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An Investigation into Low Temperature Tin-Bismuth and Tin-Bismuth-Silver Lead-Free Alloy Solder Pastes for Electronics Manufacturing Applications

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Abstract
The electronics industry has mainly adopted the higher melting point Sn3Ag0.5Cu solder alloys for lead-free reflow soldering applications. For applications where temperature sensitive components and boards are used this has created a need to develop low melting point lead-free alloy solder pastes. Tin-bismuth and tin-bismuth-silver containing alloys were used to address the temperature issue with development done on Sn58Bi, Sn57.6Bi0.4Ag, Sn57Bi1Ag lead-free solder alloy pastes. Investigations included paste printing studies, reflow and wetting analysis on different substrates and board surface finishes and head-in-pillow paste performance in addition to paste-in-hole reflow tests. Voiding was also investigated on tin-bismuth and tin-bismuth-silver versus Sn3Ag0.5Cu soldered QFN/MLF/BTC components. Mechanical bond strength testing was also done comparing Sn58Bi, Sn37Pb and Sn3Ag0.5Cu soldered components. The results of the work are reported.

Introduction
Sn3Ag0.5Cu lead-free solders are widely used for lead-free reflow applications. In general they are compatible with most reflow applications. The drawback is the relatively high melting temperature of this alloy (217ºC) which needs a reflow processing temperature between 235ºC to 260ºC. For assembly of heat temperature sensitive component and boards there is a need to look at lower temperature lead-free solder alloys as an alternative to high temperature SnAgCu solder as well as a need for a temperature hierarchy for different soldering operations on the board. The main lead-free alloy which could be used for these lower temperature soldering operations would be tin-bismuth (Sn58Bi) and tin-bismuth-silver (Sn57-57.6Bi0.4-1Ag) based with a melting temperature of 138ºC which would have a reflow processing temperature of around 180ºC. When using low melting temperature tin-bismuth based solder paste, there would also be lower energy usage versus Sn3Ag0.5Cu paste in the reflow oven as indicated in Figure 1.

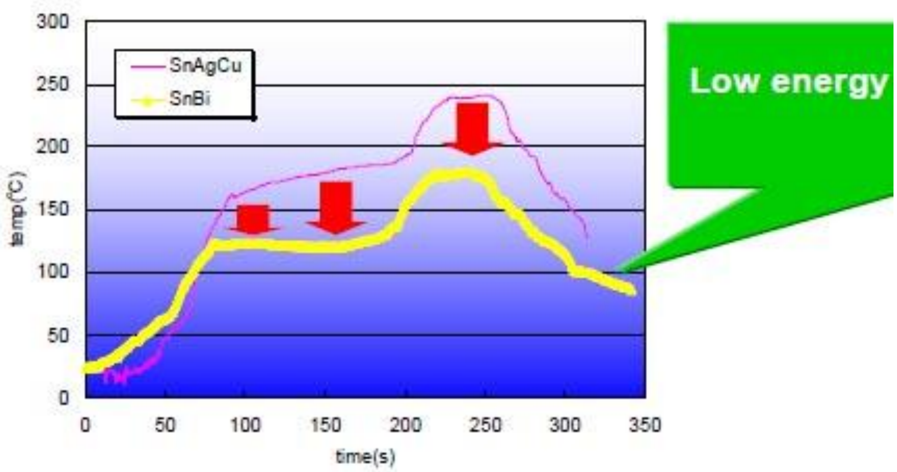

Figure 1: A comparison of a typical lead-free tin-bismuth and tin-silver-copper reflow profile.

The main drawback in bismuth usage in lead-free solder is the amount of bismuth available in the world. There is a spare capacity per year of 4,000 tonnes of bismuth so for a 180,000 tonne solder market a lead-free alloy with only 2wt% Bismuth would be useable as shown in Table 1. For niche applications for specific low melting temperature requirements, the Sn58Bi solders could be used and are being used in production today.

Table 1: Global solder market and bismuth metal usage and spare capacity per year.

Global Solder Market per year (Approximate)	Global Bismuth Metal Usage per year (Approximate)
180,000 tonnes solder	Global bismuth usage: 6,000 tonnes
Solder paste: 20,000 tonnes	World capacity: 10,000 tonnes
Wave solder: 160,000 tonnes	Spare capacity: 4,000 tonnes
	Maximum percentage of bismuth for a lead-free solder alloy: 2wt% Bi

In terms of the development in the use of tin-bismuth based lead-free solders, Hua et. al [1] conducted work comparing Sn58Bi and Sn57Bi2Ag against Sn37Pb soldered joints. The thermal fatigue life of Sn57Bi2Ag was found to be greater than Sn37Pb solder whereas Sn58Bi was less than Sn37Pb solder during thermal cycling studies from -20ºC to +110ºC. In this study, when mixing Sn58Bi solder paste with SnPb coated component terminations and board surface finishes, the Bi30Pb18Sn ternary phase was formed at 96ºC which caused a decrease in thermal cycling reliability in the soldered joints during temperature cycling from 0ºC to 100ºC which would necessitate the removal of lead from component and board coatings when assembling with tin-bismuth based solders.

Based on the need from customers to use a lower melting temperature lead-free tin-bismuth based solder evaluations on Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag solder pastes were conducted which are reported in the following sections.

Experimental

A series of evaluations were conducted in the development of tin-bismuth halide-free no-clean solder pastes. The testing included the following areas:

i) Paste Printing
ii) Reflow/ Wetting
iii) Head-in-Pillow
iv) Pin-in-Paste
v) Voiding
vi) Solder Paste Durability
vii) Solder Joint Bond Strength
viii) Solder Joint Cross-Sectional Analysis

<u>Paste Printing</u>

Paste printing studies were done on Sn58Bi Type 3 Paste A and Sn57.6Bi0.4Ag Type 4 solder paste A on 0.4mm pitch QFP and 0.3mm pitch BGA/CSP board pads over 200 paste printing strokes on a company test vehicle board to assess printability of the solder paste. In addition, viscosity measurements were conducted on Sn58Bi Type 3 Paste A at intervals after up to 3,000 continuous solder paste printing strokes with the squeegee blade to understand any changes in paste viscosity during the continuous printing process.

The Sn58Bi Type 3 paste A was also assessed after 30 minutes stencil idle time followed by printing on 0.4mm pitch QFP and 0.3mm pitch BGA/CSP board pads on the same test vehicle board.

<u>Reflow/ Wetting</u>

Sn58Bi Type 3 paste A was evaluated after reflow on different metal test pieces including Copper, Brass, Alloy 42 (Fe42Ni) and Nickel to assess the spreadability of the reflowed solder paste. The Sn58Bi Type 3 solder paste A was then used to assess soldering to 0603 [0201] pure tin coated chip and 0.65mm pitch pure tin coated QFP components on reflowed company test boards as shown in Figure 2.

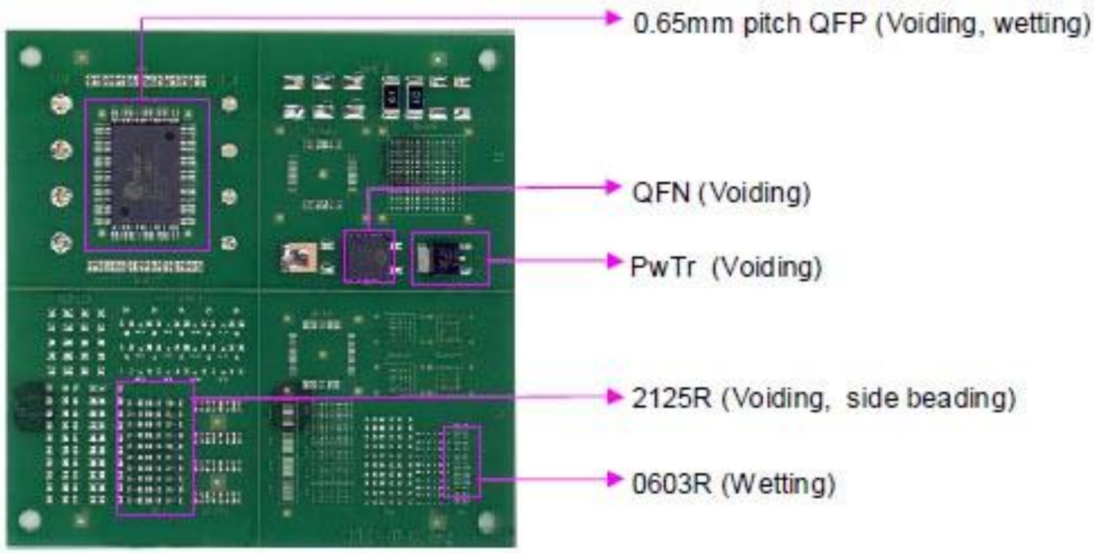

Figure 2: Solder reflow test vehicle.

Sn57.4Bi0.4Ag Type 4 paste A was also tested on assembled boards with 0603 [0201] pure tin coated chip and 0.65mm pitch pure tin coated QFP components on OSP, Sn and NiAu board surface finish versus Sn57.4Bi0.4Ag Type 4 paste B. Solder balling evaluations were conducted with Sn57.6Bi0.4Ag Type 4 paste A versus SnBi0.4Ag Type 4 paste B on 2125 [0805] pure tin coated chip components on OSP, Sn and NiAu board surface finishes.

Reflow was conducted in air atmosphere in all cases with the reflow profile in Figure 3, which had a peak temperature of 180ºC with a time over 138ºC of 65 seconds and a soak time between 120ºC to 130ºC of 110 seconds.

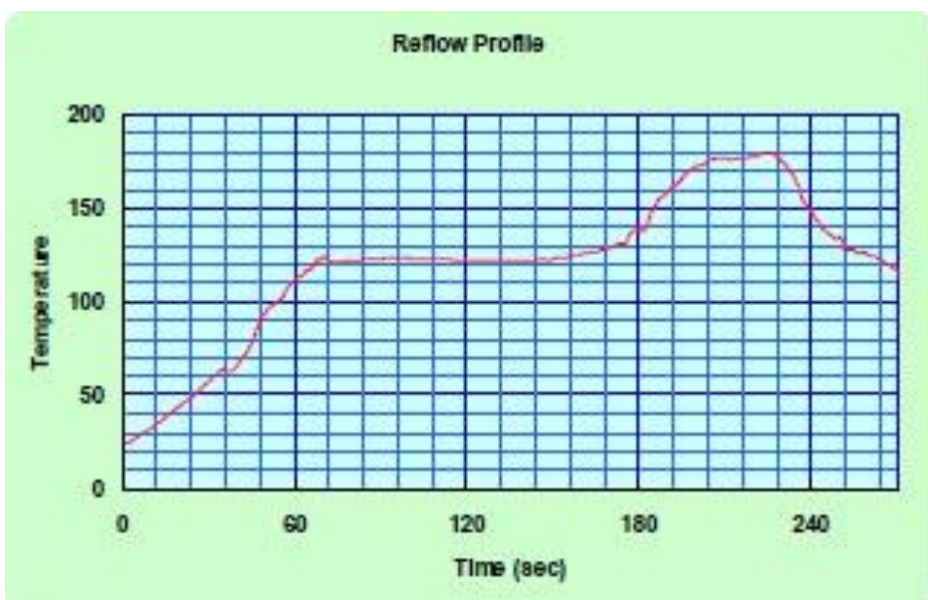

Figure 3: Sn58Bi and SnBiAg solder reflow profile.

<u>Head in Pillow</u>

Head-in-Pillow testing was conducted with Sn57.6Bi0.4Ag Type 4 Paste A versus Sn57.6Bi0.4Ag Type 4 Paste B and Sn3Ag0.5Cu Type 4 Paste C by inserting the Sn3Ag0.5Cu solder ball sphere into the reflowed solder paste at various time intervals to determine solder paste coalescence with the solder ball sphere as shown in Figure 4. The hot plate temperature for the tin-bismuth based solder pastes were 200ºC whereas that used for Sn3Ag0.5Cu paste was 275ºC.

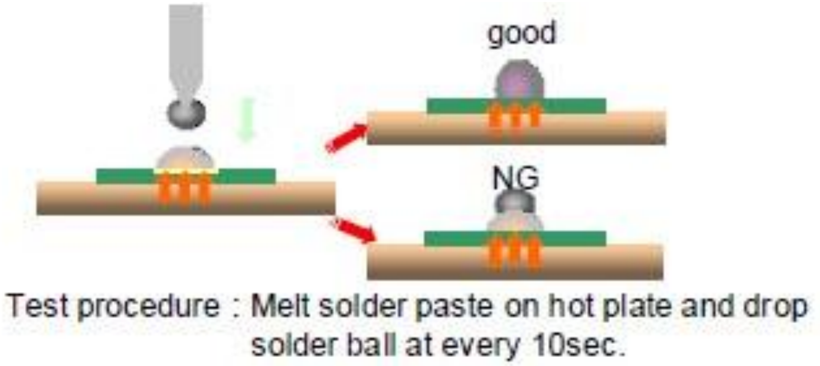

Figure 4: Heat in Pillow solder paste test procedure.

Pin-in-Paste
Pin-in-Paste testing was conducted with Sn57.6Bi0.4Ag Type 3 Paste A versus Sn57.6Bi0.4Ag Type 3 Paste B printed into 0.6mm diameter through holes on a 1.6mm thick (63mil) OSP coated company test vehicle with 0.5mm diameter brass lead wires inserted into the through holes after paste printing followed by reflow in air atmosphere using the reflow profile in Figure 3.

Voiding studies
Voiding studies were conducted on 6432 [2512] pure tin coated chip component, Sn3Ag0.5Cu 1mm pitch BGA and pure tin coated Power transistor components using Sn58Bi Type 3 paste A versus Sn3Ag0.5Cu Type 3 paste C on the OSP coated company test vehicle in air atmosphere. The reflow profile used for the Sn58Bi paste was as shown in Figure 3. The reflow profile used for Sn3Ag0.5Cu paste was as shown in Figure 1.

This was followed by voiding evaluations on Sn57.6Bi0.4Ag Type 4 Paste A versus Sn57.6Bi0.4Ag Type 4 Paste B using the pure tin coated power transistor component on OSP, Sn and NiAu board surface finishes on the company test vehicle in air atmosphere.

A follow on study was then conducted to evaluate the affect of silver in the lead-free solder on voiding with the pure tin coated power transistor component using Sn58Bi Type 3 Paste A versus Sn57.6Bi0.4Ag Type 4 Paste A versus Sn57Bi1Ag Type 4 Paste A. Reflow was conducted in an air atmosphere.

Solder Paste Product Durability
Once initial studies were conducted on paste printing, reflow, head-in-pillow, pin-in-paste and voiding, evaluations were conducted on Sn57.6Bi0.4Ag Type 3 paste A over a period of 5 days continuous use to determine if there were any variations in viscosity and thixotropic index of the paste. Print quality on 0.3mm pitch BGA/CSP and 0.4mm pitch QFP components was assessed along with reflow behavior on 0603[0201] pure tin coated chip components and large 6330 [2512] chip board pads on the OSP coated company test vehicle.

In addition Sn57.6Bi0.4Ag Type 3 Paste A was assessed for voiding behavior on the pure tin coated power transistor components during the continuous print and reflow studies over the 5 days in air atmosphere with the reflow profile used in Figure 3.

Bond strength data
Once print and reflow assessments were completed solder joint bond strength was assessed for various soldered chip and lead-frame components. The chip testing equipment used is shown in Figure 5 and the QFP pull testing methodology used is shown in Figure 6.

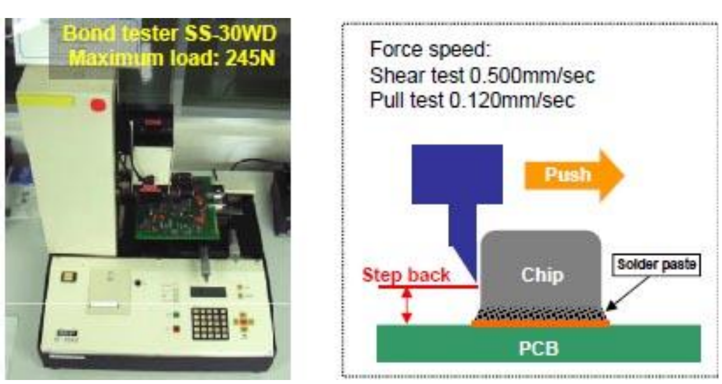

Figure 5: Chip testing equipment.

