Fig.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 Fig. 6.

With the mixed powder solder, an improved wetting was observed, comparing to Bi/Ag and Bi/Ag/Sn as shown in Fig.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 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-containing solders. Generally speaking, Bi-rich solder is strong, but brittle. In Fig. 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 a comparable TCT results can be obtained for both mixed powder and high lead-containing solders.

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 quarter inch tensile bars. In the quarter inch Bi/11Ag tensile bar, Ag dendrites of several hundred microns are observed, as shown in Fig. 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 μm to 40 μm , and the fine particles (sub-microns) forming the network band to isolate the Bi colonies (Fig. 8 and Fig. 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 Bi/Ag tensile bars. After TCT

tests, although the fine Ag-rich particles become coarser and the spacing between the particles enlarged, they are still well dispersed in the joint and in submicron size, as shown in Fig. 18. The relatively well-maintained microstructure indicates that the mechanical properties may be well preserved during TCT test. Secondly, the well-controlled IMC thickness (Fig. 12) may also contribute to the improved reliability. More studies on the joint microstructure and the microstructural evolution are in progress.

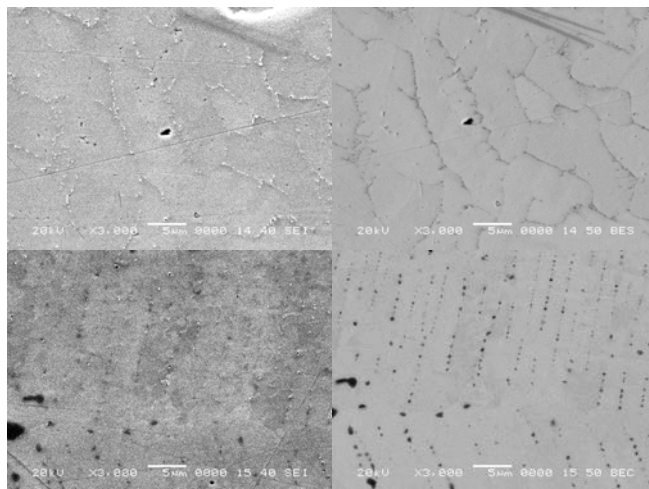


Figure 18 - The microstructure of the Bi/Ag/X solder joint before TCT tests (top left: SE image and top right: BS image) and after TCT tests (bottom left: SE image and bottom right: BS image).

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 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°C was verified by DSC and TMA data. The mixed powder solders show a significantly improved wetting comparing 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 do show a considerable increase. The underlying mechanism of the enhanced reliability for the Bi/Ag/X system has been investigated based on observation of the joint microstructure and the microstructural evolution.

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Requirements for High Temperature Lead-free (HTLF) Solders

- RoHS, WEEE regulations etc
- Processing temperature below 400°C
- Resisting the re-melt of the subsequent reflow at around 260°C
- Compatible with current mainstream surface finishes, including wetting
- Good thermal fatigue resistance
- Low cost

Potential HTLF Solders

Sn-Sb+ alloys

- Sn-Sb, Sn-Sb-Ag etc.

