Advantages of Bismuth-based Alloys for Low Temperature Pb-Free Soldering and Rework

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Introduction

The increased function of personal electronic devices, such as mobile phones and personal music devices, has driven the need for smaller and smaller active and passive components. This trend toward miniaturization, occurring at the same time as the conversion to RoHS-compliant lead-free assembly, has been a considerable challenge to the electronics assembly industry. The main reason for this is the higher reflow process temperatures required for Pb-free assembly. These higher temperatures can thermally damage the PCB and the components. In addition, the higher reflow temperatures can negatively affect the solder joint quality, especially when coupled with the smaller paste deposits required for these smaller components. If additional thermal processing is required, the risk increases even more.

A low temperature solder is advantageous in this process in that its lower temperature thermal processing requirements can reduce the total thermal damage caused by using higher melting temperature alloys. Defects, such as delamination or "pop-corning" of moisture sensitive devices (MSD), could be minimized or eliminated by using lower temperature solders. Delamination or pop-corning failure modes occur when moisture diffuses into plastic components that rapidly expand upon heating. These lower temperature alloys may also be considered for use with temperature sensitive components, the step soldering process, or rework.

The base metal for most solders is tin, which melts at 232^{o}C. In low temperature soldering a number of alloying elements can be used to reduce tin's melting temperature. Ga, In, Bi, and Cd are effective in reducing the melting temperature of solder alloys, although Cd is not often considered due to its toxicity. Gallium-containing alloys are not practical as they are typically liquidus at room temperature or slightly above. This leaves bismuth and indium as alloying candidates for a low temperature tin-based solder alloy. Indium has some unique properties, but it is much more costly than other alloying elements, which are generally used in solders. Bismuth is a low cost alloying option, especially in light of rising metals costs, and will be considered in this paper. More specifically, we will investigate the BiSnAg alloy with a composition of 57Bi/42Sn/1Ag. Many companies have evaluated this alloy, with much of work done by Hewlett-Packard (HP). Some of this work will be re-visited in this paper.

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Metal	Source	Price/lb.	
Bismuth	Metal Bulletin	$11.45	Avg.
Copper	Metal Bulletin	$4.37	4/27/2011
Indium	Metal Bulletin	$343.00	Avg.
Lead	Metals Week	$1.27	Avg.
Silver	NYMEX	$674.00	4/27/2011
Tin	Metals Week	$14.63	4/27/2011

Figure 1. Metals chart.

This BiSnAg alloy has a lower melting temperature than eutectic tin-lead solder's (Sn63Pb37 or Sn63) 183°C, yet it is high enough for most soldering applications. In addition, its mechanical properties are similar to Sn63, but contain no lead. The alloy is near eutectic at its 137-139°C. Although a reflow temperature of 20-40oC above liquidus is typically recommended, the BiSnAg alloy still only requires a maximum reflow processing temperature of about 180°C. Sn63 assembly generally requires 205-215°C (or higher if reflowing Pb-free BGAs -225-230°C) and process temperatures of 240-245°C are common for Pb-free assembly. Work performed by HP on shear strength, creep resistance, fatigue resistance, and other mechanical testing showed BiSnAg to have properties approaching or surpassing Sn63 under most conditions, including reasonable strength up to 90°C.[1]

There are some concerns with bismuth-containing alloys, as Bi tends to be fairly brittle. Bismuth (and many bismuth alloys) are unique in the sense that they expand upon cooling, which can cause issues, such as fillet lifting, with through-hole components, and if used in an application where lead is present, can form a low-melting eutectic at 96°C. This concern was a real issue when the industry was first transitioning into the lead-free arena because most assemblies were only partially lead-free and lead contamination was a real concern. As the transition has progressed this situation has become much less an issue.

In addition to reviewing the work HP has done with this alloy, new work on stencil printing characteristics, reflow profile optimization, and solder joint quality will be presented.

The Hewlett-Packard Work

Wetting

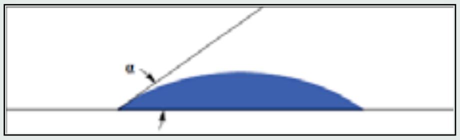
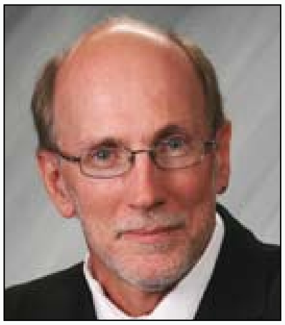


Figure 2. Wetting angle α on CuOSP [1].