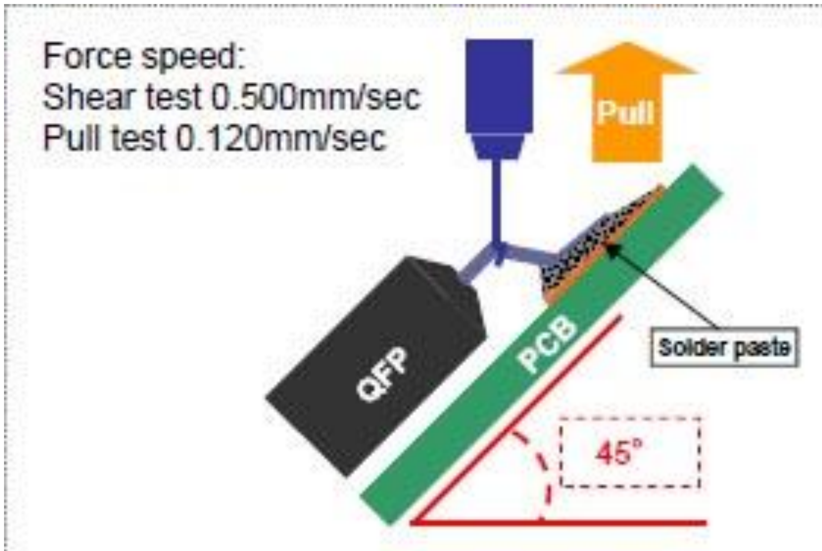

Figure 6: QFP Pull testing methodology.

Initial pull tests was done using 0.65mm pitch pure tin coated QFP components and initial shear testing was done using pure tin and NiAu coated 3216 [1206] coated chips, pure tin 2012 [0805] and pure tin 1608 [0603] coated chips reflowed with Sn58Bi Paste A, Sn3Ag0.5Cu Paste C and Sn37Pb Paste D.

Follow on studies looked at pull testing of 0.65mm pitch pure tin coated QFP and shear testing of pure tin coated 3216 [1206] chip and 2012 [0805] chip components with Sn58Bi Paste A, Sn57.6Bi0.4Ag Paste A and Sn57Bi1Ag Paste A to understand the affect of silver content in the lead-free SnBi based solders on mechanical pull and shear test solder joint results.

<u>Cross-sectional analysis</u>
Cross-sectional analysis was done on 3216[1206] pure tin coated chip components reflow soldered with Sn58Bi Paste A, Sn57.6Bi0.4Ag Paste A and Sn57Bi1Ag Paste A.

The results of the experiments are reported in the following section.

Results and Discussion
<u>Paste Printing</u>
Continual printing tests for Sn58Bi Type 3 Paste A and Sn57.6Bi0.4Ag Type 4 Paste A on 0.4mm pitch QFP and 0.3mm pitch BGA/CSP pads after over 200 print strokes showed good results in terms of solder paste deposition on the board pads as indicated in Figures 7, 8 and 9.

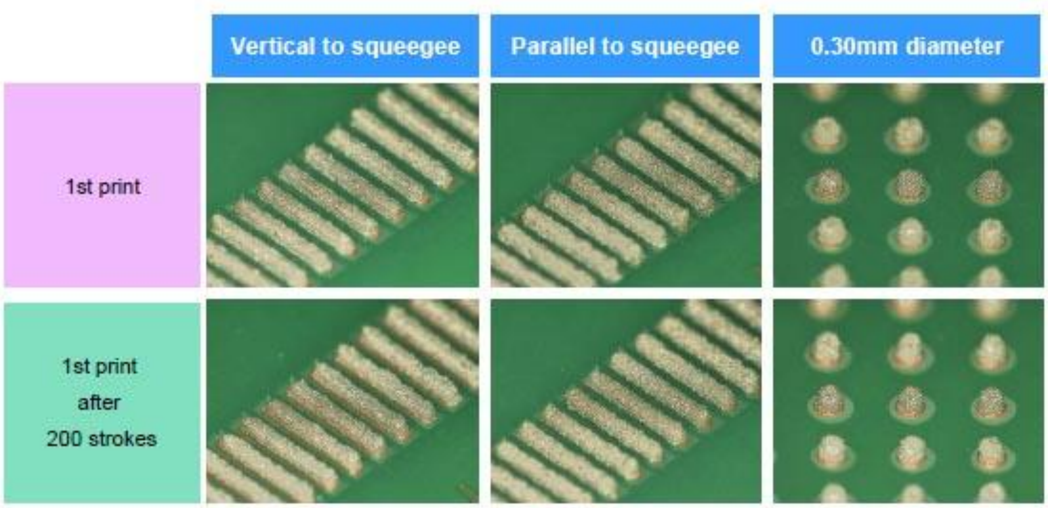

Figure 7: Continual paste printing results with Sn58Bi Type 3 paste A on 0.4mm pitch QFP and 0.3mm pitch BGA/CSP board pads.

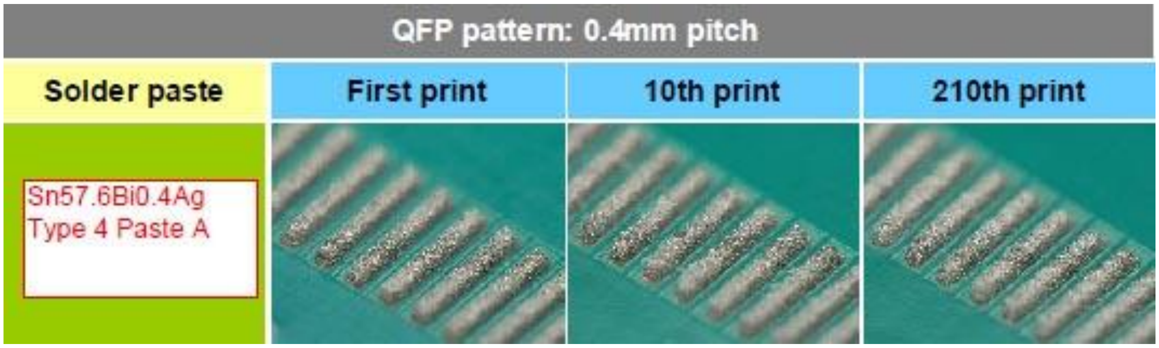

Figure 8: Continual paste printing results with Sn57.6Bi0.4Ag Type 4 paste A on 0.4mm pitch QFP and 0.3mm pitch BGA/CSP board pads.

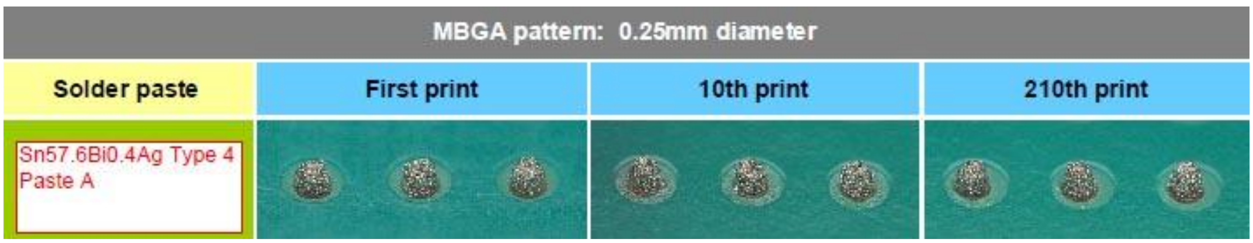

Figure 9: Continual paste printing results with Sn57.6Bi0.4Ag Type 4 paste A on 0.3mm pitch BGA/CSP board pads.

The viscosity variation of the Sn58Bi Type 3 Paste A was found to be minimal over 3,000 paste print strokes tested as shown in Figure 10.

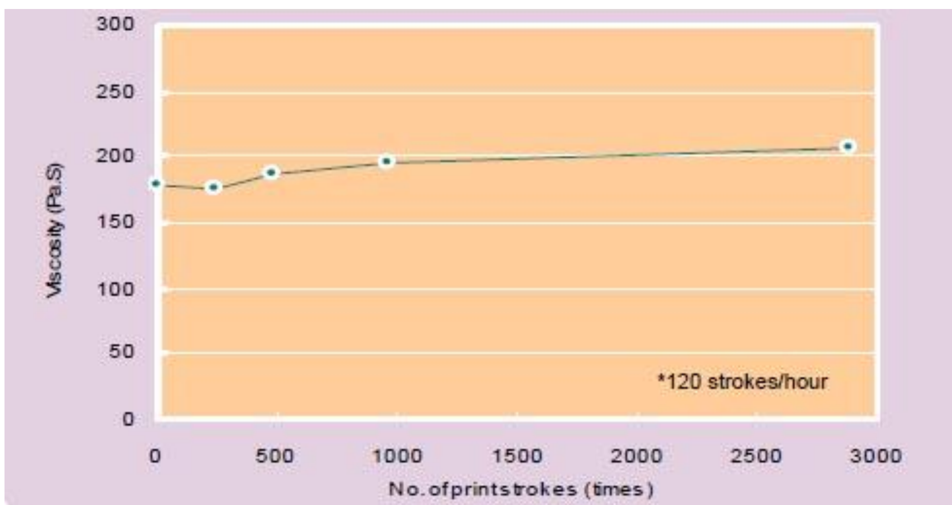

Figure 10: Viscosity variation during continuous printing of Sn58Bi Type 3 paste A.

Evaluation of paste printed deposits after a stencil idle time of 30 mins showed good results for Sn58Bi Type 3 paste A in terms of paste deposits on the 0.4mm pitch QFP and 0.3mm pitch BGA/CSP board pads as shown in Figure 11.

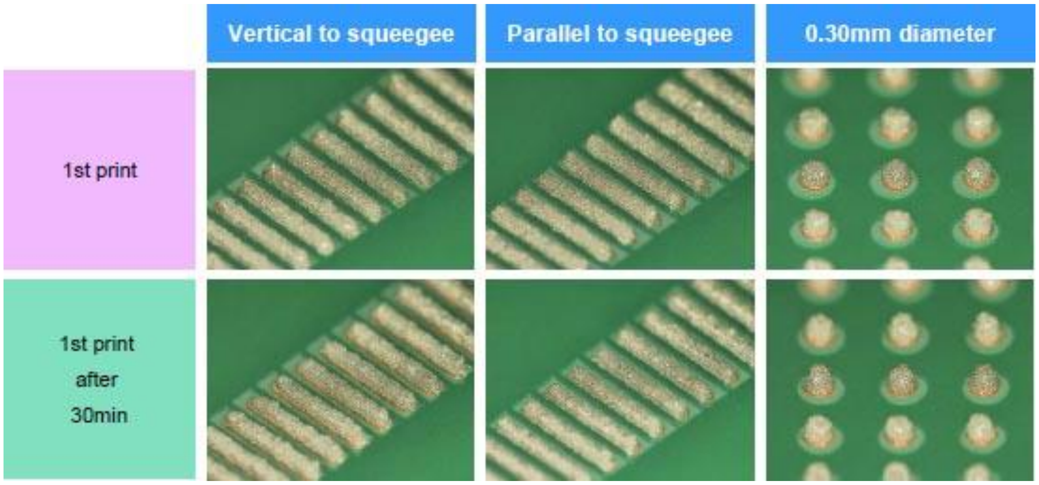

Figure 11: Printing after 30 minutes stencil idle time with Sn58Bi Type 3 paste A on 0.4mm pitch QFP and 0.3mm BGA/CSP board pads.

Reflow/ Wetting

Sn58Bi Type 3 paste A was evaluated after reflow for spreading on different material test pieces including Copper, Brass, Alloy 42 and Nickel as shown in Figure 12. The spreading on the copper and brass substrate was over the area that the solder paste was printed after reflow which was a good result. There was partial spreading on the Alloy 42 and Nickel substrates after reflow which was to be expected for these hard to solder surfaces. Reflow was done in an air atmosphere with the reflow profile used in Figure 3.

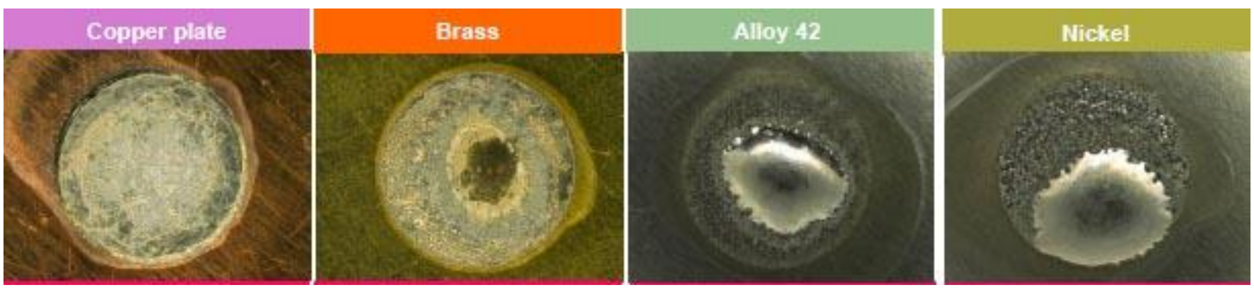

Figure 12: Sn58Bi Type paste A reflow spreading on Copper, Brass, Alloy 42 and Nickel material test pieces.

Sn58Bi Type 3 paste A was then assembled on test boards with 0603 [0201] chip and 0.65mm pitch QFP components with good wetting to the components at time zero and after 8 hours of rolling the solder paste on the stencil before printing the paste on the test board followed by reflow as shown in Figure 13.

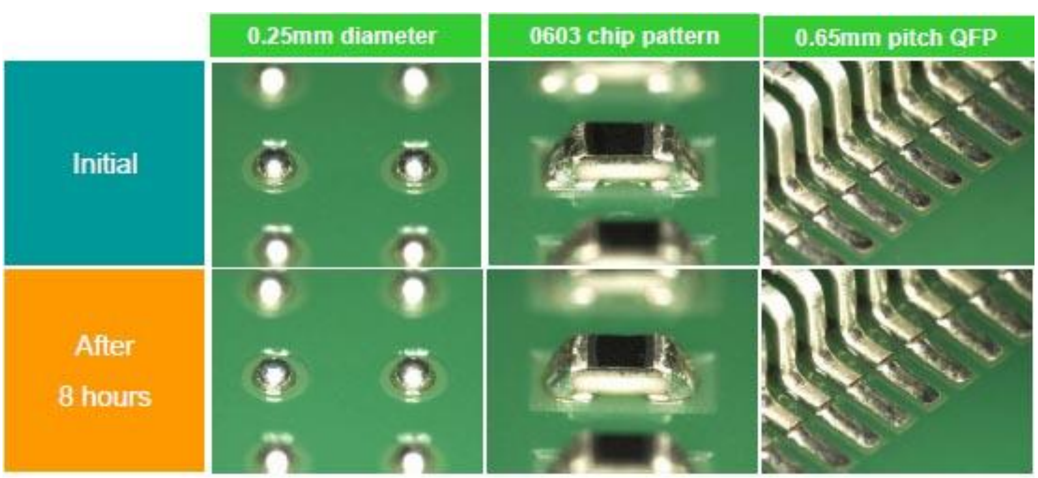

Figure 13: Sn58Bi paste A wetting on 0603 [0201] chip and 0.65mm pitch QFP components at time zero and after 8 hours of rolling the solder paste on the stencil before printing on the test board followed by reflow.

Sn57.6Bi0.4Ag Type 4 paste A was used to reflow 0603 [0201] chips and 0.65mm pitch QFP components on OSP, Sn and NiAu board surface finish test boards in comparison with Sn57.6Bi0.4Ag Type 4 paste B. The results from Figures 14 and 15 show good wetting with each paste used for the chip components and reasonable wetting on the QFP components with each paste.