Zn based alloys

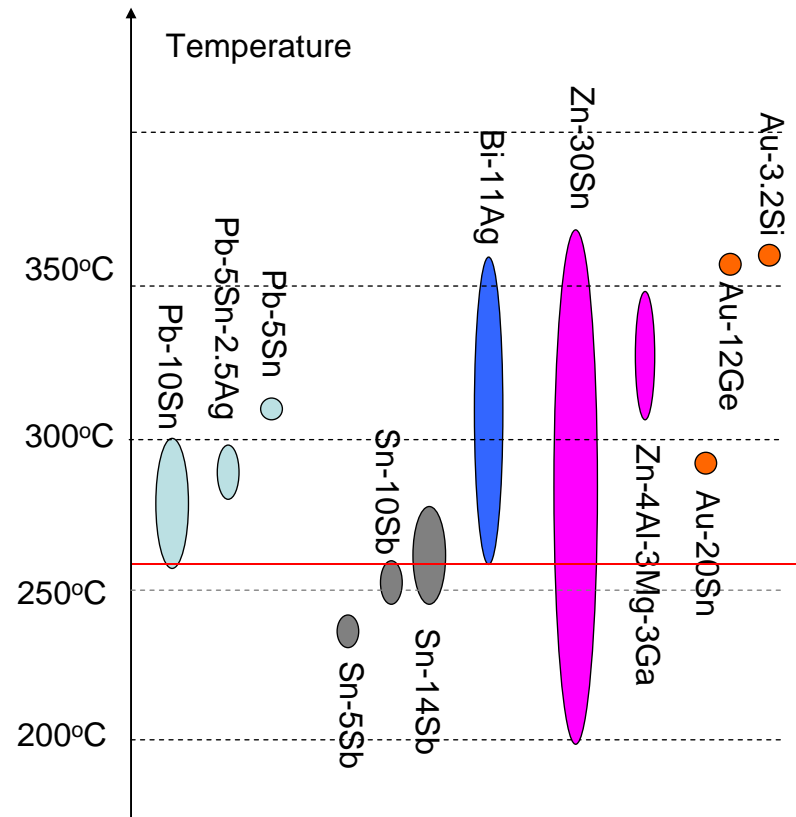
- Zn-Al & Zn-Sn

Au based alloys

- Au-Sn, Au-Si, Au-Ge

Bi based alloys

- Bi-11Ag, Bi-Cu, Bi-Zn & Bi-2Sn-3Cu

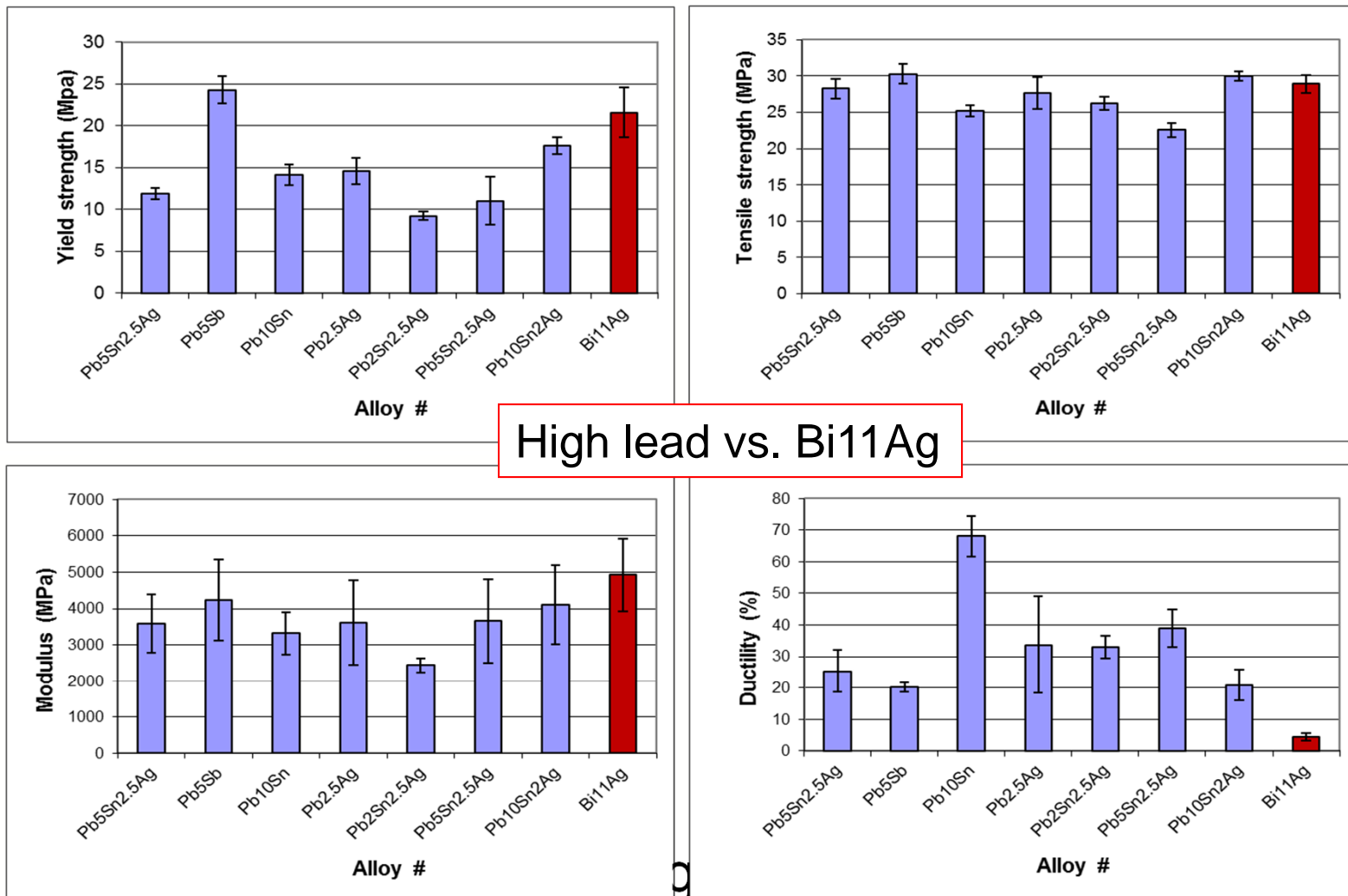




Overview of Potential HTLF Solders

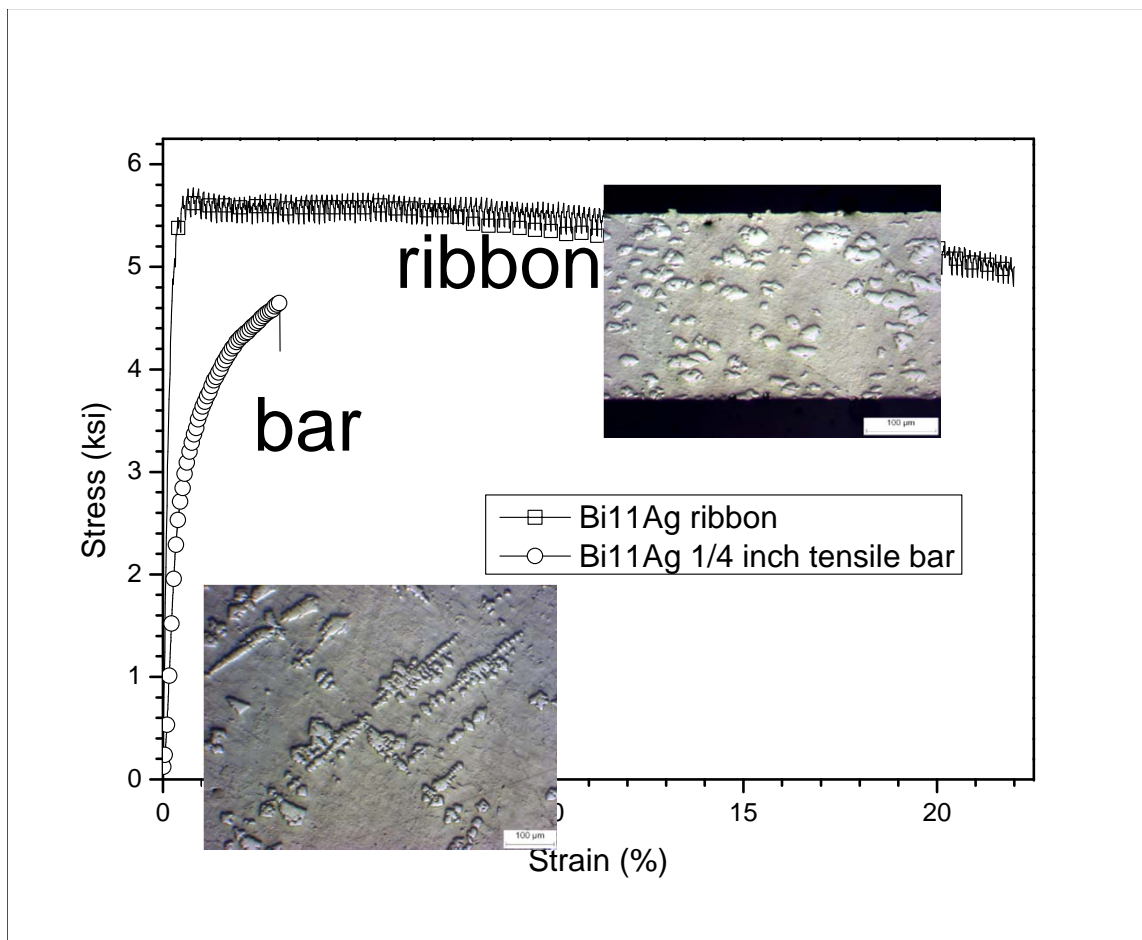
- **Sn-10Sb**
Good mechanical properties
Good thermal and electrical conductivity
Solidus temperature below 250°C
- **Zn-(25-35)Sn**
Good strength and ductility
Excellent thermal conductivity
Solidus temperature ~200°C
Thick IMC layer after reflow and thermal aging
- **Au-Sn, Au-Si & Au-Ge**
Excellent electronic & thermal conductivity
Good reflow temperature resistance
Too Expensive
- **Bi-11Ag**
High strength **but low ductility**
Acceptable electric conductivity
Poor wettability

Mechanical Properties (Bi11Ag vs Pb)



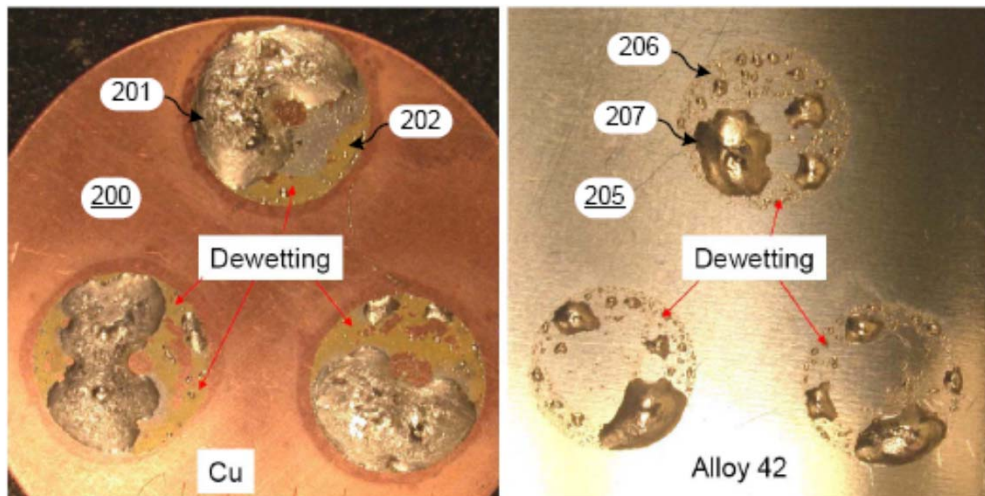


Mechanical Properties of Bi11Ag

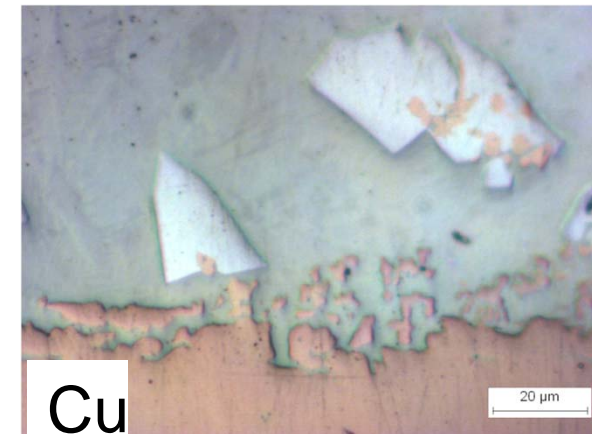


Although bar is poor in ductility, the ribbon show ~20% elongation. It indicates that ductility could be achieved in Bi11Ag system if the microstructure is optimized.