There are a number of factors that affect wetting behavior, such as the surface tension of the solder, PCB pad metallization, and flux activity. Early work by HP [1] showed that the flux activity of the materials that were tested was vital to the results, but once the proper flux chemistry was achieved, the results (spread test and wetting angle as pictured in Figure 2) were near those of Sn63. The lower melting temperature BiSnAg alloy requires a flux with a lower activation temperature. Most tin-lead fluxes activate at 160-170°C and are not optimal for the BiSnAg process.

ED BRIGGS



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Shear

Solder joints experience shear stress caused by differences in CTE (coefficient thermal expansion) mismatch in temperature cycling. The HP study found that the BiSnAg alloy had a higher shear strength than Sn63 at 20°C, a comparable shear strength at 65°C, and lower (but comparable) shear strength than Sn63 at 110°C. For more detail on the test procedure and results please refer to *57Bi-42Sn-1Ag: A Lead Free, Low Temperature Solder for the Electronic Industry.* [2]

Creep:

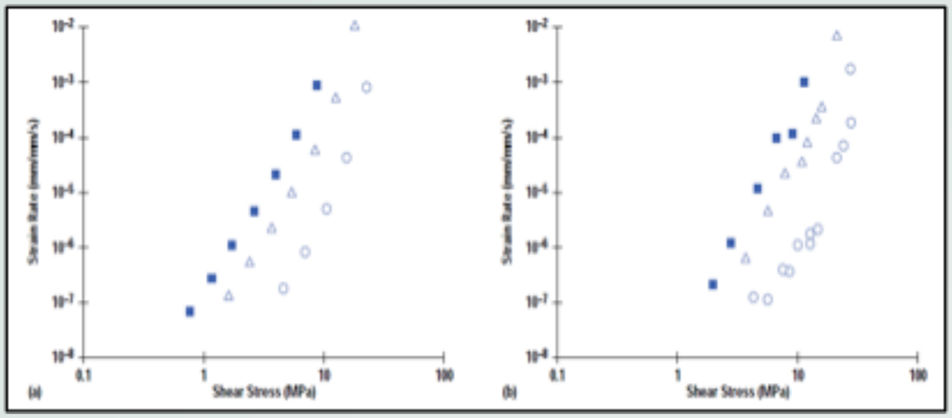

Figure 3. Strain Rate vs. Shear (a) Sn63 (b) SnBi.[1]

Creep is defined as a constant load applied at an elevated temperature causing deformation or flow over time. Results from the HP study are shown in Figure 3. The steady state strain rates as a function of shear stress are plotted at 25°C, 65°C, and 90°C (for BiSn and Sn63, no data were available for the BiSnAg). Creep resistance of BiSn exceeds Sn63 at 25-65°C. [1]

Thermal Fatigue

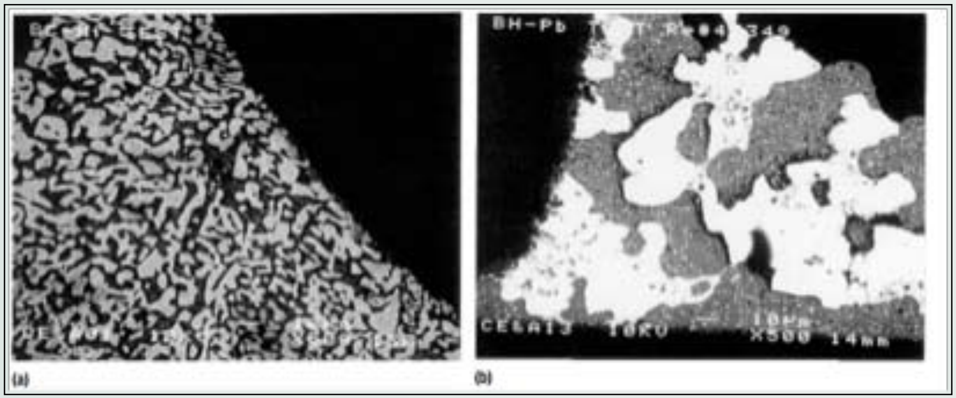

Figure 4. SEM cross section of solder joints the same magnification after thermal cycling (a) BiSn on CuOSP (b) BiSn on Sn63 HASL.. (Note the large grain structure.) [3] .