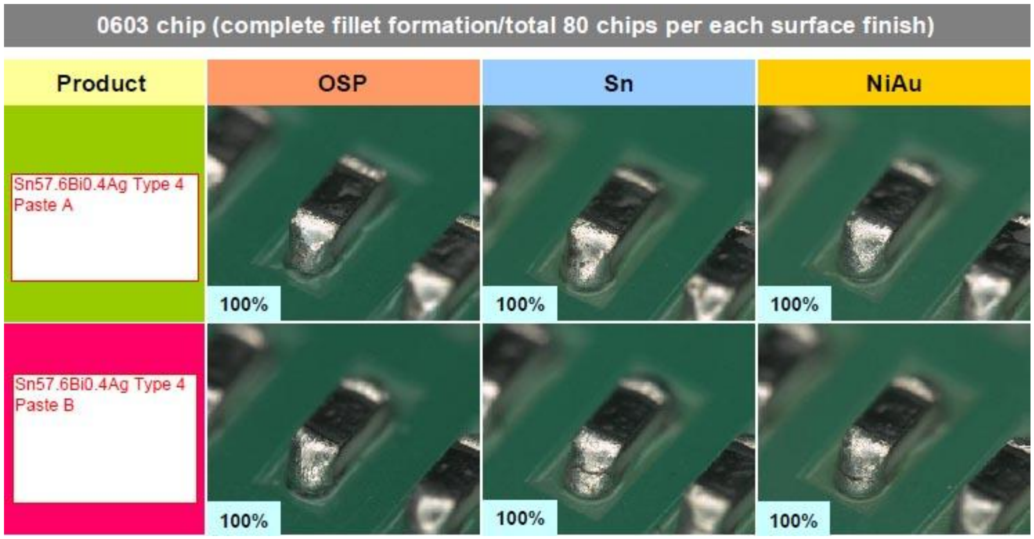

Figure 14: Sn57.6Bi0.4Ag Paste A versus Paste B wetting on 0603 [0201] chip components.

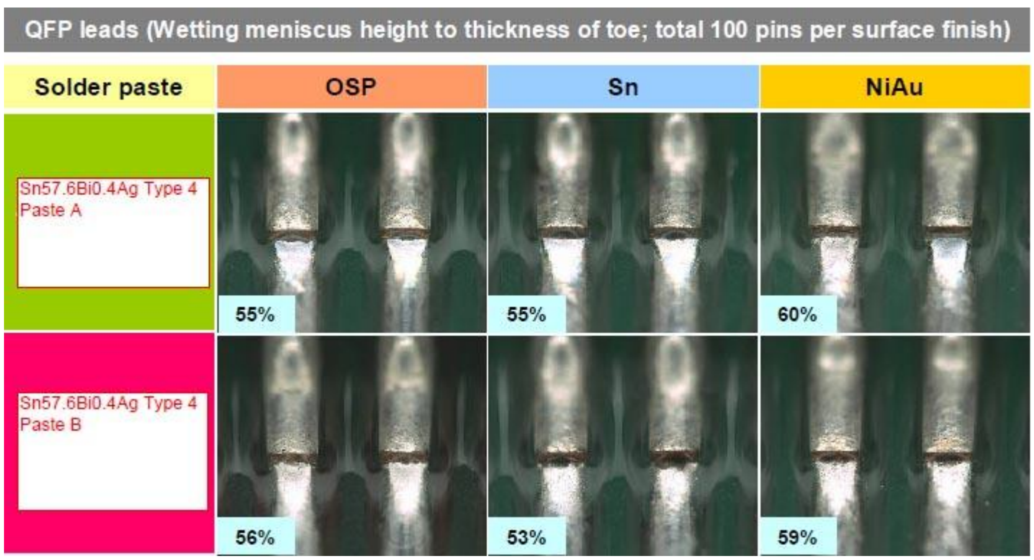

Figure 15: Sn57.6Bi0.4Ag paste wetting versus Paste B wetting on 0.65mm pitch QFP components.

Solder balling evaluations were conducted with Sn57.6Bi0.4Ag Type 4 paste A versus Sn57.6Bi0.4Ag Type 4 paste B on 2125 [0805] pure tin coated chip components on OSP, Sn and NiAu board surface finishes with a reduced amount of solder balling with Sn57.6Bi0.4Ag Paste A versus Sn57.6Bi0.4Ag Paste B after reflow as shown in Figure 16.

Figure 16: Sn57.6Bi0.4Ag Paste A versus Paste B solder balling on 2125 [0805] soldered pure tin coated chip components.

Head-in-Pillow

Head-in-Pillow testing was conducted with Sn57.6Bi0.4Ag Paste A versus Sn57.6Bi0.4Ag Paste B and Sn3Ag0.5Cu Paste C with Sn3Ag0.5Cu ball spheres. The two lead-free Sn57.6Bi0.4Ag pastes had complete merger of the solder sphere after up to 180 seconds versus 60 seconds with the Sn3Ag0.5Cu paste as shown in Figure 17. The lower hot plate temperature used for the tin-bismuth based pastes compared with the Sn3Ag0.5Cu solder paste meant that the flux was not used up as much with the tin-bismuth based solder pastes with an improvement in head-in-pillow test performance.

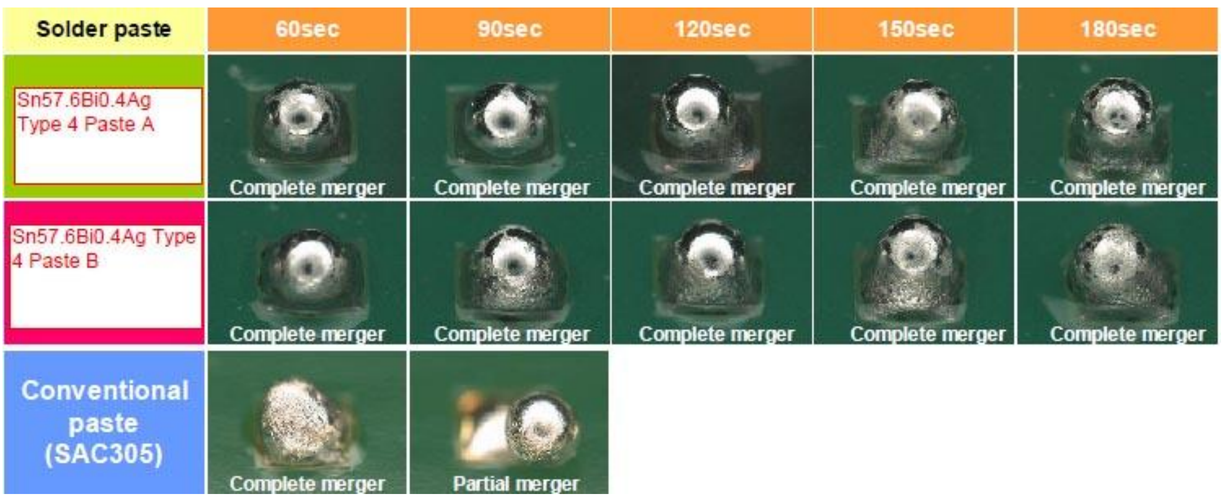

Figure 17: SnBi0.4Ag Type 4 paste A versus SnBi0.4Ag Type 4 paste B versus Sn3Ag0.5Cu paste C head-in-pillow testing.

Pin-in-Paste

Pin-in-Paste testing was conducted with Sn57.6Bi0.4Ag Type 3 Paste A versus Sn57.6Bi0.4Ag Type 3 Paste B. The SnBi0.4Ag Paste A results showed better wetting after reflow versus SnBi0.4Ag Paste B as indicated in Figure 18.

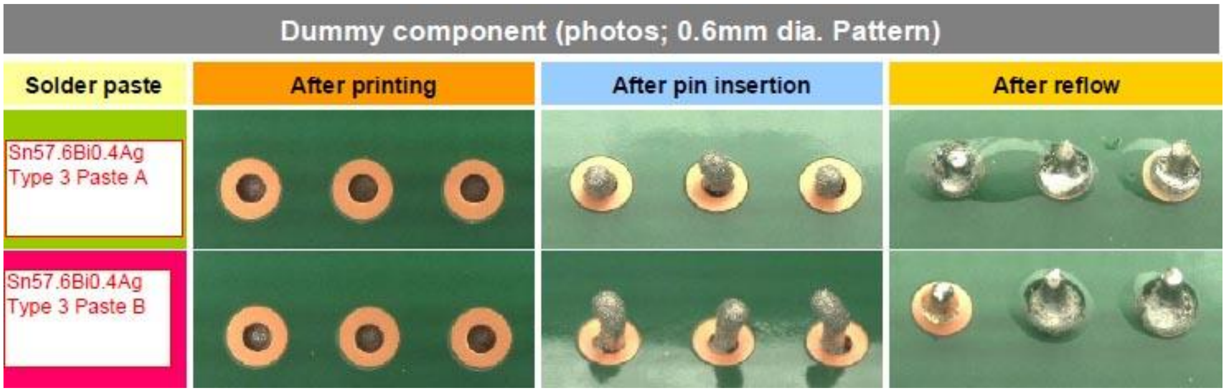

Figure 18: SnBi0.4Ag paste A versus Paste B pin-in-paste reflow testing.

Voiding studies

Voiding studies were conducted on 6432 [2512] pure tin coated chip, Sn3Ag0.5Cu 1mm pitch BGA and pure tin coated Power transistor components using Sn58Bi Type 3 paste A versus SnAgCu Type 3 paste C which generally showed a lower voiding amount with Sn58Bi Paste A as shown in Figure 19. The surface tension of the Sn58Bi solder paste would be lower than Sn3Ag0.5Cu solder paste during reflow so it would be easier for the voids to escape with the Sn58Bi solder paste during reflow.

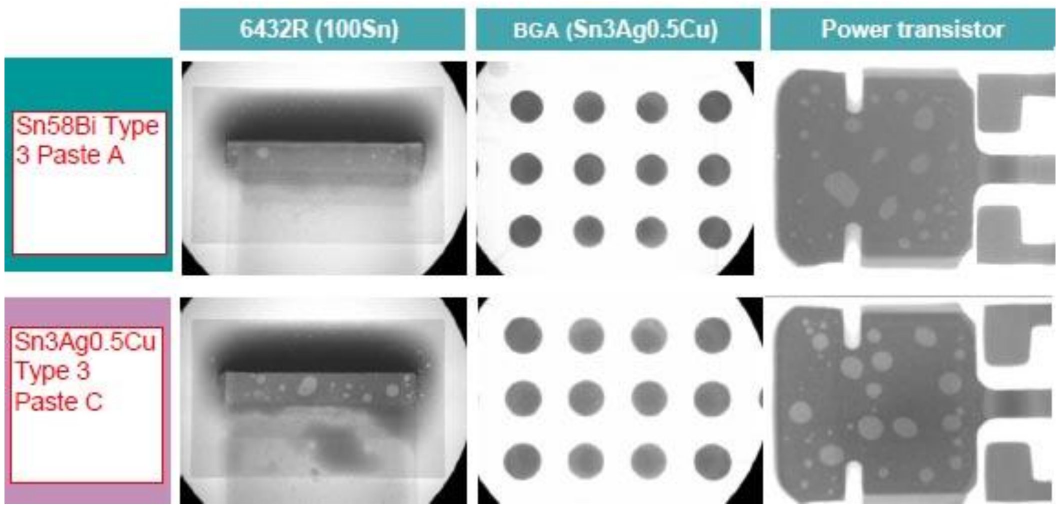

Figure 19: Sn58Bi paste A versus Sn3Ag0.5Cu paste C voiding on soldered 6432 [2512] chip, BGA and Power transistor components.

This test was followed by voiding evaluations on Sn57.6Bi0.4Ag Type 4 Paste A versus Sn57.6Bi0.4Ag Type 4 Paste B using the pure tin coated power transistor component on OSP, Sn and NiAu board surface finishes. Sn57.6Bi0.4Ag Type 4 Paste A showed minimal voiding on all three board surface finishes compared with Sn57.6Bi0.4Ag Type 4 Paste B as shown in Figure 20.

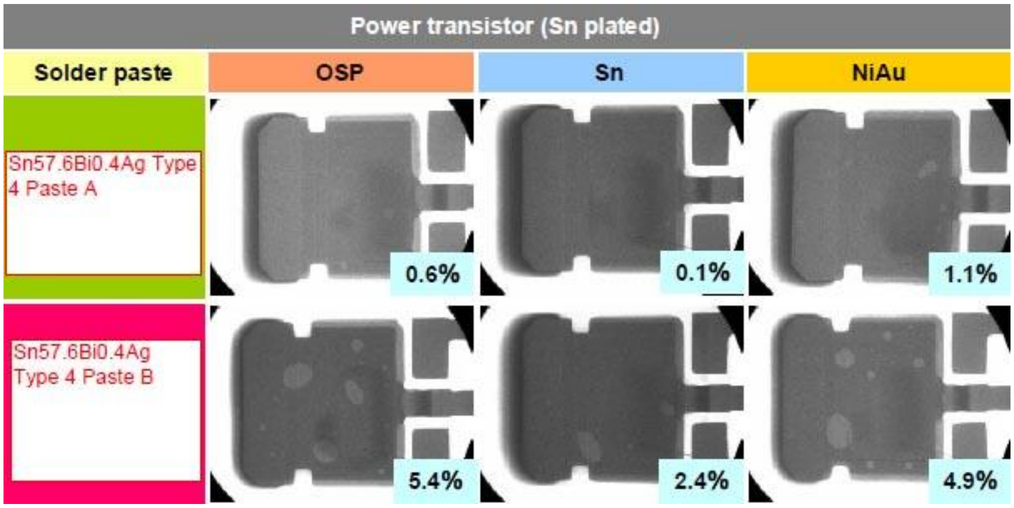

Figure 20: Sn57.6Bi0.4Ag Paste A versus Sn57.6Bi0.4Ag Paste B voiding on soldered power transistor components on OSP, Sn and NiAu board surface finishes.

A follow on study was then conducted to evaluate the affect of silver additions to the tin-bismuth solder on voiding with the power transistor component using Sn58Bi Type 3 Paste A versus Sn57.6Bi0.4Ag Type 4 Paste A versus Sn57Bi1Ag Type 4 Paste A. There was generally no real difference between the three solder pastes evaluated as shown in Figure 21 which indicated that the voiding was more dependent on the flux type in the paste rather than silver content in the solder paste.

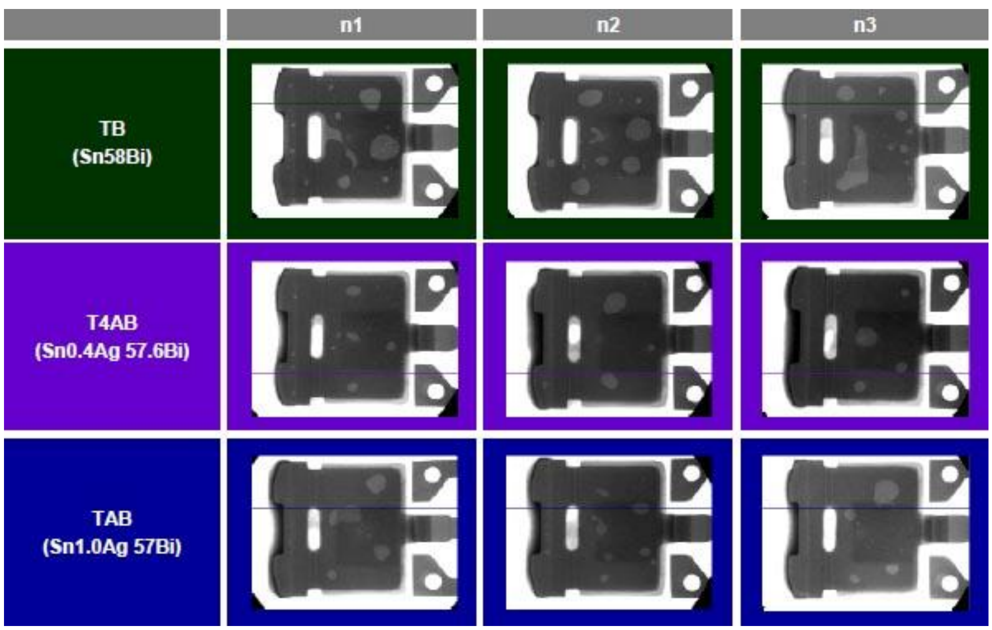

Figure 21: Sn58Bi paste A versus SnBi0.4Ag paste A versus SnBi1Ag paste A voiding with the soldered power transistor component.

<u>Solder Paste Product Durability</u>

Evaluations were conducted on Sn57.6Bi0.4Ag Type 3 paste A over a period of 5 days continuous use to understand if there were any variations in viscosity or thixotropic index of the paste. Based on the results shown in Figure 22, there was minimal variation in viscosity or thixotropic index of the paste over the 5 day period.