Wetting Problem of Bi11Ag



Bi11Ag pastes show very poor wetting on Cu and Alloy42.



There is no IMCs formed at the interface between solder and Cu substrate.

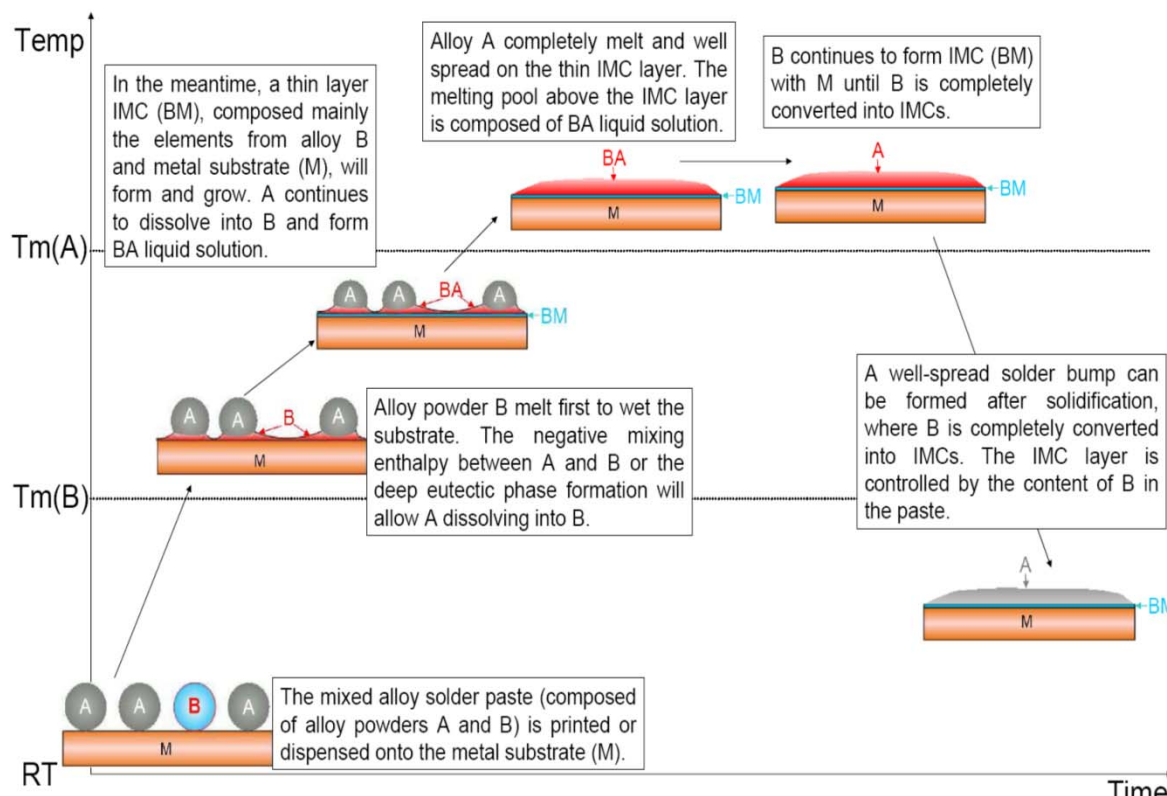
Bi-Ag can exhibit high strength together with good ductility if refined & well dispersed Ag particles are achieved within Bi matrix. Poor wetting is the major concerns in Bi-Ag system.



Design of Mixed Powder Paste System

Paste is mixed with two or more different metal powders. The first alloy powders consisted of the majority metal load in paste. The secondary powders are additives.

Alloy A: high melting temperature $T_m(A)$ but poor reaction chemistry with metal substrate. A is majority part of the paste.
 Alloy B: low melting temperature $T_m(B)$ but good reaction chemistry with metal substrate. Alloy B is chosen to have the negative mixing enthalpy with Alloy A and/or to form deep eutectic phase with alloy A. B is the minor additives in the paste.



First alloy powders in the paste dominate the melting behavior, the mechanical properties and thus the reliability.

Secondary alloy powders in the paste improve the wetting and dominate the formation of the IMCs. They should not harm the melting behavior of first alloy.

Using Bi-Ag system as the first alloy, Sn, In and Zn or their alloys as the secondary alloy powders.