An interesting finding occurred during HP's thermal fatigue testing. Twenty boards were assembled with Sn63 and 58Bi/42Sn using PCBs with CuOSP and Sn63 HASL finish on the pads. All passed visual and functional testing, but during thermal cycling (-20°C - 110°C) a thermal failure was observed with the BiSn solder on the SnPb HASL finished PCB pads when some of the components fell off after about 500 cycles (whereas the Sn63 failed after 900 cycles). It was noted before testing that the solder joint surfaces of the SnBi on CuOSP and Sn63 HASL were smooth, but afterwards the SnBi on SnPb HASL was grainy, while the BiSn on CuOSP was still smooth. This roughness was due to large grain growth (Figure 4). HP concluded that the grain growth was due to Pb from the surface finish dissolving into the BiSn solder, forming a low melting eutectic at 96°C. Since each cycle reached 100°C, that phase became liquid at the grain boundaries, accelerating the formation of the large grains. [1]

Due to the concern with this low melting point phase, lead contamination studies found that the lead content of <0.3% wt. does not significantly degrade the mechanical properties of BiSnAg even when aged at 100°C. However, it was suggested that the maximum allowable target should be 0.1% wt. Pb.

In later work, HP observed that small additions of Ag (or Au) increased the thermal fatigue life of the BiSn alloy. At -25° to 75°C (BiSnAg), all assemblies survived 7000 cycles, and actually outperformed Sn63. BiSnAg thermal fatigue is comparable or superior to

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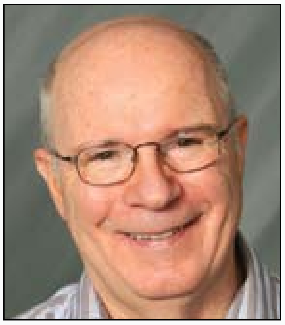

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Sn63 (even in range of 0-100°C and in the absence of Pb contamination). It was suggested by HP that the Ag may decrease the grain size and stabilize the microstructure (a finer microstructure typically is ideal for better mechanical properties). [4]

Bend Test BGAs

In this test, HP incorporated 3 PCB pad surface finishes - CuOSP, ENIG, and ImSn - and a plastic ball grid array (PBGA) with the following solder spheres: 96.5Sn/3.5Ag, Sn95.8/Ag3.5/0.7Cu, 99.3Sn/0.7Cu, and Sn63. A 4-point bend test was performed on assembled boards after aging them isothermally at 90°C for 1, 3, and 10 days.

It was found that the high tin-containing solder spheres (with liquidus ≥217°C) did not melt/collapse using the low temperature profile required for the SnBi solder paste. It was also found that with the SnBi solder paste that the volume of paste deposited on the pad is vital. When the volume was insufficient, all solder joints failed in the solder between the PCB and the BGA ball. However, with adequate paste volume, the SnBi solder joint strength improved enough to force failure by pullout of the Cu pad. Joint strength was about 65% of Sn63. [4]

Summary of HP Testing

BGAs: It was recommended to use SnBi or SnBiAg solder spheres so that the solder joints will collapse and improve the joint microstructure, thus improving the mechanical properties. Current Sn63 or SAC stencil aperture designs can be used. As mentioned, SAC alloy balls will not collapse due to the lower reflow process associated with SnBi or SnBiAg alloys. Therefore, to get the best properties when using the higher melting SAC solder balls, the correct volume of SnBiAg paste is vital. In order to approach Sn63 solder paste performance, more paste is required than current stencil designs for Sn63 or lead-free processes deliver. In HP's study for a 30mil solder sphere where 4000-4500 mil3 was sufficient, 8000-9000 mil3 of SnBi/SnBiAg solder paste was required. The appearance of the reflowed solder joint changed from an hourglass shape to a barrel-like shape. One approach to optimize this issue is to use square vs. circle apertures. For the same area ratio, a square aperture will provide more volume.

Backside components: The SnBi and SnBiAg alloys have a lower surface tension than either Sn63 or lead-free alloys. This lower surface tension may be problematic in double-sided reflow for heavier components on the underside. The lower surface tension of bismuth solder may not hold components in place during the second reflow.

Surface finishes: HP concluded that CuOSP PCB pad surface finishes consistently showed the best mechanical and process results. ImAg, ENIG, and ImSn all produce acceptable wetting and subsequent performance. Thick coatings of Ag or Au should be avoided, as with any Sn bearing solder, due to embrittlement issues.

Bake out: Post baking procedures (if a bake is required) may need to be altered. Twelve hours at 125°C is too harsh for this low melting alloy. A maximum temperature of 90°C for 12-15 hours should be sufficient.

Component placement: Because of the lower surface tension of the SnBi and SnBiAg alloys, the registration of the solder paste deposit to the PCB pad and component placement may be more critical as less self-alignment may occur.