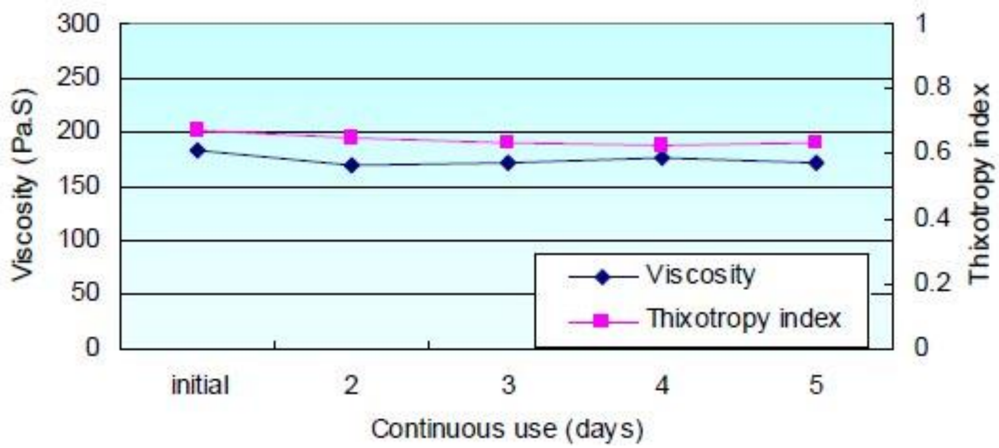

Figure 22: Sn57.6Bi0.4Ag Type 3 paste A viscosity and thixotrophy index evaluation over 5 days continuous printing

Over the 5 day printing study, solder paste print quality on the 0.3mm pitch BGA/CSP and 0.4mm pitch QFP components was assessed and found to be good along with reflow behavior on reflowed soldered 0603 [0201] chip components and large 6330 [2512] board pads as indicated in Figure 23.

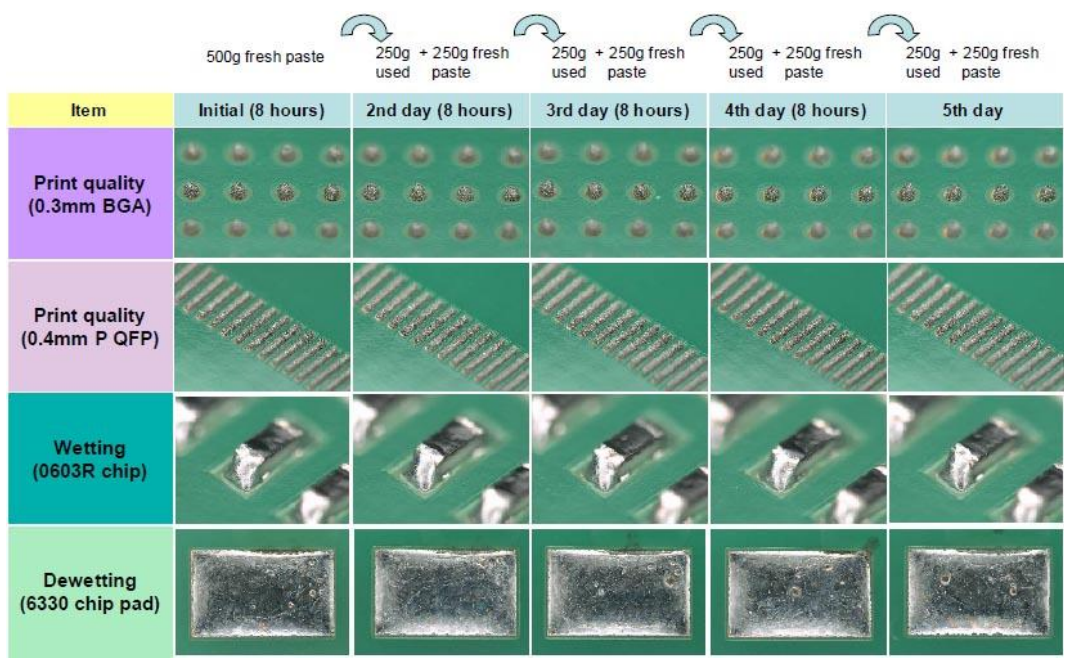

Figure 23: Sn57.6Bi0.4Ag Type 3 paste A printing and reflow/wetting evaluations over 5 days of testing.

There was low Sn57.6Bi0.4Ag Paste A voiding behavior on reflow soldered power transistor components during the continuous print and reflow studies over the 5 days as indicated in Figure 24.

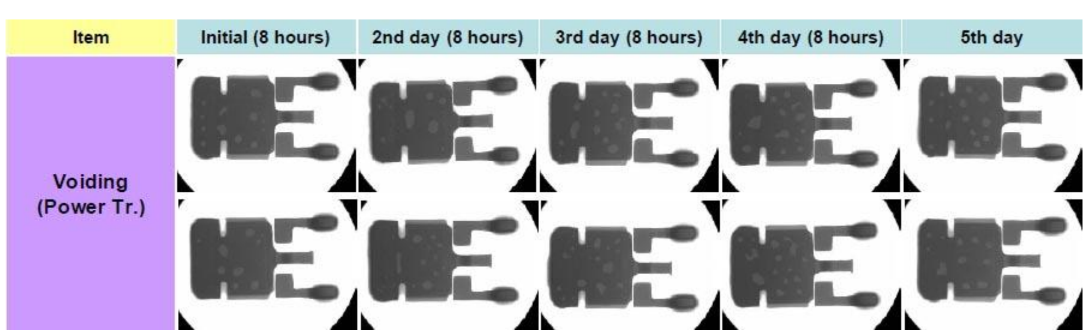

Figure 24: Sn57.6Bi0.4Ag Type 3 Paste A voiding study on soldered power transistor components over 5 days of testing.

Bond strength data

Initial solder joint bond strength tests were done using 0.65mm pitch QFP, 3216[1206] chip, 2012[0805] chip and 1608[0603] chip components reflowed with Sn58Bi Paste A, Sn3Ag0.5Cu Paste C and Sn37Pb Paste D as shown in Figure 25. The results indicate that the bond strength with Sn58Bi paste A soldered components was equivalent or better than Sn3Ag0.5Cu or Sn37Pb paste soldered components.

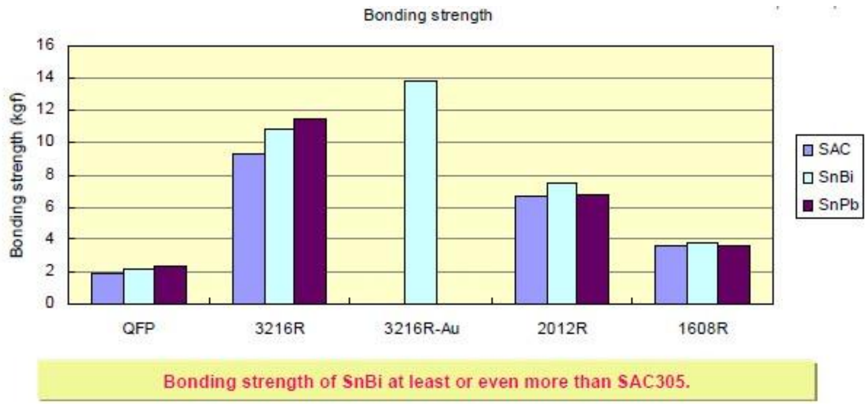

Figure 25: Sn58Bi versus Sn3Ag0.5Cu versus Sn37Pb bond strength results on soldered 0.65mm pitch QFP, 3216[1206] chip, 2012[0805] chip and 1608[0603] chip components.

Additional studies looked at the effect of silver additions to tin-bismuth solder on the bond strength results. Pull testing results of 0.65mm pitch pure tin coated QFP components and shear testing results of 3216[1206] chip and 2012[0805] chip components reflow soldered with Sn58Bi Paste A, Sn57.6Bi0.4Ag Paste A and Sn57Bi1Ag Paste A are shown in Tables 2 and 3. The results indicate minimal differences in pull and shear test data between the Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag paste soldered components.

Table 2: Sn58Bi versus Sn57.6Bi0.4Ag versus Sn57Bi1Ag shear test results on soldered 3216[1206] chip and 2012[0805] chip components from 5 component tests.

Unit: Newtons	Sn58Bi	Sn58Bi	Sn57.6Bi0.4Ag	Sn57.6Bi0.4Ag	Sn57Bi1Ag	Sn57Bi1Ag
Component Number	3216 chip	2012 chip	3216 chip	2012 chip	3216 chip	2012 chip
1		67.5		41.3		41.1
2	109.8	45.7	81.6	59.8	95.2	66.0
3	91	76.1	101.0	69.6	92.2	41.6
4	100.1	59.1	83.5	66.2	94.5	58.1
5	104.2	51.6	83.5	56.9	95.6	61.7
Average	101.3	60.0	87.4	58.8	94.4	53.7
Stdev.	7.9	12.2	9.1	11.0	1.5	11.6
Min.	91.0	45.7	81.6	41.3	92.2	41.1
Max.	109.8	76.1	101.0	69.6	95.6	66.0

Table 3: Sn58Bi versus Sn57.6Bi0.4Ag versus Sn57Bi1Ag pull testing results on soldered 0.65mm pitch QFP components from 10 component tests.

Unit: Newtons	Sn58Bi	Sn57.6Bi0.4Ag	Sn57Bi1Ag
Component Number			
1	20.3	18.9	19.9
2	19.6	19.6	19.7
3	19.7	17.2	17.4
4	18.5	20.0	19.6
5	20.7	19.7	20.8
6	21.2	20.6	21.1
7	20.1	19.0	22.1
8	21.8	21.2	21.8
9	19.2	21.6	21.2
10	24.0	22.4	22.6
Average	20.5	20.0	20.6
Stdev.	1.6	1.5	1.5
Min.	18.5	17.2	17.4
Max.	24.0	22.4	22.6

Cross-sectional analysis

Cross-sectional analysis was done on 3216 [1206] pure tin coated chip components soldered with Sn58Bi Paste A, Sn57.6Bi0.4Ag Paste A and Sn57Bi1Ag Paste A. The results indicate good soldering to the chip components and the board for all three solder alloy pastes as shown in Figure 26.

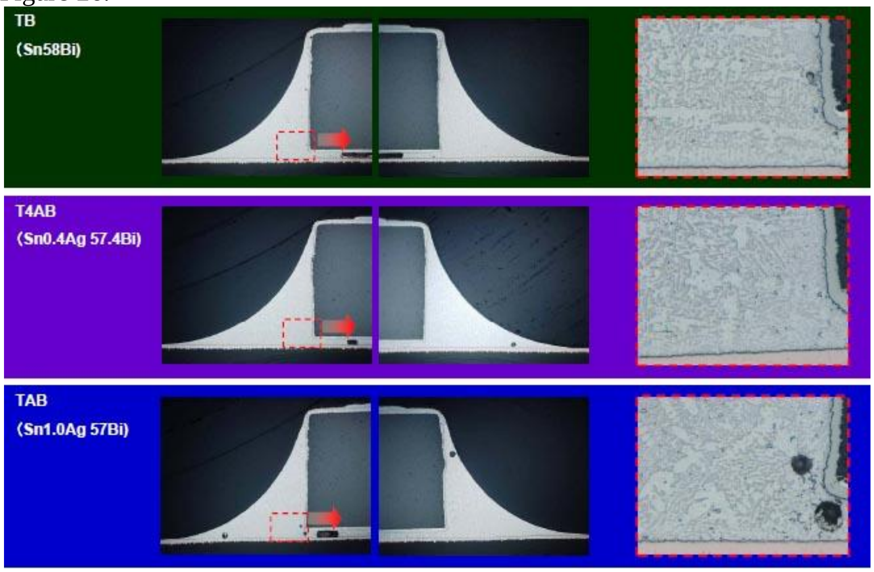

Figure 26: Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag soldered 3216 [1206] chip component cross-sections.

The microstructures shown in Figures 27, 28 and 29 indicate tin and bismuth phases in the microstructure with some evidence of Cu_6Sn_5 IMC in the bulk microstructure with good soldering to the board and component interfaces.

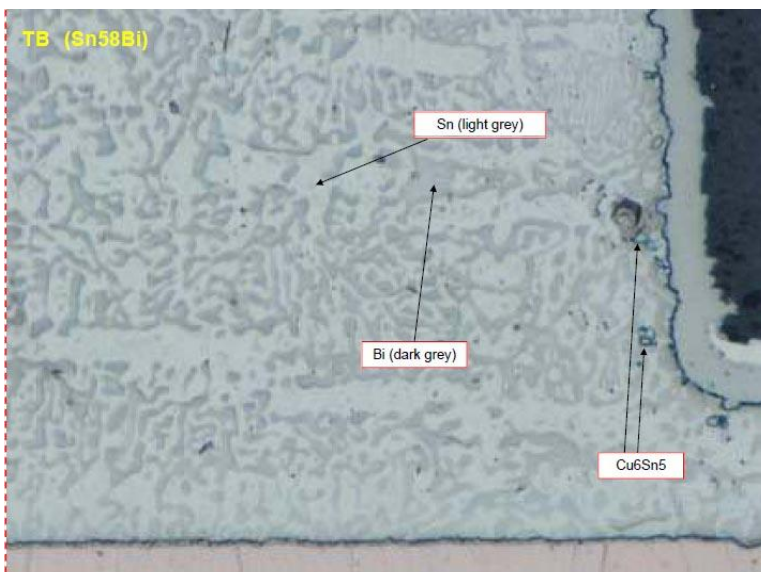

Figure 27: Sn58Bi soldered 3216 [1206] chip component cross-section.

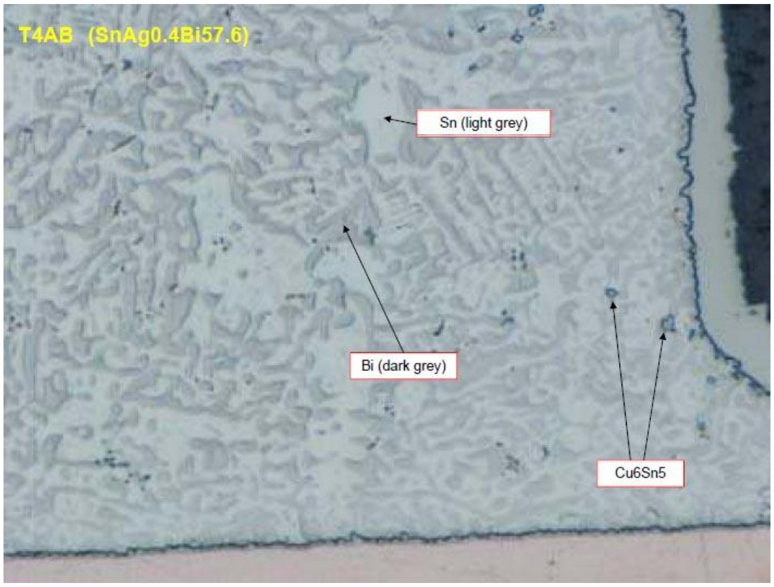

Figure 28: Sn57.6Bi0.4Ag soldered 3216[1206] chip component cross-section.

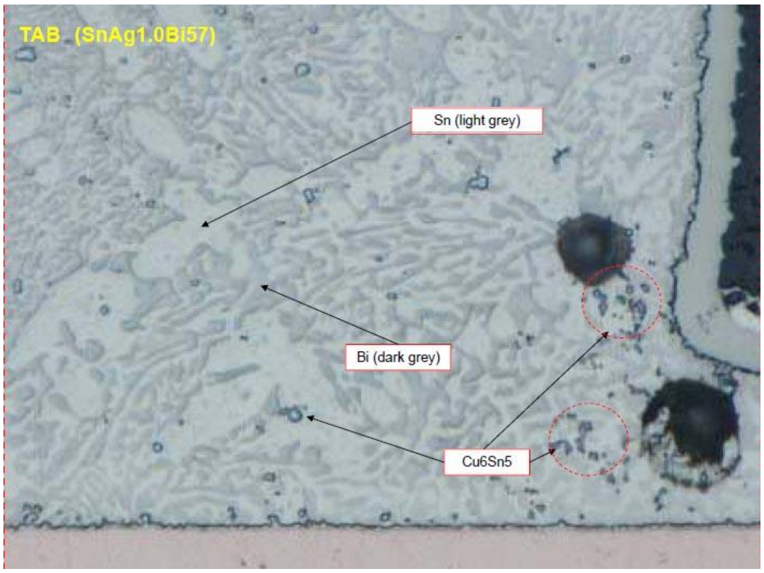

Figure 29: Sn57Bi1Ag soldered 3216[1206] chip component cross-section.