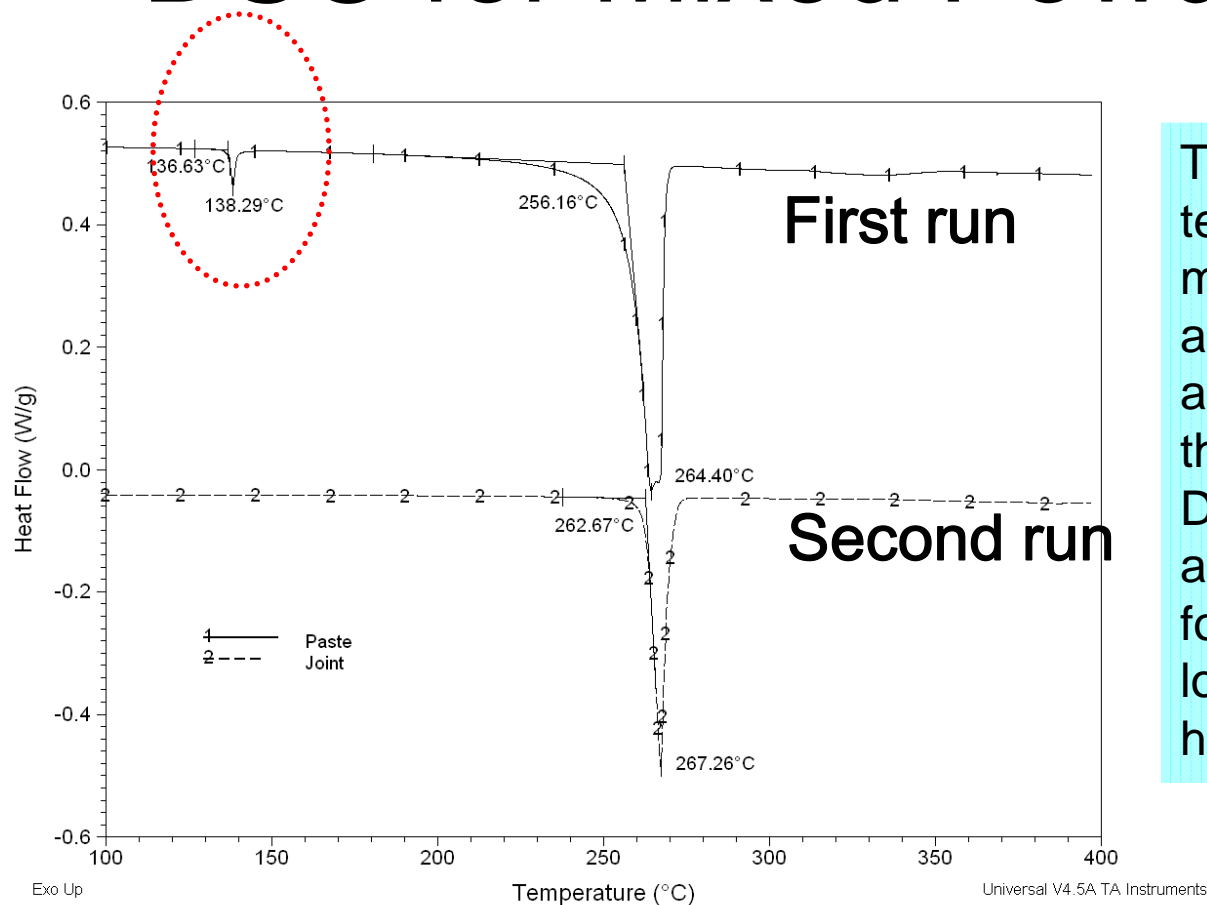


Design of Experiments

- Melting behavior – DSC & TMA
- Wetting - Visual
- Voiding test – X-ray
- Thermal aging resistance (@175°C for up to 1000hrs) – Cross-section
- Temperature cycling test (-55°C to 125°C for up to 2000cycles) – parts integrity



DSC for Mixed Powder Paste

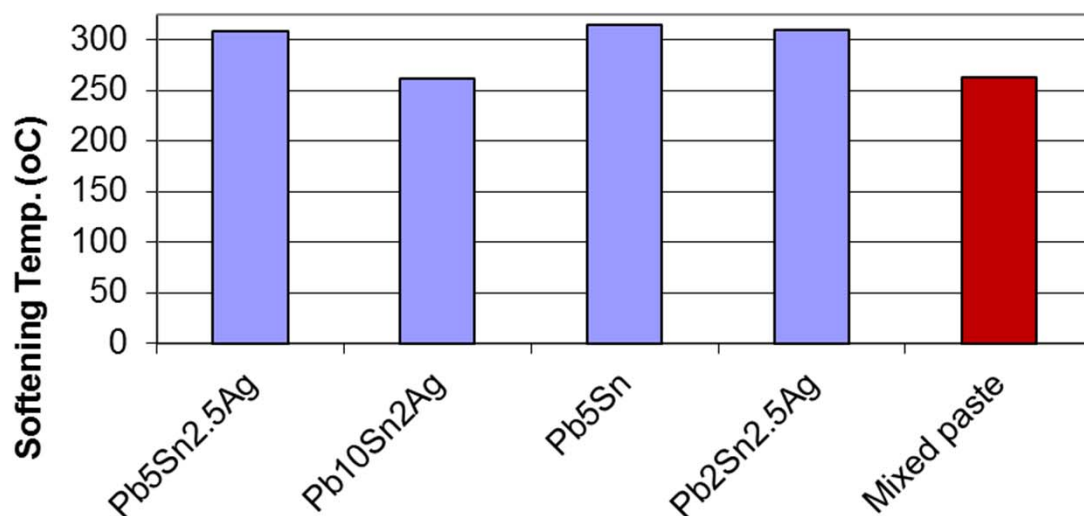


The additives melt at low temperature to wet the metallization surface finish and form IMCs. Then the first alloy start to melt and wet on the IMCs formed early. During soldering, the additives are consumed to form IMCs, with little or no low melting phase remain. A high temp joint thus formed.



TMA Data Support DSC Findings

TMA tests



Solder paste is sandwiched between two 0.25" Cu coupons and reflowed to form the joints.

TMA tests are performed on these joints.

Heating rate: 5°C/min.

Temp range: 20 to 400°C.

The softening temperature for the mixed solder paste being comparable to Pb10Sn2Ag, but lower than Pb5Sn2.5Ag, Pb5Sn and Pb2Sn2.5Ag. This observation is in accordance with DSC results.

Wetting of Mixed Powder Superior

The mixed solder powder pastes exhibit the improved wetting on Cu, alloy 42, & Ag thick film.

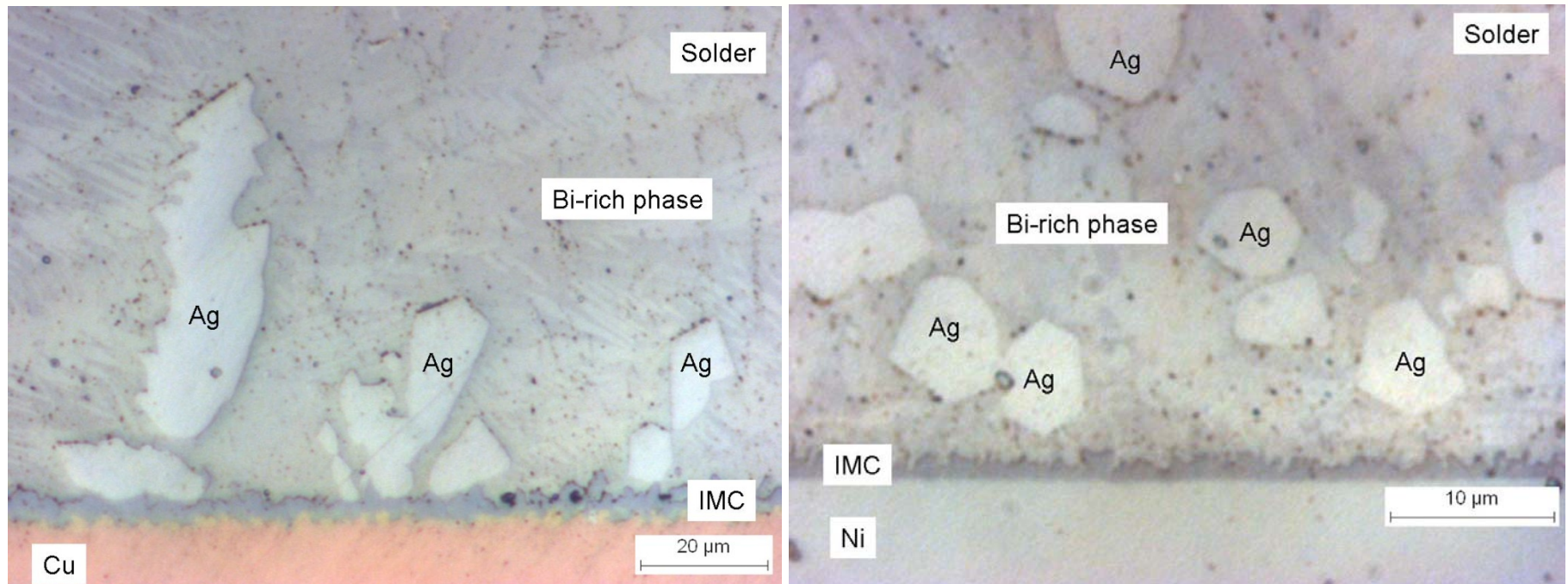


Left: mixed solder paste on Cu
Right: mixed solder paste on Alloy 42

Left: mixed solder paste /Ag-Pd-Alumina
Right: mixed solder paste /Ag-Pt-Alumina



Cross-section of Interface Shows Reaction



The additives formed IMC layer at the interface between the solder and the substrate. The IMC layer thickness is controlled by amount of the additives in the pastes.