Depanelization: Use adequate fixturing and board support, as the BiSnAg has a more sensitive strain rate. [2]

New Study Results

Printing

The focus of this printing experiment was to observe the transfer efficiency of the SnBiAg solder paste to note any discernable difference in process parameters from the typical Sn63 or lead-free solder pastes. Therefore, in an effort to minimize the number of variables, the same stencil, squeegee blades, and printer parameters were utilized as in previous experiments with the Sn63 and Pb-free solder pastes.

A 4mil laser-cut/electropolished stencil, 250mm squeegee with edge guards, foiless clamps, and landscape vacuum support blocks were used on the stencil printer. The solder paste was printed at 50mm/second squeegee speed with a blade pressure of 4kg.

A test board with 16, 14, 12mil circular and square, (and 11mil squares) was evaluated, 0201, land grid array (LGA), and various rectangles in both solder mask defined (SMD) and non-solder mask defined (NSMD) pads were evaluated. A no-clean solder paste with Type 3 particle size of 57Bi/42Sn/1Ag was chosen. Eight PCBs were printed with no stencil wipe performed and data collected via a Koh Young KY-3020T laser scanning system to measure the volume of the stencil printed deposits.

Area Ratio

The stencil aperture area ratio (AR) is a critical metric in successful stencil printing. It is the area of the stencil aperture opening divided by the area of the aperture side walls. Figure X shows a schematic for a circular aperture. A simple derivation shows that the AR is simplified to the diameter (D) of the circle divided by 4 times the stencil thickness (t) or AR = D/4t. Somewhat surprisingly, the results are the same for square apertures, with D now equal to the side of the square. For the AR of a rectangular aperture, the formula is a little more complicated: ab/2(a+b)t, where a and b are the sides of the rectangle.

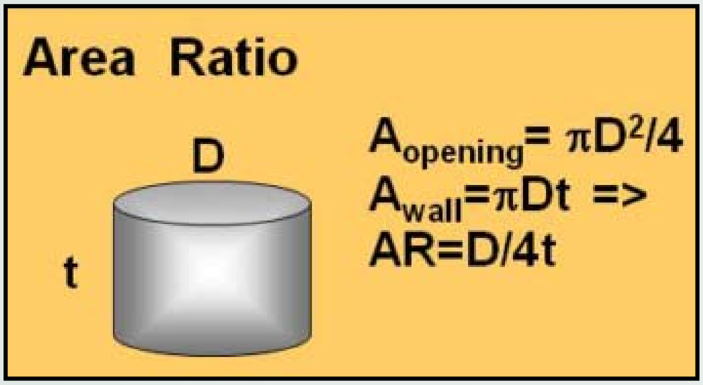

Figure 5. A schematic showing the definition of the area ratio for a circular stencil.

It is widely accepted in the industry that in order to get good stencil printing the AR must be greater than 0.66. Experience has shown that if the AR < 0.66, the transfer efficiency will be low and erratic. Transfer efficiency, another important stencil printing metric, is defined as the volume of the solder paste deposit divided by the volume of the aperture. [5]

Stencil Printing Results

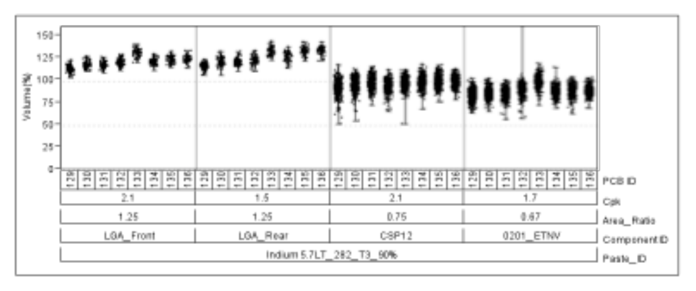

Figure 6.

The transfer efficiency of the LGA pad, 12mil CSP, and 0201 as shown in Figure 6 was excellent. The 0201 area ratio of 0.67 was the greatest challenge and included 6400 data points for reference in this test. With the exception of a couple of outliers, the transfer efficiency was very good.