Conclusions

Based on the tests conducted during the evaluation the following was determined:

1. Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag solder pastes show good printing and reflow performance over the variety of components tested.
2. The tin-bismuth solder pastes were found to have good head-in-pillow performance and were acceptable for pin-in-paste soldering.
3. Voiding studies on power transistor components showed low voiding with the developed tin-bismuth pastes with minimal effect on voiding from silver additions to the tin-bismuth pastes.
4. Paste durability studies showed good results over the 5 day print and reflow testing for the developed tin-bismuth paste.
5. Pull and shear testing data for tin-bismuth soldered components were equivalent or better than Sn3Ag0.5Cu and Sn37Pb soldered components.
6. There were minimal differences in pull and shear testing of Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag soldered components.
7. Cross-sectional analysis of Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag soldered components showed good bonding to the board and component interfaces.

Future Work

More developments would be done with tin-bismuth based lead-free solder pastes to improve print and reflow performance as well as further work to assess solder joint reliability.

Acknowledgements
The authors would like to thank the research and development engineers at Koki in Japan who conducted the tin-bismuth solder paste development and analysis tests reported in this paper.

References

1. F. Hua, Z. Mei, J. Glazer and A.Lavagnino, Eutectic Sn-Bi as an Alternative Pb-Free Solder, IPC Works Conference, 1999.

An Investigation Into Low Temperature Tin-bismuth and Tin-bismuth-silver Lead-free Alloy Solder Pastes for Electronics Manufacturing Applications

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[1]Koki Company Limited, Japan,
[2]Christopher Associates Inc., Santa Ana, CA, USA

Agenda

- Introduction
- Experimental
- Results and Discussion
- Future Work

Introduction

Sn3Ag0.5Cu lead-free solders are widely used for lead-free reflow applications.

- Main drawback is the relatively high melting temperature of this alloy (217ºC) with a reflow processing temperature between 235ºC to 260ºC.

For assembly of heat temperature sensitive component/boards need to look at:

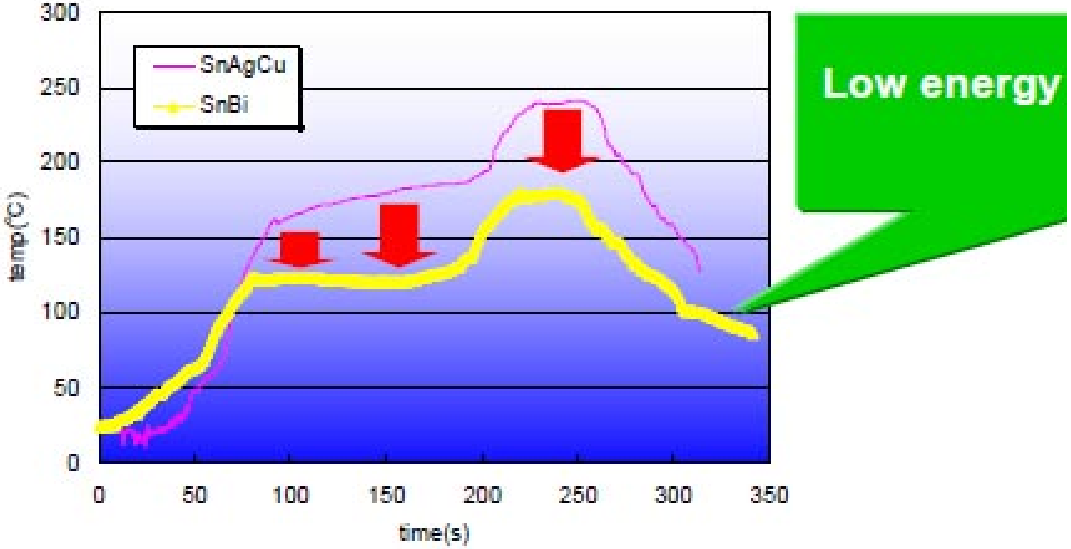
- lower temperature lead-free solder alloys
- temperature hierarchy for different soldering operations.

Introduction

Main lead-free alloy used for lower temperature soldering operations would be:

- Tin-bismuth (Sn58Bi)
- Tin-bismuth-silver (Sn57-57.6Bi0.4-1Ag)

Melting temperature of 138ºC with reflow around 180ºC.



Using low melting temperature tin-bismuth based solder would lower energy usage in reflow oven.

Introduction

Main drawback in bismuth usage in lead-free solder is reduced amount of bismuth available in the world.

- Spare capacity per year of 4,000 tonnes of bismuth
- For a 180,000 tonne solder market a lead-free alloy with only 2wt% Bismuth would be useable.
- For niche applications, the Sn58Bi solders could be used and are being used in production today.

Global Solder Market per year (Approximate)	Global Bismuth Metal Usage per year (Approximate)
180,000 tonnes solder	Global bismuth usage: 6,000 tonnes
Solder paste: 20,000 tonnes	World capacity: 10,000 tonnes
Wave solder: 160,000 tonnes	Spare capacity: 4,000 tonnes
	Maximum percentage of bismuth for a lead-free solder alloy: 2wt% Bi

Introduction

Based on the need from customers to use a lower melting temp. lead-free tin-bismuth based solder evaluations conducted on the following solder pastes:

1. Sn58Bi
2. Sn57.6Bi0.4Ag
3. Sn57Bi1Ag

Experimental

Testing of tin-bismuth halide-free no-clean solder pastes included the following areas:

- Paste Printing
- Reflow/ Wetting
- Head-in-Pillow
- Pin-in-Paste
- Voiding
- Solder Paste Durability
- Solder Joint Bond Strength (Pull/ Shear)
- Solder Joint Cross-Sectional Analysis

Experimental (Paste Printing)

Paste printing studies were done on Sn58Bi Type 3 (Paste A) and Sn57.6Bi0.4Ag Type 4 (Paste A) on the following board pads over 200 print strokes:

- 0.4mm pitch QFP
- 0.3mm pitch BGA/CSP

- Viscosity measurements were conducted on Sn58Bi Type 3 (Paste A) after up to 3,000 printing strokes.

- Sn58Bi Type 3 (Paste A) also assessed after 30 minutes stencil idle time followed by printing on 0.4mm pitch QFP & 0.3mm pitch BGA/CSP board pads.

Experimental

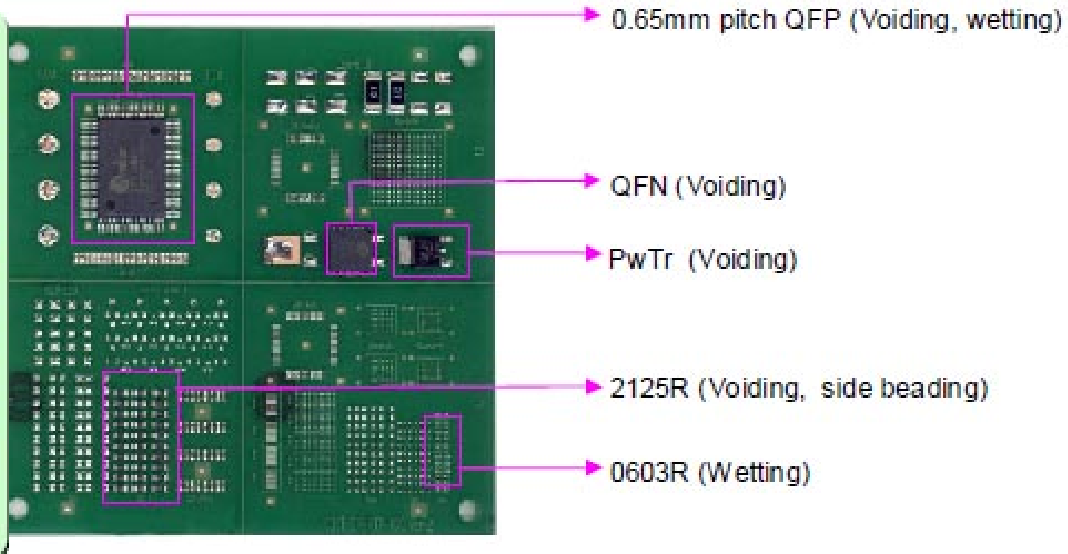
Reflow/ Wetting

Sn58Bi Type 3 (Paste A) was reflowed on different metal test pieces to assess spreadability including:

- Copper
- Brass
- Alloy 42 (Fe42Ni)
- Nickel

Experimental (Reflow/Wetting)

Sn58Bi Type 3 (Paste A) was also used to assess soldering to 0603 [0201] chip and 0.65mm pitch QFP components on reflowed company test boards in air atmosphere.

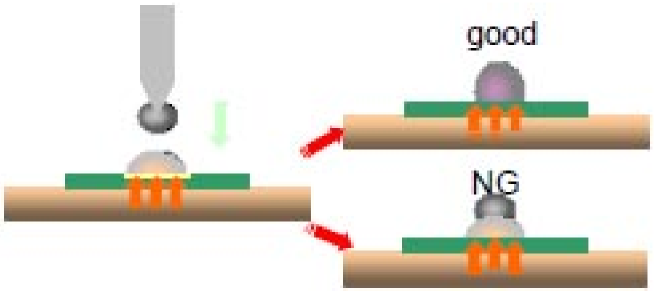


Peak temperature of 180ºC with a time over 138ºC of 65 seconds.
Soak time between 120ºC to 130ºC of 110 seconds.

Experimental (Head-in-Pillow Test)

Testing conducted using Sn3Ag0.5Cu solder ball spheres with:

- Sn57.6Bi0.4Ag Type 4 (Paste A and Paste B)
- Sn3Ag0.5Cu Type 4 (Paste C)



Test procedure : Melt solder paste on hot plate and drop solder ball at every 10sec.

- Hot plate temperature for the tin-bismuth based solder pastes were 200ºC versus 275ºC for Sn3Ag0.5Cu solder paste.

Experimental (Pin-in-Paste)

Testing conducted with:

- Sn57.6Bi0.4Ag Type 3 (Paste A)
- Sn57.6Bi0.4Ag Type 3 (Paste B)

Paste printed into 0.6mm diameter through holes on 1.6mm thick (63mil) OSP coated company test vehicle

0.5mm diameter brass lead wires then inserted into board followed by reflow in air atmosphere.

Experimental (Voiding Studies)

1. Studies on soldered 6432 [2512] pure tin coated chip component, Sn3Ag0.5Cu 1mm pitch BGA and pure tin coated power transistor components using:

- Sn58Bi (Paste A)
- Sn3Ag0.5Cu (Paste C)

2. Evaluations using power transistor components on OSP, Sn and NiAu board finishes with:

- Sn57.6Bi0.4Ag Type 4 (Paste A)
- Sn57.6Bi0.4Ag Type 4 (Paste B)

Experimental (Voiding Studies- cont.)

3. Voiding assessment with power transistor to assess affect of silver content using:

- Sn58Bi Type 3 (Paste A)
- Sn57.6Bi0.4Ag Type 4 (Paste A)
- Sn57Bi1Ag Type 4 (Paste A)

Experimental (Solder Paste Durability)

Evaluations with Sn57.6Bi0.4Ag Type 3 (Paste A) over 5 days continuous use to determine:

- Variations in viscosity and thixotropic index of paste.
- Print quality on 0.3mm pitch BGA/CSP and 0.4mm pitch QFP components.
- Reflow behavior on 0603[0201] pure tin coated chip components and large 6330 [2512] chip board pads.
- Voiding behavior on pure tin coated power transistor components.

Experimental (Bond Strength Tests)

1. Solder joint bond strength assessed for various soldered chip and lead-frame components using:

   0.65mm pitch QFP, 3216[1206] chip, 2012[0805] chip, 1608[0603] chip reflowed with Sn58Bi, Sn3Ag0.5Cu & Sn37Pb paste.

2. Additional studies looked at effect of silver additions to tin-bismuth solder using:

   0.65mm pitch QFP

3216[1206] chip, 2012[0805] chip

reflowed with Sn58Bi, Sn57.6Bi0.4Ag,Sn57Bi1Ag paste.

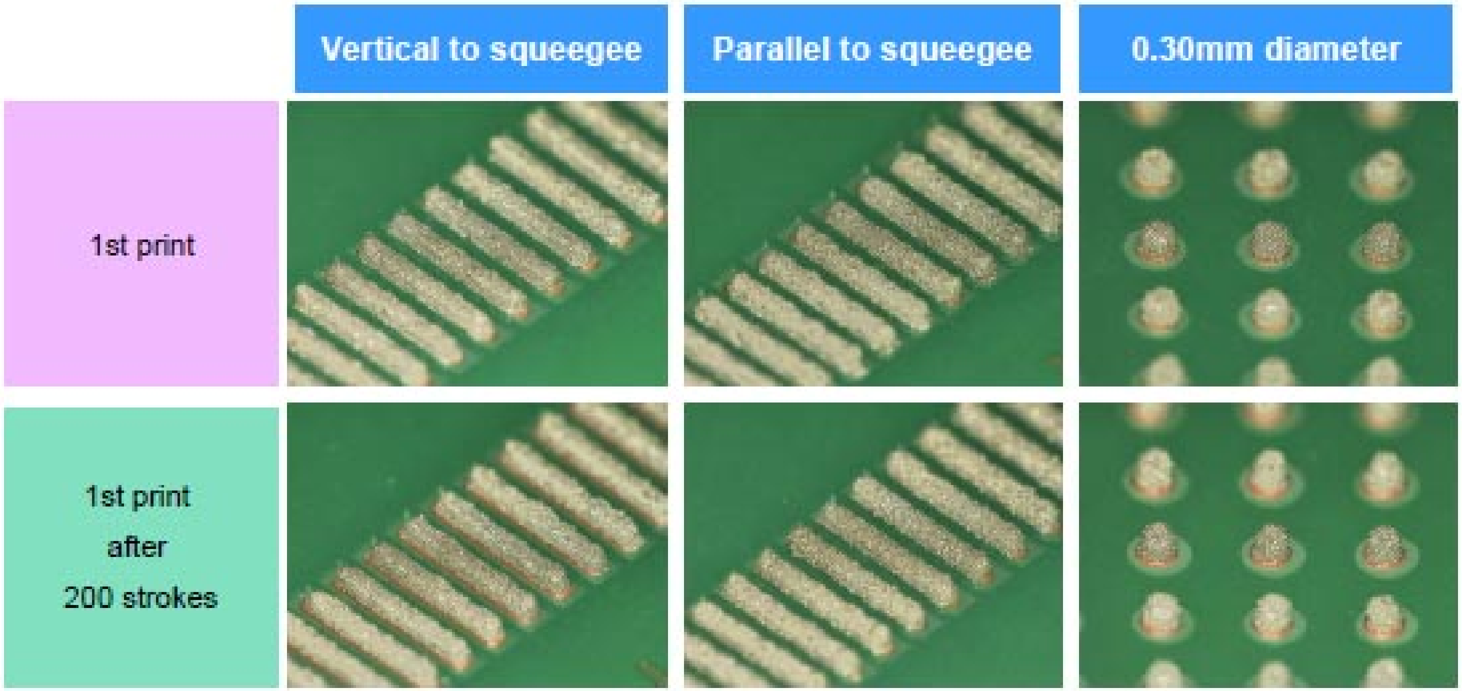
Experimental (Cross-sectional Analysis)

Cross-sectional analysis done using:

- Sn58Bi (Paste A)
- Sn57.6Bi0.4Ag (Paste A)
- Sn57Bi1Ag (Paste A)

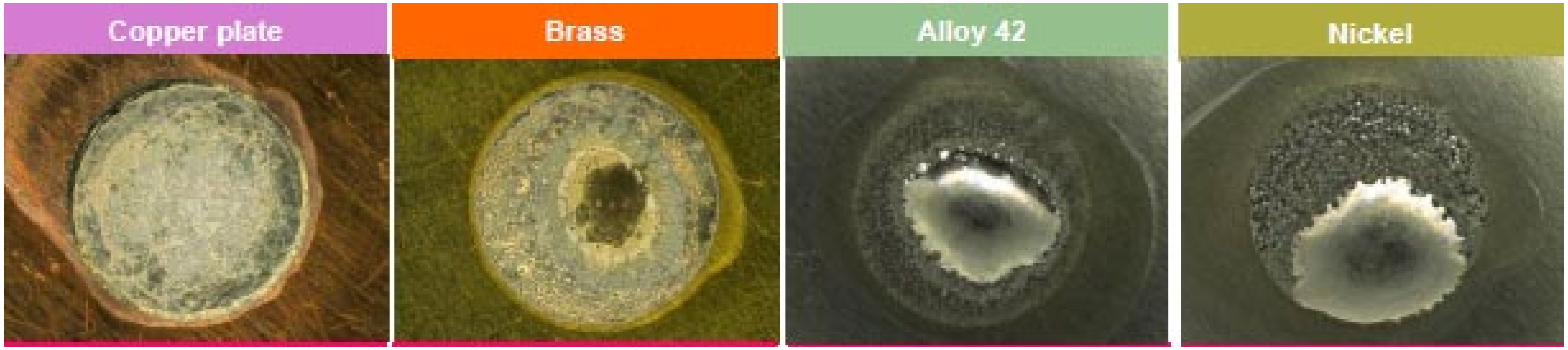
on reflowed 3216[1206] chip components.