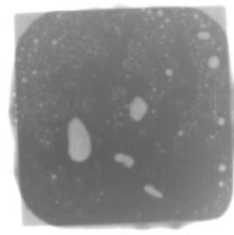
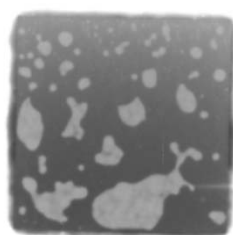
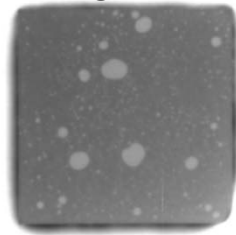
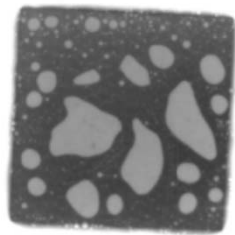
Well-dispersed and refined particles are observed in the joints, similar in size to that in ribbons.



Voiding of Mixed Powder Looks Good

Pb5Sn2.5Ag

The mixed solder paste



656-63-1

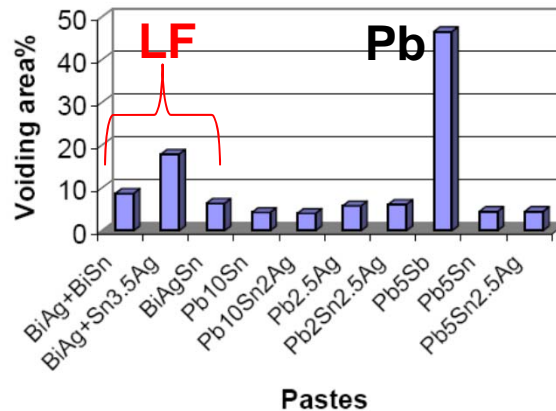
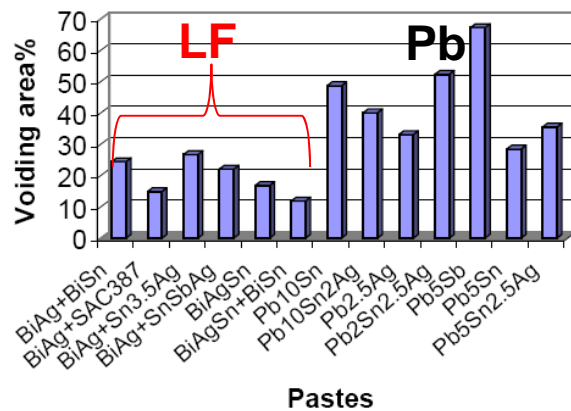
656-63-2

656-65-3

656-65-5

Flux: A B
Voiding_Q75 flux series

A B
Voiding_5.1AT flux series



Joints between a 0.25''x0.25'' Cu cap and Cu substrate achieved. Voiding inspected by X-ray.

Voiding performance of the mixed solder paste system is comparable with or better than high lead pastes.

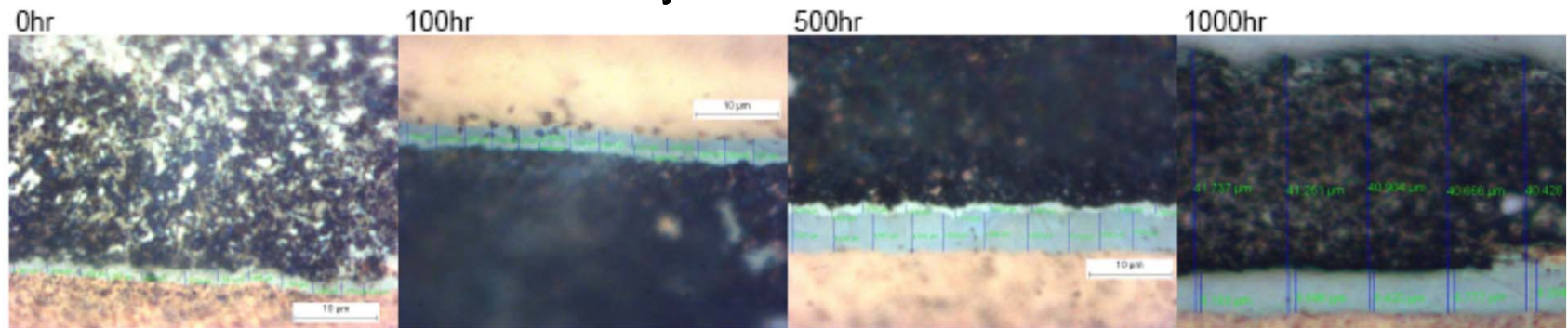


Controllable IMC Thickness of Mixed Powder Pastes

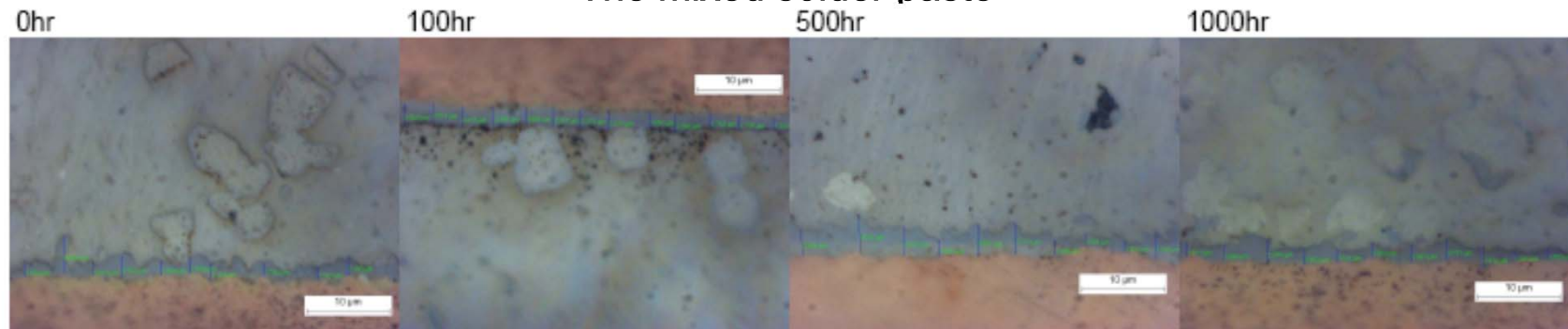
Aging temperature: 175°C

Negligible IMC thickness change for mixed powder paste.