Results and Discussion (Paste Printing)



Continual printing tests for Sn58Bi Type 3 (Paste A) and Sn57.6Bi0.4Ag Type 4 (Paste A) on 0.4mm pitch QFP & 0.3mm pitch BGA/CSP pads gave good solder paste deposition on board pads.

Results and Discussion (Reflow/Wetting)



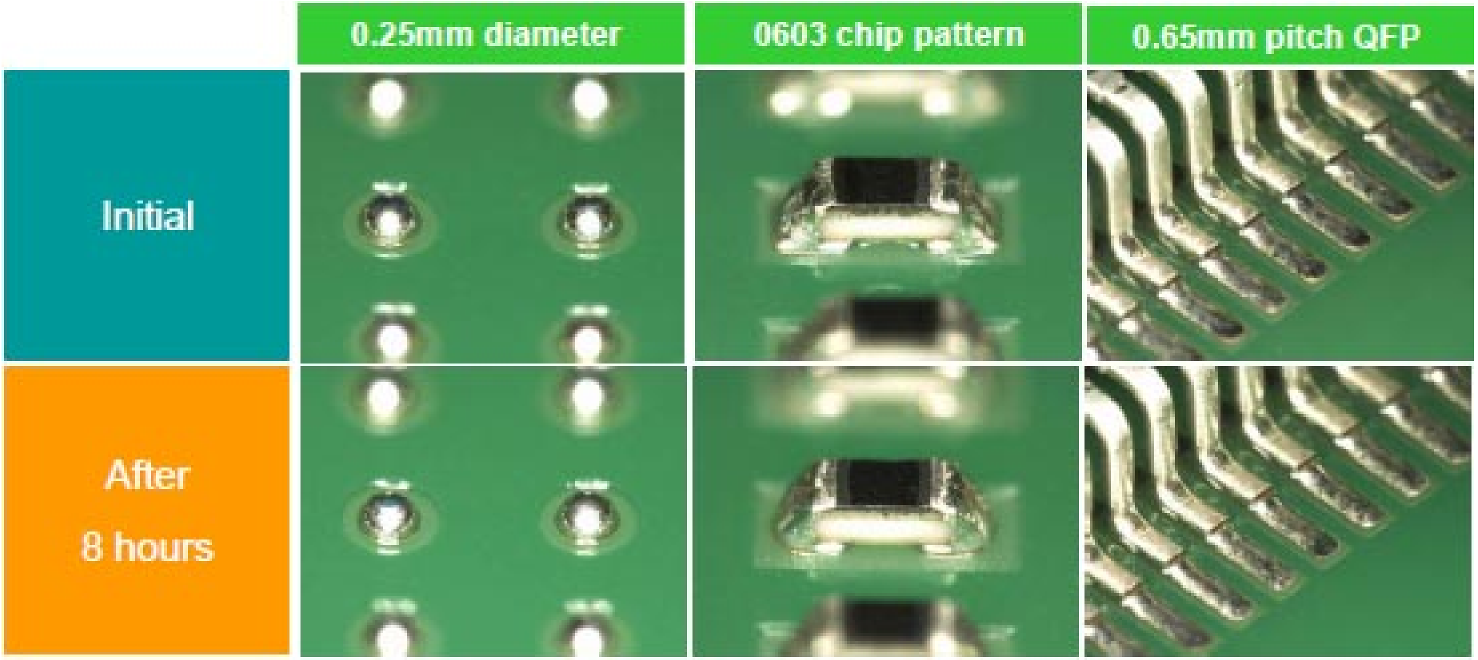
Sn58Bi Type 3 (Paste A) spreading after reflow on Copper, Brass, Alloy 42, Nickel substrates showed:

- Good spreading on copper and brass substrates over the area that the solder paste was printed.
- Partial spreading on Alloy 42 and Nickel substrates which was expected for these hard to solder surfaces.

Results and Discussion (Reflow/Wetting)

Sn58Bi Type 3 (Paste A) assembled on test boards with:

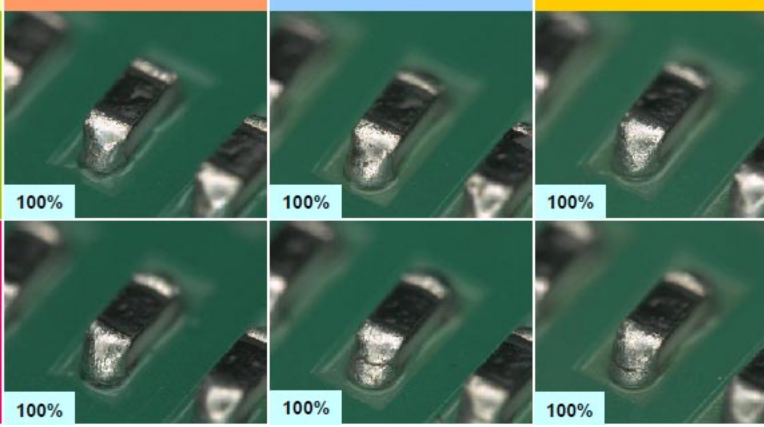
- 0603 [0201] chip
- 0.65mm pitch QFP components had good wetting to the components at time zero & 8 hours of rolling the solder paste on stencil before printing and reflow.

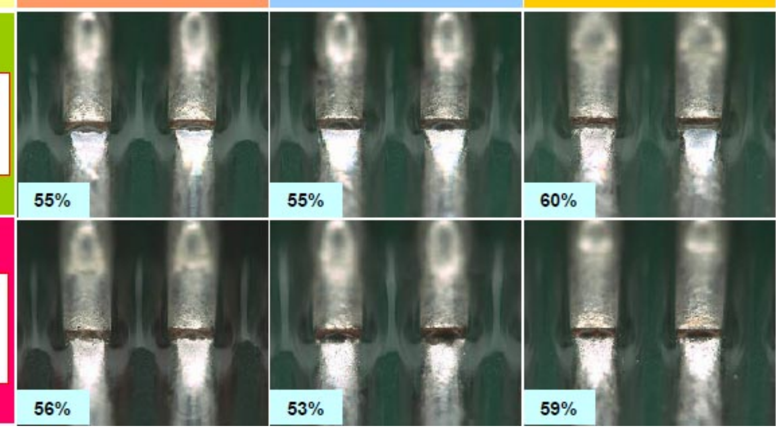


Results and Discussion (Reflow/ Wetting)

Sn57.6Bi0.4Ag Type 4 (Paste A) and (Paste B) printing and reflow with 0603 [0201] chips and 0.65mm pitch QFP components on OSP, Sn and NiAu board surface finish test boards

0603 chip (complete fillet formation/total 80 chips per each surface finish)				QFP leads (Wetting meniscus height to thickness of toe; total 100 pins per surface finish)			
Product	OSP	Sn	NiAu	Solder paste	OSP	Sn	NiAu
Sn57.6Bi0.4Ag Type 4 Paste A	100%	100%	100%	Sn57.6Bi0.4Ag Type 4 Paste A	55%	55%	60%
Sn57.6Bi0.4Ag Type 4 Paste B	100%	100%	100%	Sn57.6Bi0.4Ag Type 4 Paste B	56%	53%	59%

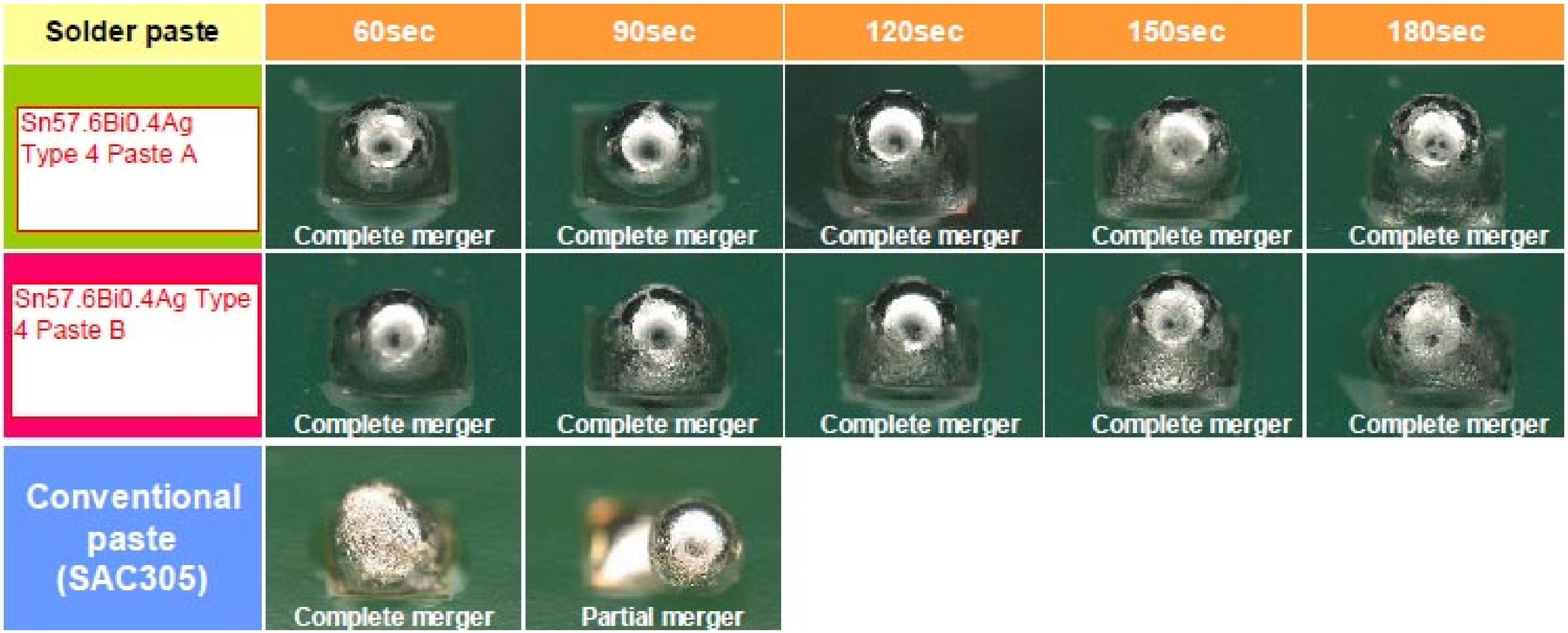




- Good wetting for chip components and reasonable wetting on QFP components with each paste.

Results and Discussion (Head-in-Pillow)

- Head-in-Pillow testing with Sn57.6Bi0.4Ag (Paste A) vs Sn57.6Bi0.4Ag (Paste B) vs Sn3Ag0.5Cu (Paste C).

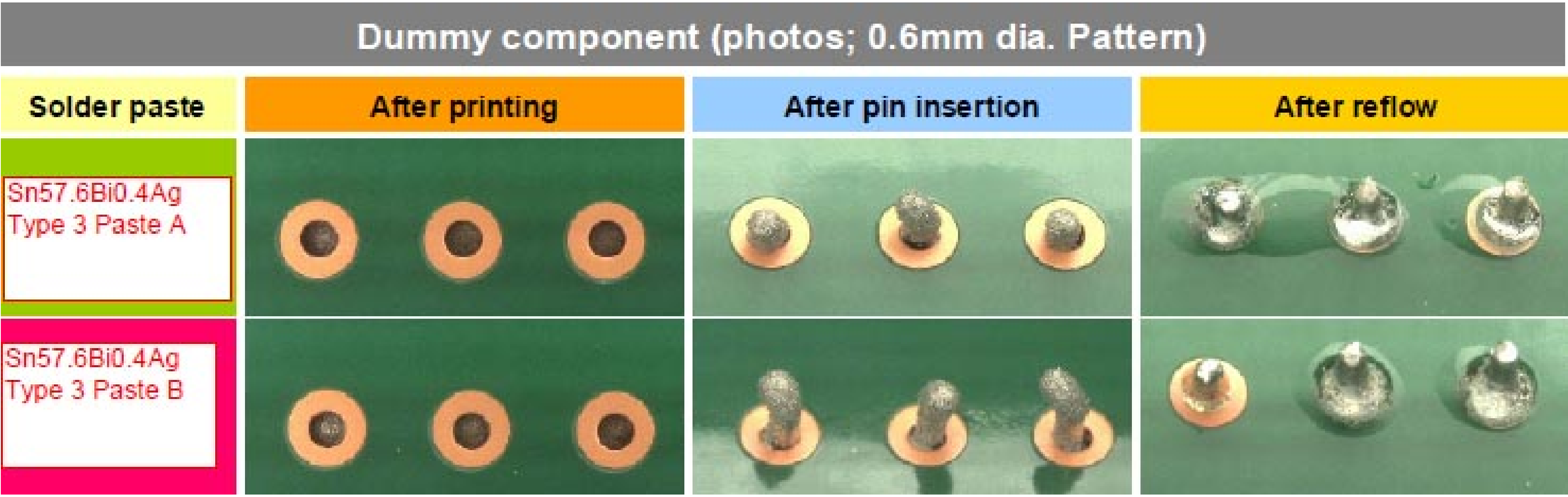


- Both Sn57.6Bi0.4Ag pastes had complete merger of solder sphere after 180 seconds vs 60 seconds with Sn3Ag0.5Cu.
- Lower hot plate temperature used with tin-bismuth based pastes meant that flux was not used up with improved head-in-pillow performance.

Results and Discussion (Pin-in-Paste)

Testing conducted with:

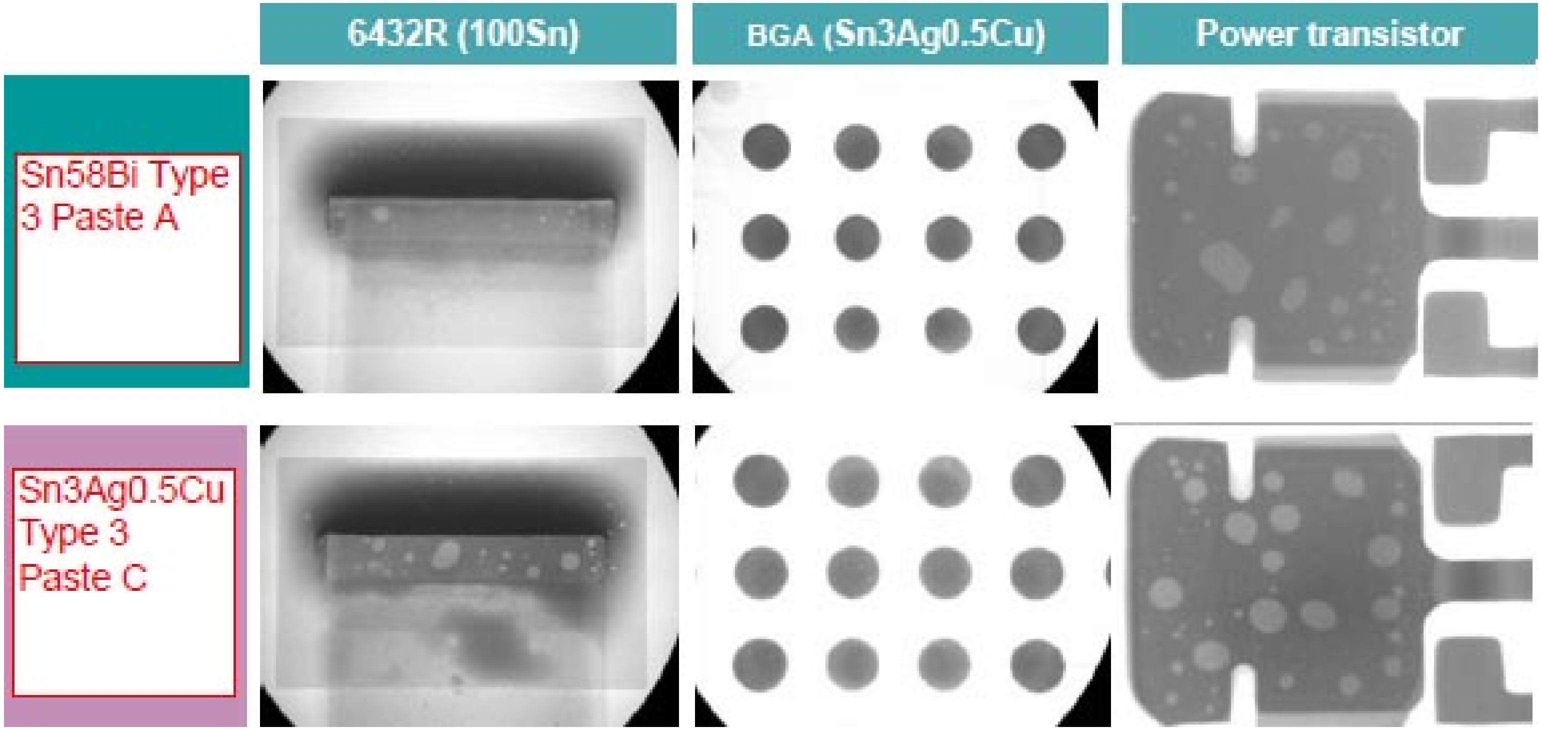
- Sn57.6Bi0.4Ag Type 3 (Paste A) vs Sn57.6Bi0.4Ag Type 3 (Paste B).



- SnBi0.4Ag (Paste A) results showed better wetting after reflow versus SnBi0.4Ag (Paste B).

Results and Discussion (Voiding)

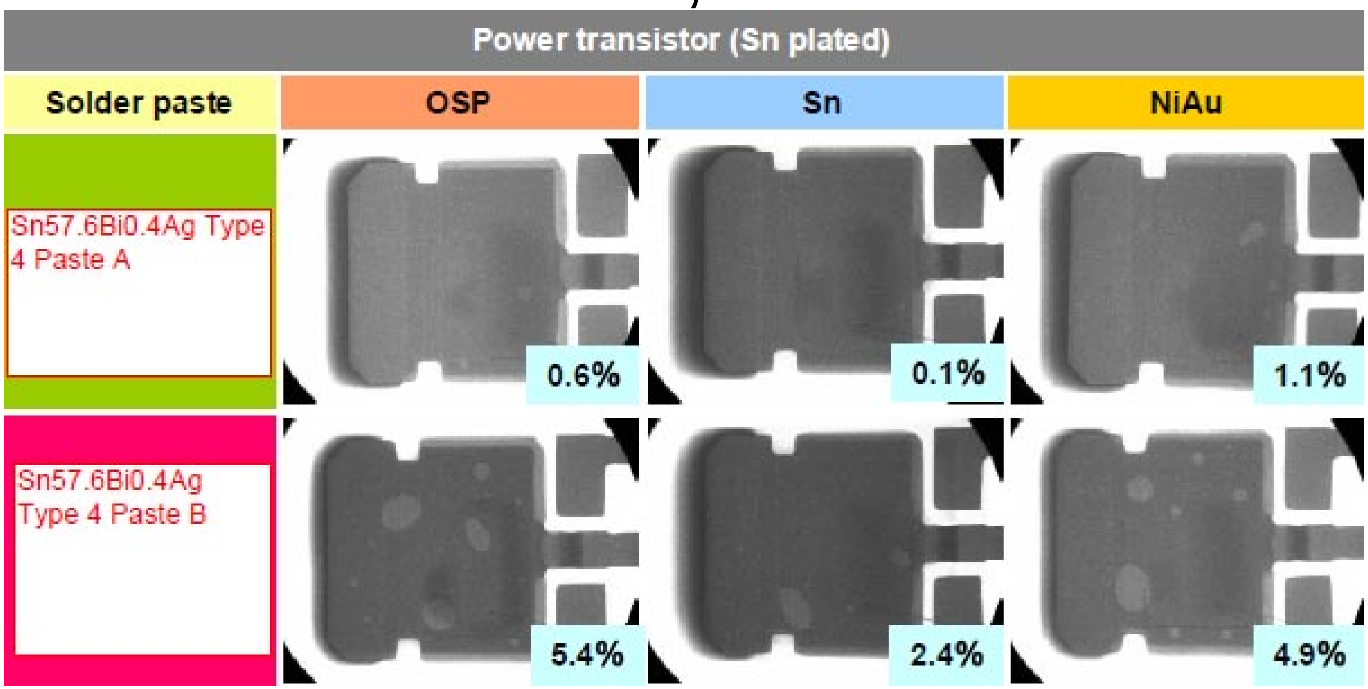
Voiding conducted on 6432 [2512] chip, Sn3Ag0.5Cu 1mm pitch BGA and Power transistors using Sn58Bi Type 3 (Paste A) vs SnAgCu Type 3 (Paste C).



- Generally lower voiding amount with Sn58Bi (Paste A).
- Surface tension of Sn58Bi solder would be lower than Sn3Ag0.5Cu solder during reflow so easier for voids to escape

Results and Discussion (Voiding- cont.)

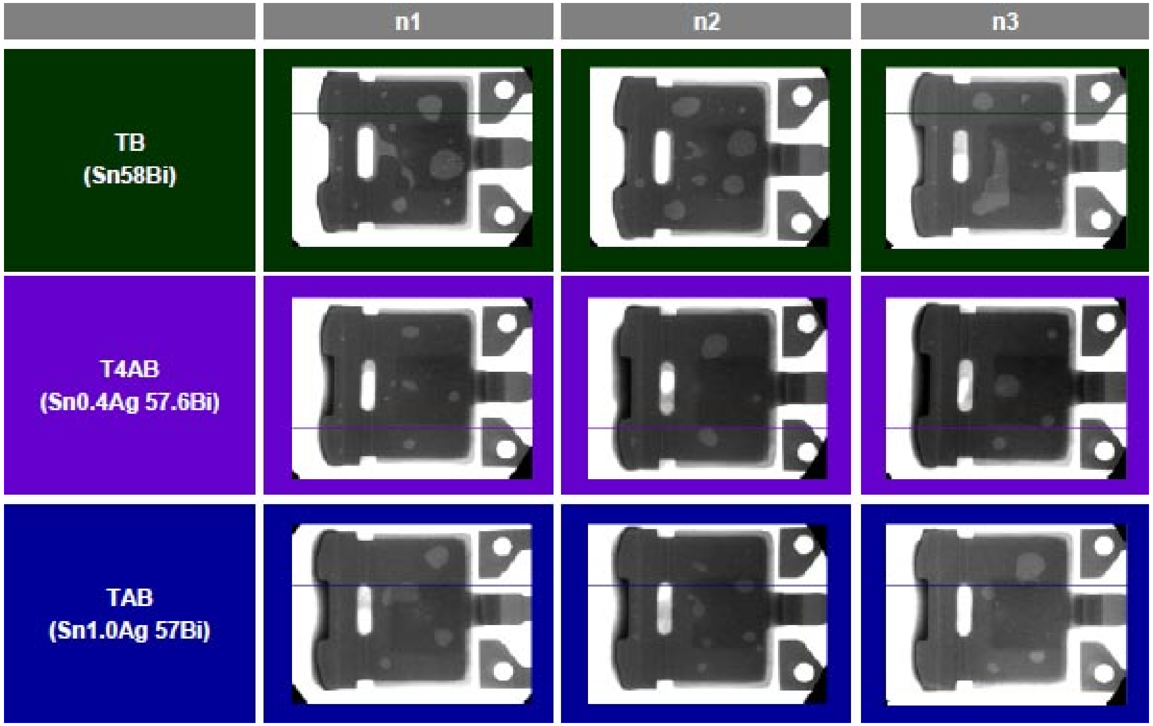
Voiding evaluations conducted on Sn57.6Bi0.4Ag Type 4 (Paste A) vs Sn57.6Bi0.4Ag Type 4 (Paste B) with power transistor on OSP, Sn and NiAu boards.



Sn57.6Bi0.4Ag (Paste A) showed min. voiding on all 3 board surface finishes vs Sn57.6Bi0.4Ag (Paste B).

Results and Discussion (Voiding- cont.)

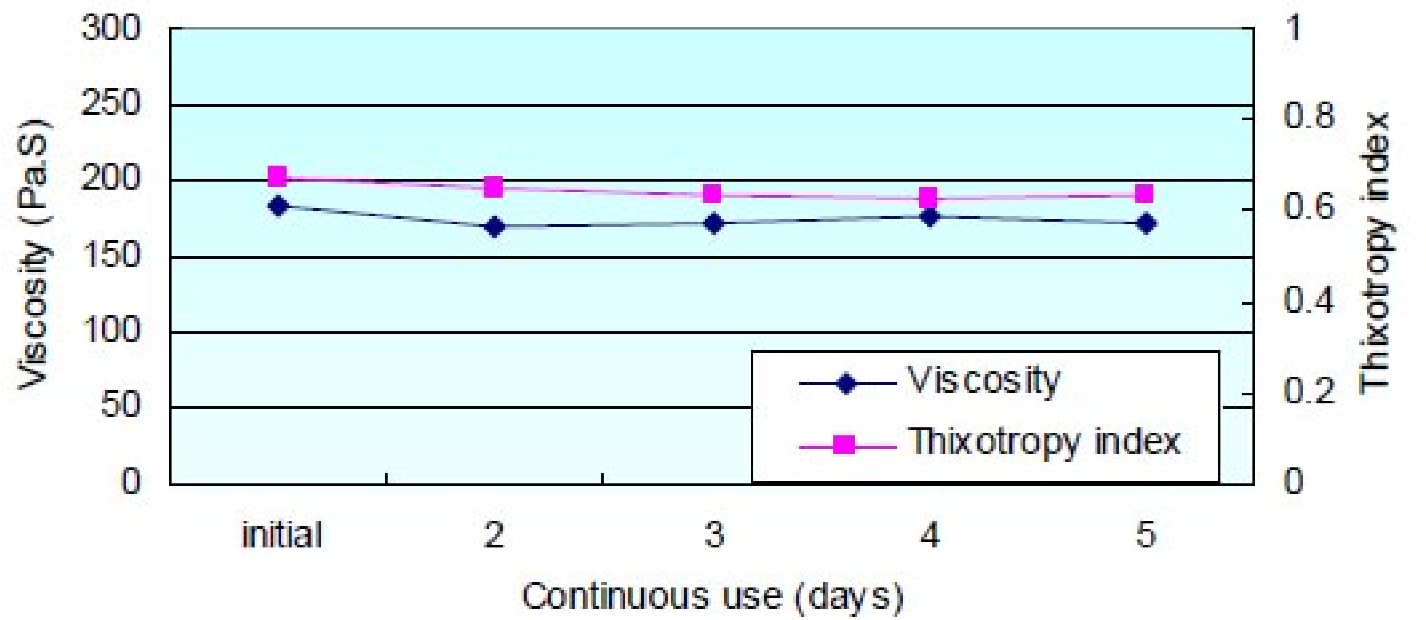
Voiding study with power transistor using Sn58Bi (Paste A) vs Sn57.6Bi0.4Ag (Paste A) vs Sn57Bi1Ag (Paste A).



- Generally no real difference between the three solder pastes indicating voiding more dependent on the flux type in the paste than silver content.

Results and Discussion (Solder Paste Durability)

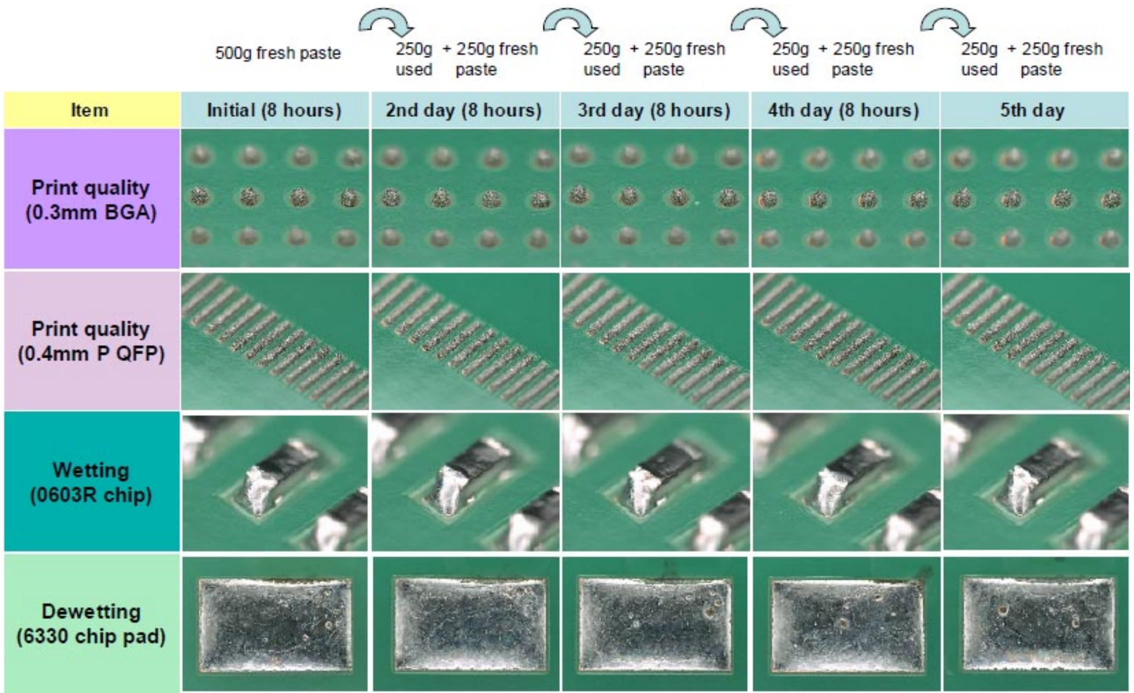
Evaluations conducted on Sn57.6Bi0.4Ag Type 3 (Paste A) over 5 days continuous use



- Minimal variation in viscosity or thixotropic index of the paste over the 5 day period.

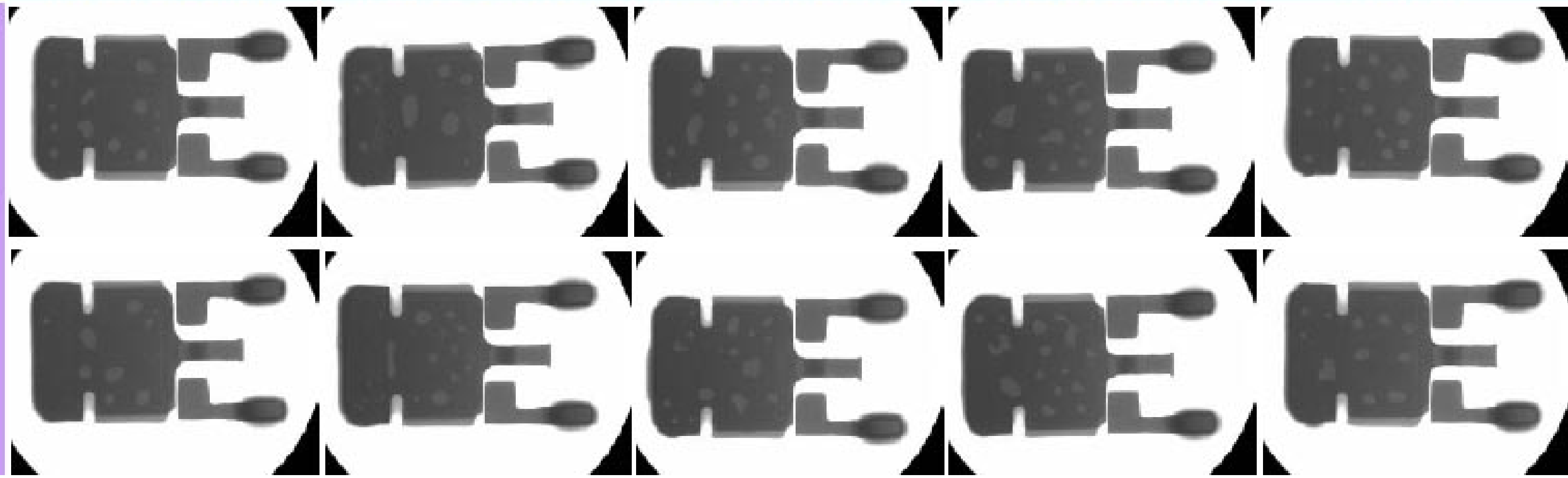
Results and Discussion
Solder Paste Durability- cont.