Indalloy #159: Pb-10Sn

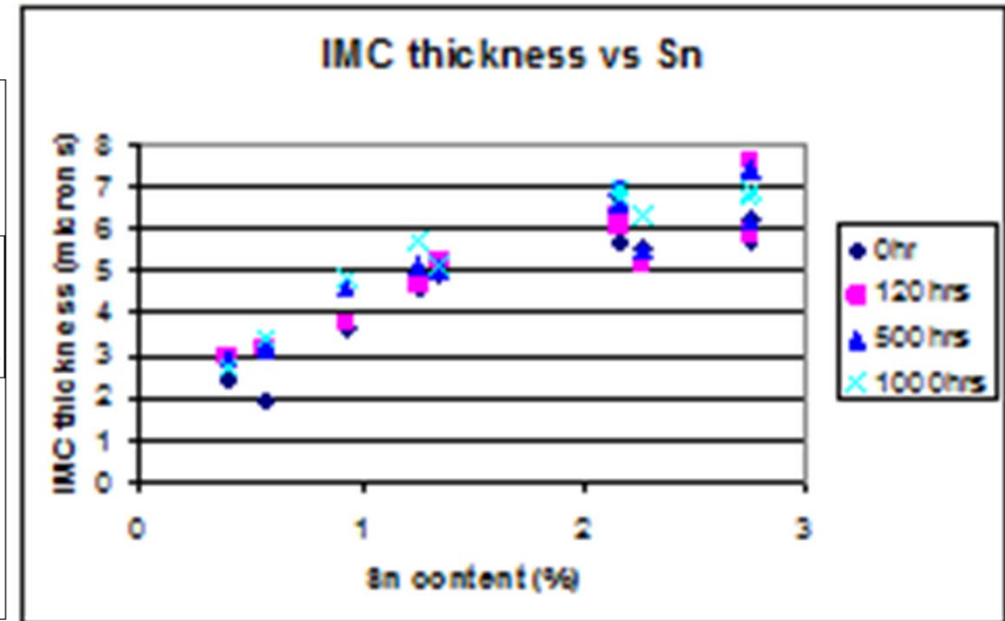
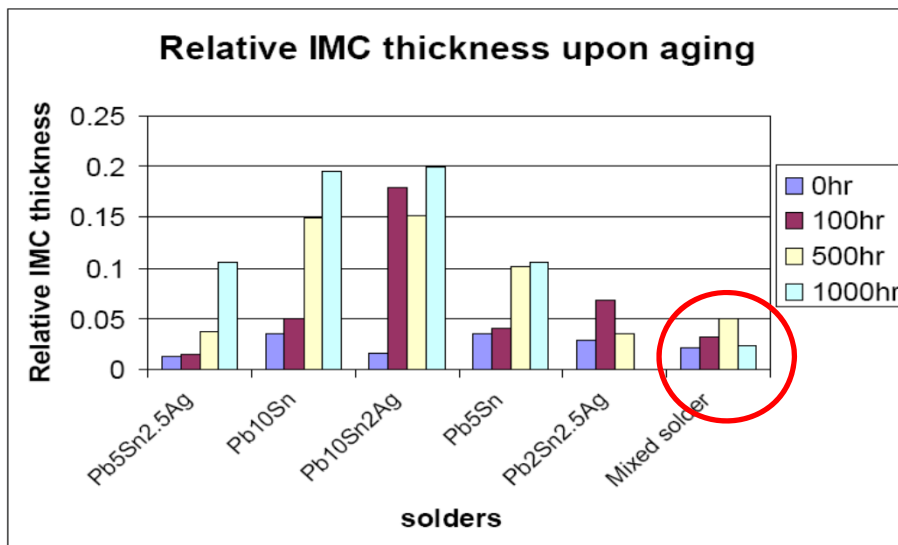


The mixed solder paste





IMC Thickness Of Mixed Powder Insensitive to 175°C Aging



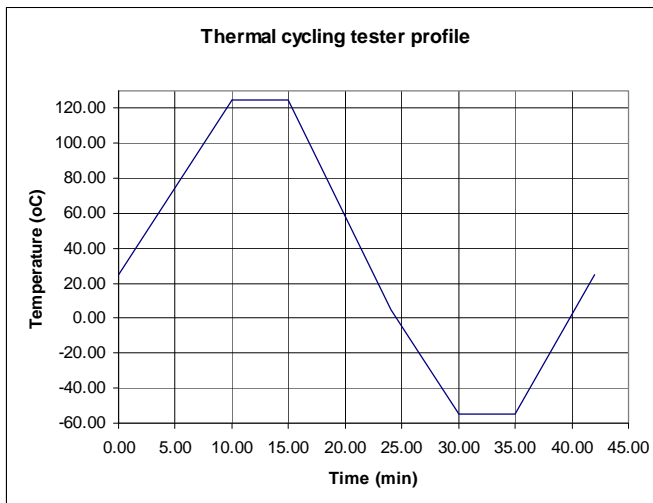
* Relative IMC thickness=IMC thickness/Bondline thickness

IMC thickness is closely related to Sn content in solder. The mixed solder pastes, with the controlled Sn content, shows the smallest changes of IMC thickness upon aging.

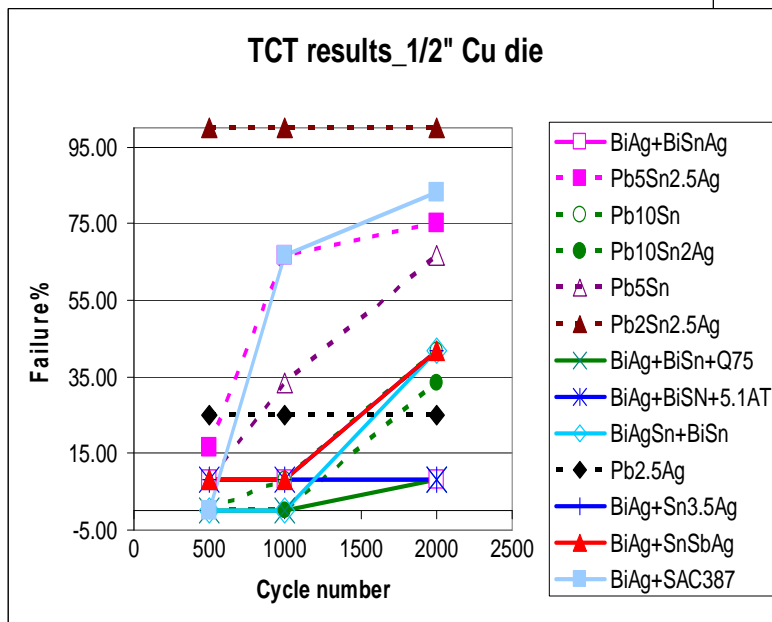


TCT Test Design

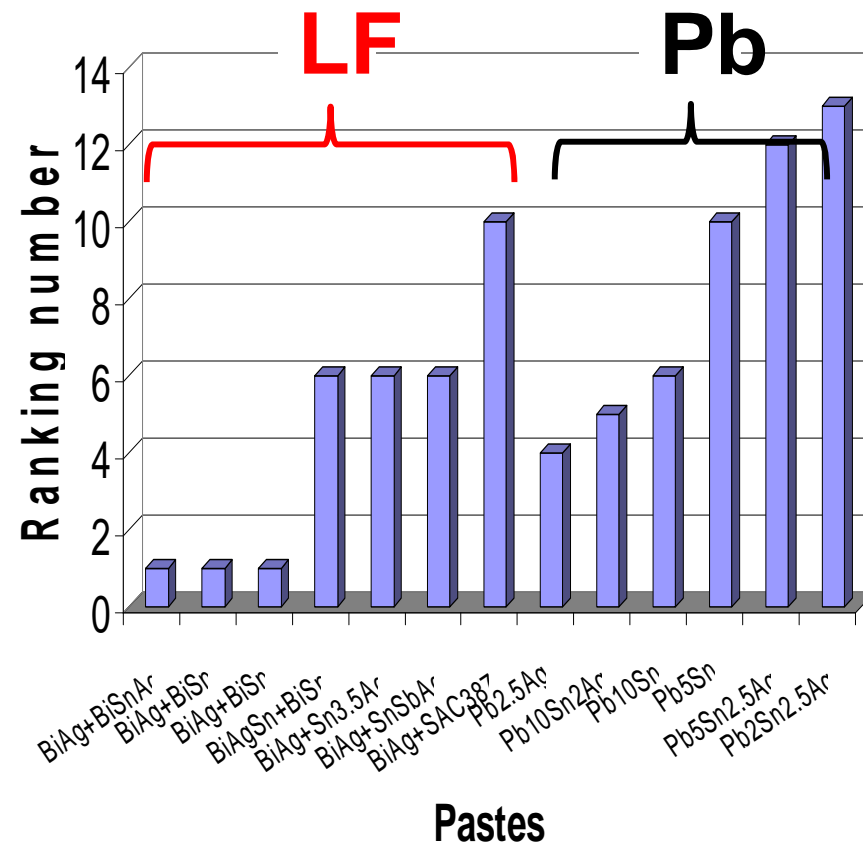
- Ag-Pt thick film pads on Alumina coupon
- 4mil thick stencil
- 2 x 0.5"x0.5" Cu dies
- 4 x 0.25"x0.25" Cu dies
- 6 x 0.125"x0.125" Cu dies
- Checkpoints: 500,1000 and 2000 cycles
- Number of broken parts is counted at each check point, & form the base of ranking. The ranking of all the high temperature solders under TCT results varied with die size.



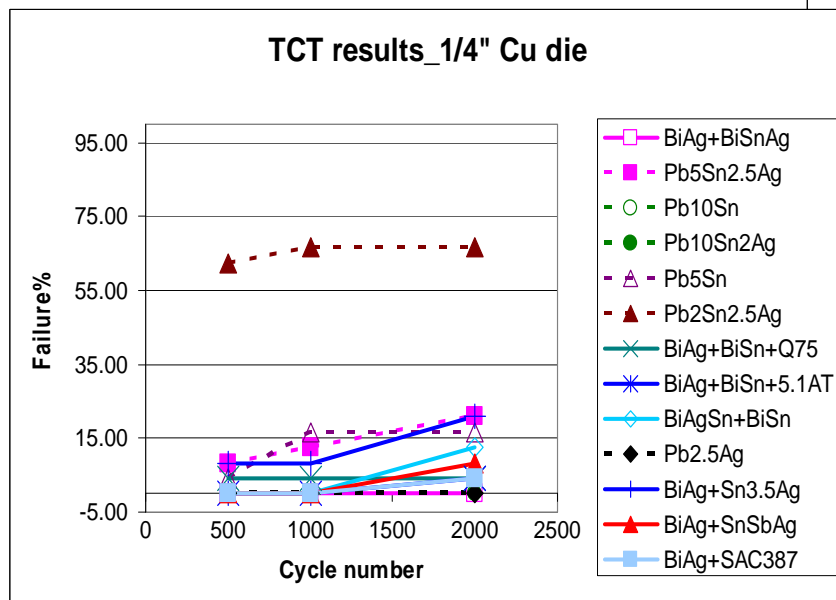
TCT Ranking of 0.5" Cu Die



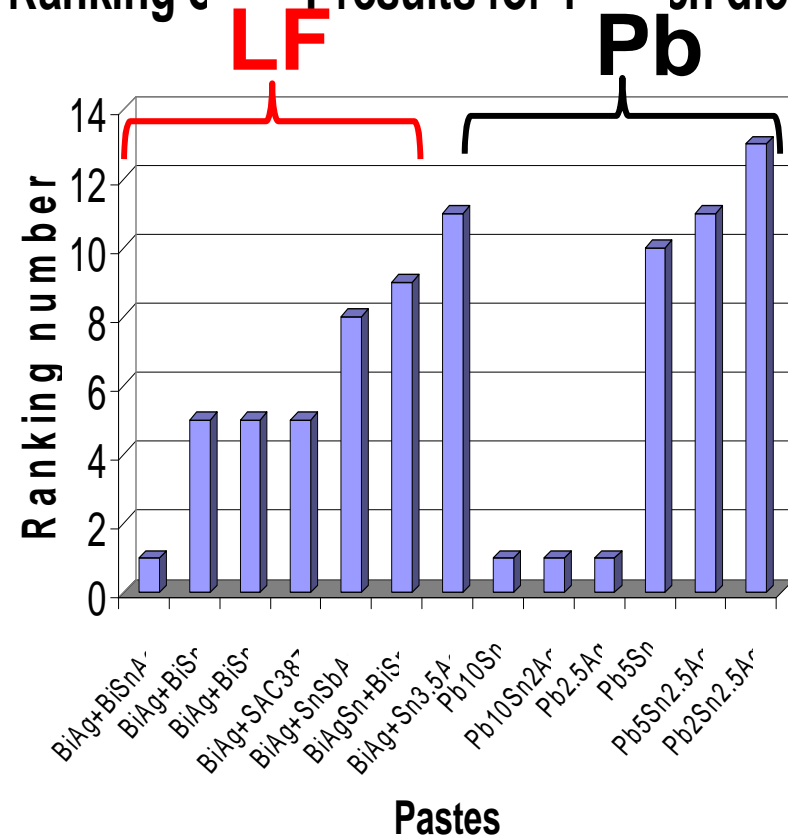
Ranking of TCT results for 0.5 inch die



TCT Ranking of 0.25" Cu Die

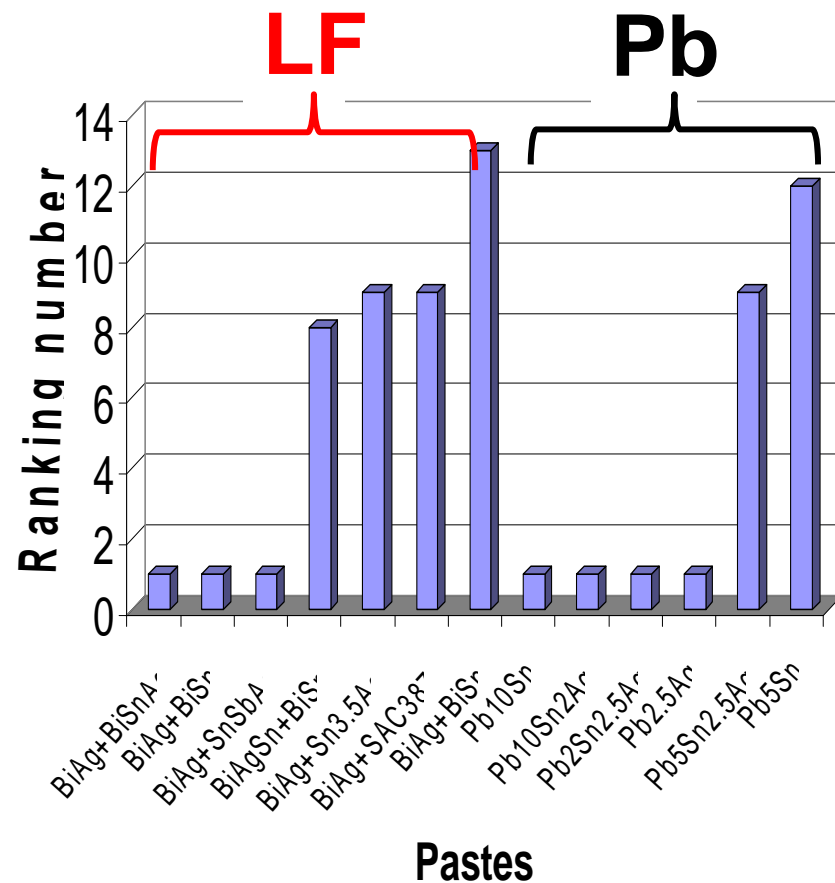
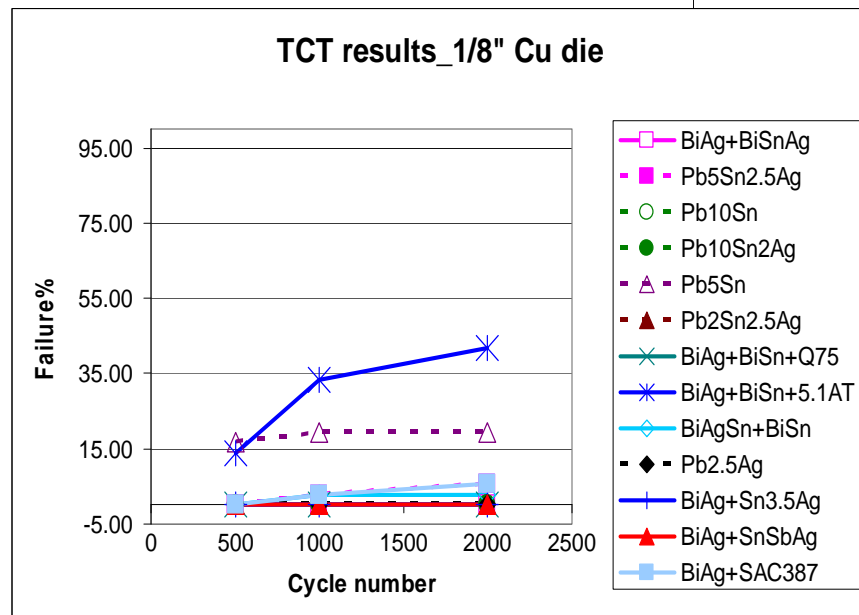