Over 5 day printing study, solder paste print quality was good on 0.3mm pitch CSP & 0.4mm pitch QFP components with good reflow on soldered 0603 [0201] chip & large 6330 [2512] board pads.



Results and Discussion
Solder Paste Durability- cont.

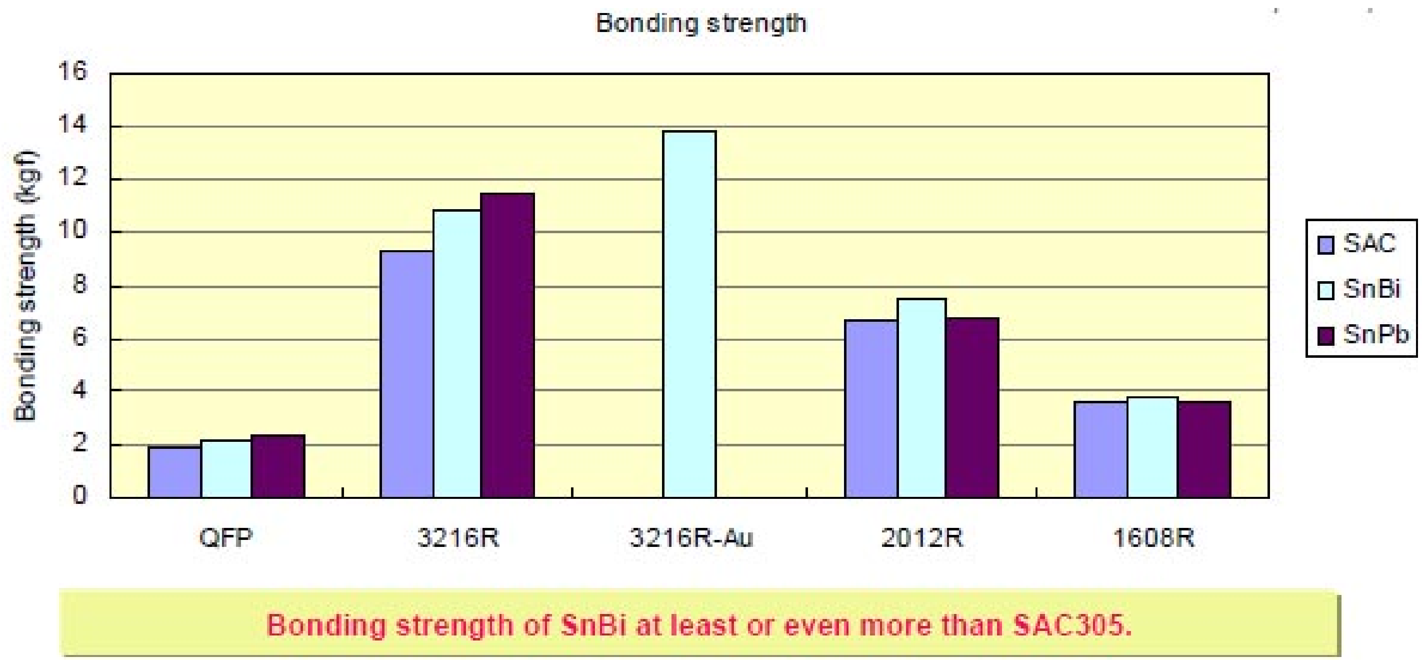
Voiding was low with Sn57.6Bi0.4Ag (Paste A) on reflow soldered power transistor during the 5 day print and reflow study.

Item	Initial (8 hours)	2nd day (8 hours)	3rd day (8 hours)	4th day (8 hours)	5th day
Voiding (Power Tr.)					

Results and Discussion (Bond Strength)

Initial solder joint bond strength tests done using:

0.65mm pitch QFP, 3216[1206] chip, 2012[0805] chip and 1608[0603] chip reflowed with Sn58Bi, Sn3Ag0.5Cu and Sn37Pb.

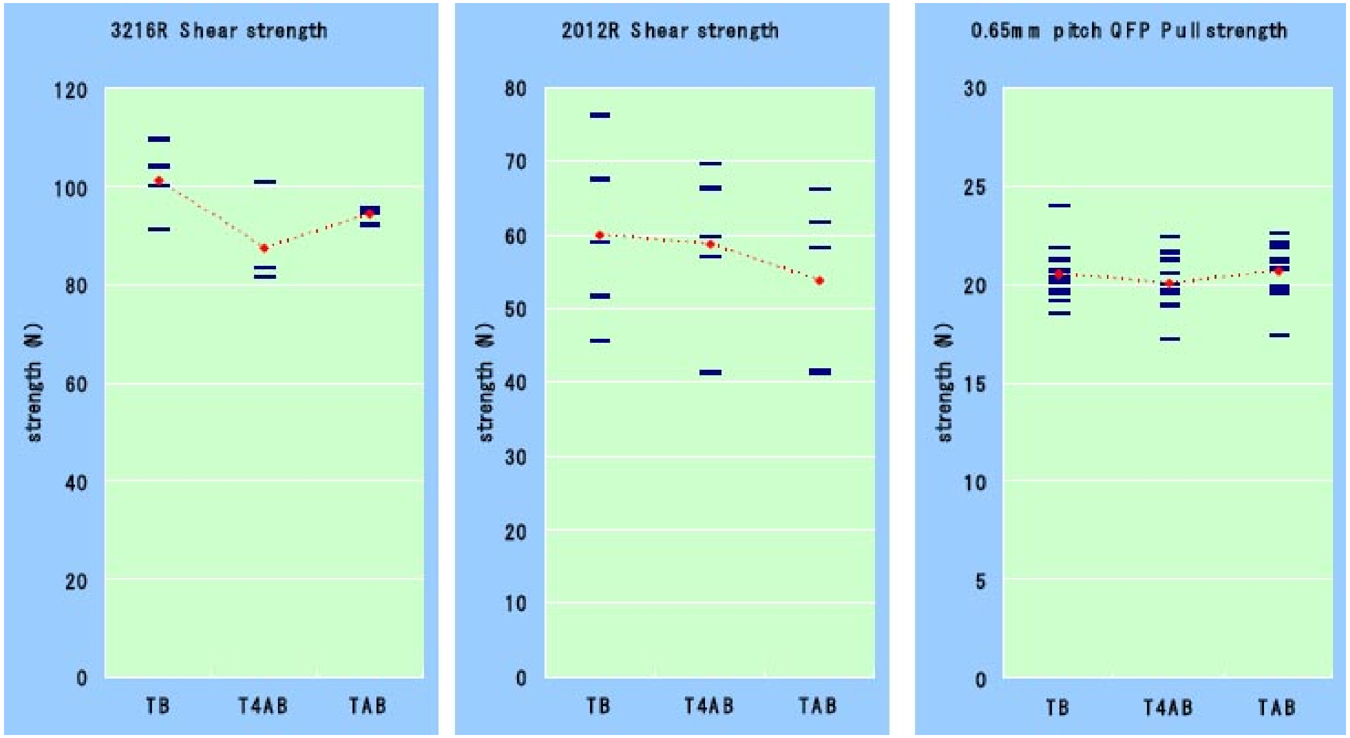


- Bond strength with Sn58Bi was equivalent or better than Sn3Ag0.5Cu or Sn37Pb.

Results and Discussion Bond strength – cont.

Additional studies on effect of silver additions in tin-bismuth solder on bond strength results.

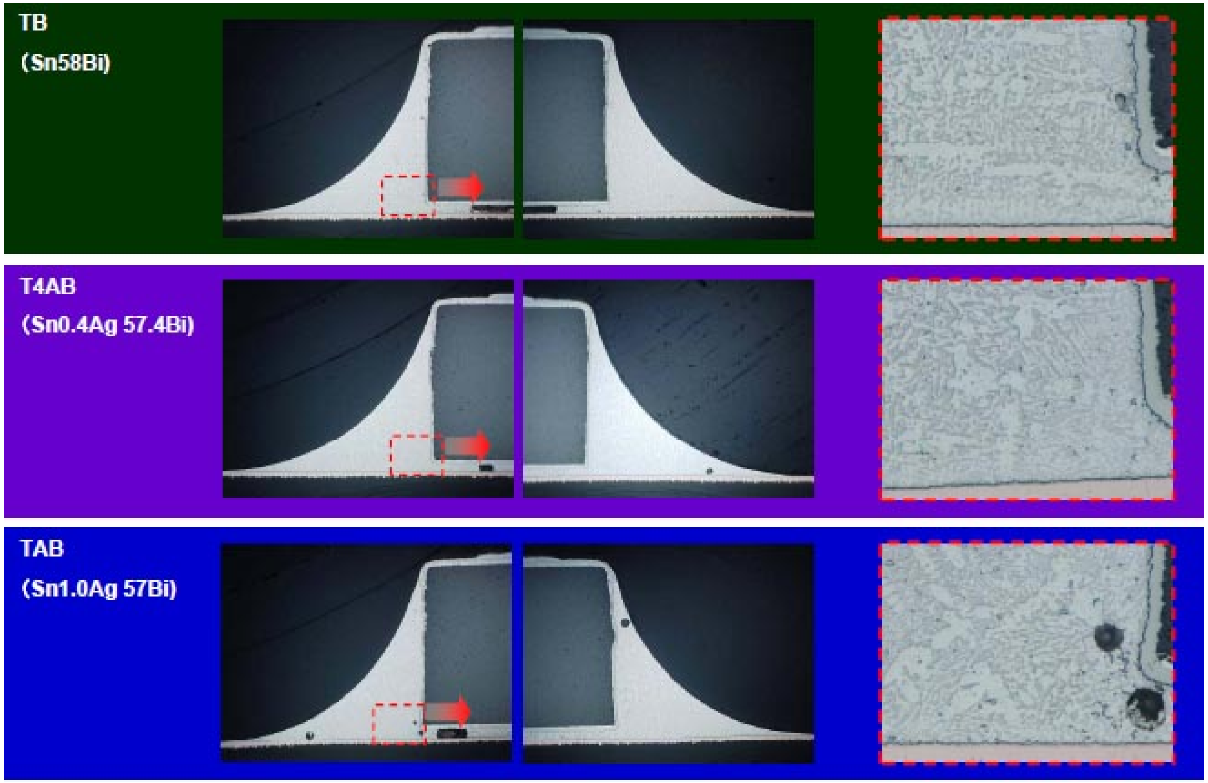
- Results indicated minimal differences in pull & shear test results between Sn58Bi (TB), Sn57.6Bi0.4Ag (T4AB) and Sn57Bi1Ag(TAB) solders.



Results and Discussion

Cross-sectional Analysis

Cross-sectional analysis on 3216 [1206] chip components soldered with Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag.



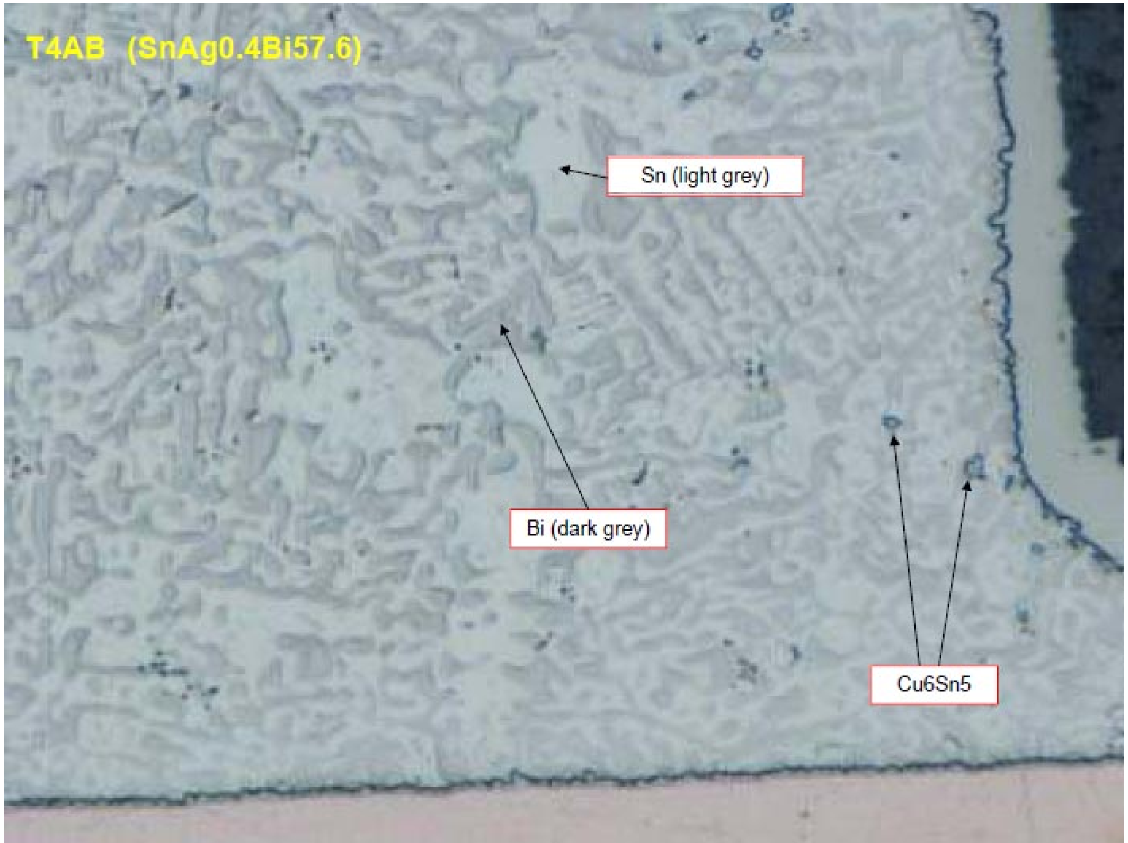
- The results indicate good soldering to the chip components and the board for all three solder alloys.

Results and Discussion

Cross-sectional Analysis –cont.

Microstructures for all three tin-bismuth soldered alloys indicate:

- Tin and bismuth phases in all microstructures
- Some evidence of Cu_6Sn_5 IMC in bulk microstructure
- Good soldering to the board and component interfaces.



Conclusions

Based on the tests conducted the following was determined:

- Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag solder pastes show good printing and reflow performance over the variety of components tested.
- The tin-bismuth solder pastes were found to have good head-in-pillow performance and were acceptable for pin-in-paste soldering.
- Voiding studies on power transistor components showed low voiding with the developed tin-bismuth Paste A with minimal effect on voiding amount from silver additions to the tin-bismuth pastes.

Conclusions (Cont.)

- Paste durability studies showed good results over the 5 day print and reflow testing for the developed tin-bismuth paste.
- Pull and shear testing data for tin-bismuth soldered components were equivalent or better than Sn3Ag0.5Cu and Sn37Pb soldered components.
- There was minimal differences in pull and shear test results for Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag soldered components.
- Cross-sectional analysis of Sn58Bi, Sn57.6Bi0.4Ag and Sn57Bi1Ag soldered components showed good bonding to the board and component interfaces.

Future Work

- More developments would be done with tin-bismuth based lead-free solder pastes to:
  - improve print and reflow performance
  - further assess solder joint reliability

Acknowledgements

The authors would like to thank the research and development engineers at Koki in Japan who conducted the tin-bismuth solder paste development and analysis tests reported in this paper.

- Appendix

Results and Discussion
Solder balling analysis

Evaluations conducted with Sn57.6Bi0.4Ag Type 4 (Paste A) vs Sn57.6Bi0.4Ag Type 4 (Paste B) on 2125 [0805] chip components on OSP, Sn and NiAu boards.

2125R chip (Solder beading; total 60 chips per surface finish)

Solder paste	OSP	Sn	NiAu
T4AB58-M741	7	9	2
Competitive product (Sn/Bi57.6/Ag0.4)	19	24	34

- A reduced amount of solder balling with Sn57.6Bi0.4Ag (Paste A) vs Sn57.6Bi0.4Ag (Paste B) was found after reflow.