Ranking of TCT results for 1/4" Cu die



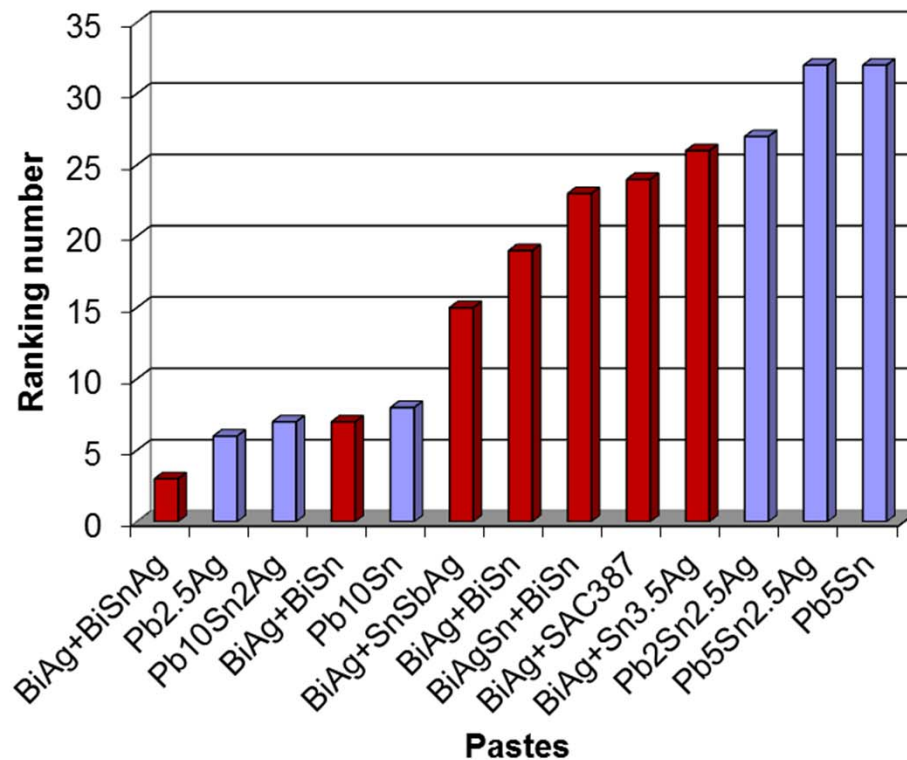
TCT Ranking of 0.125" Cu Die

Ranking TCT results for 8th inch die



TCT Ranking for All Pastes

Ranking of high temp pastes under TCT

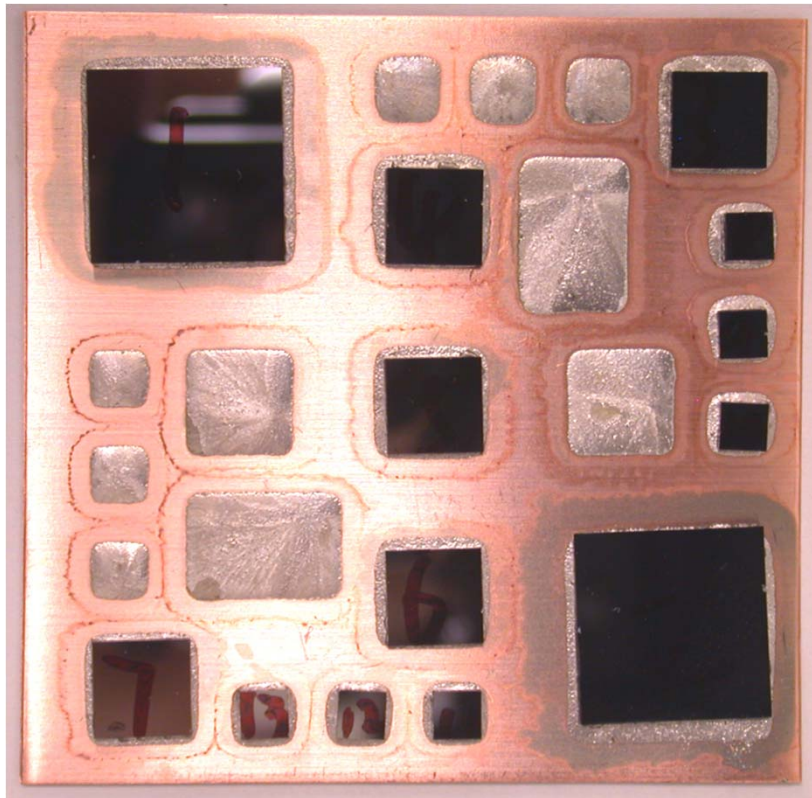


TCT ranking of mixed powder BiAgX system and the high Pb solders shows comparable performance.

Total ranking number is calculated by summing up all three ranking number of all three die sizes for each paste.



Ongoing Tests



Testing methodology:

Three sizes of Si dies: $\frac{1}{2}$ ", $\frac{1}{4}$ ", $\frac{1}{8}$ ".

Two $\frac{1}{2}$ " dies, five $\frac{1}{4}$ " dies and six $\frac{1}{8}$ " dies are bonded in each coupon.

X-ray inspection for voiding performance is being done before and after 3X additional reflow with a peak temp of 260°C.

TCT test from -55 to 125°C performed on these assemblies ongoing



Conclusion

- A novel high temperature Pb-free solder system, **mixed powder paste (BiAgX)**, was developed, with melting temperature of $\sim 260^{\circ}\text{C}$, verified by DSC and TMA.
- Mixed powder pastes BiAgX show wetting comparable with high Pb solders, and is much better than BiAg.
- IMC thickness increase due to thermal aging
 - Mixed powder pastes – moderate
 - High Pb solder pastes – significant
- Voiding of mixed powder pastes is comparable or better than high Pb solders.
- TCT ranking for mixed powder system & the high lead pastes show comparable performance.