Circles vs. Squares

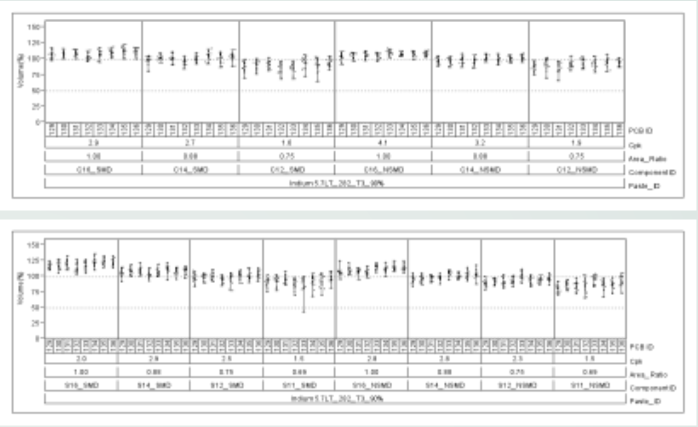

Figure 7.

For the larger apertures, circles provided a bit better Cpk (http://en.wikipedia.org/wiki/Process_capability_index), but as the apertures became smaller the squares began to outperform the circles (Figure 7). The smaller apertures are more challenging in regards to transfer efficiency and the paste volume becomes critical. It's important to note that for a circular and square stencil aperture of the same area ratio, the square (radius corners recommended) aperture delivers more paste volume. The increased volume for these smaller area ratios increases the transfer efficiency as evidenced in the test data.

SMD vs. NSMD

For larger apertures (>14mil), the non-solder mask defined (or pad defined) PCB pads provided better transfer efficiency than the solder mask defined. For the larger pads the non-solder mask defined pads provide a better stencil to PCB gasket. However as the PCB pads become smaller (<14mil) the data shows that the mask defined pads provided better transfer efficiency. Paste release from the stencil aperture relies partially on the adhesion of the solder paste to the PCB pad. As the PCB is lowered from the stencil aperture, adhesion of the solder paste to the PCB helps the paste to "pull" out of the stencil aperture. With the smaller pad there is little surface area for adhesion; the wall of the solder mask (mask defined pad) may increase the surface area for adhesion improving paste release.

In summary the printing process for SnBiAg solder paste was very similar, if not identical, to the Sn63 or lead-free process.

Reflow Profile Results

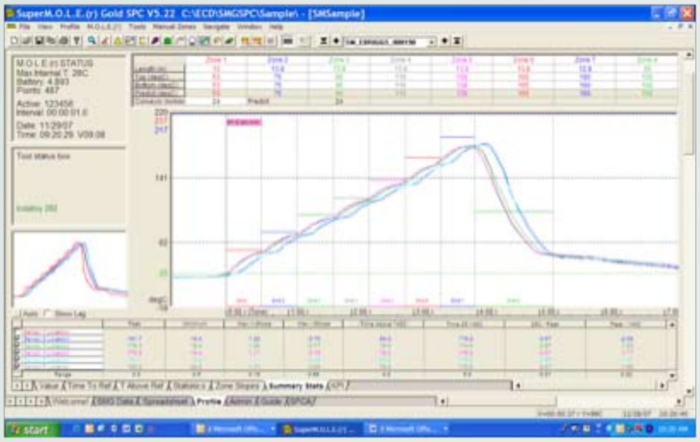

Figure 8.

In our reflow experiments, a ramp-to-peak profile (Figure 8), with a peak temperature of 170-180°C and time above liquidus (TAL) of 70-80 seconds was used. Due to the lower processing temperature, a longer TAL is often necessary to allow for intermetallic formation.

A common test vehicle having apertures of 38.5mil X 390mil with pitch size 90mil was used. The paste was first printed and reflowed on CuOSP finished PCB pads immediately after printing and the solder joints were then evaluated (Figure 9). Additional samples were then printed on ENIG, CuOSP, and ImAg PCB pads and placed in humidity chambers - the first sample for 3 hours at 76% RH and the second sample for 3 hours at 90%RH. The samples were then reflowed to observe the humidity resistance in the solder joint formation (Figures 10 and 11).

Results

Wetting

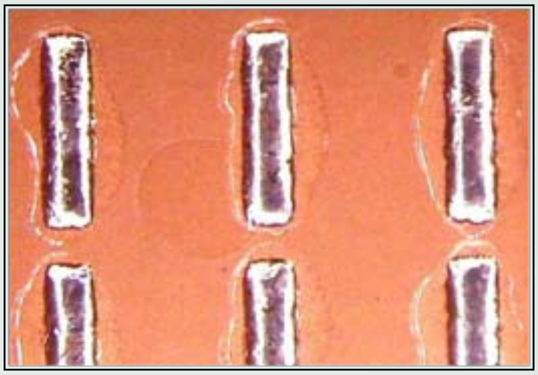

Figure 9. Printed and Immediately Reflowed.

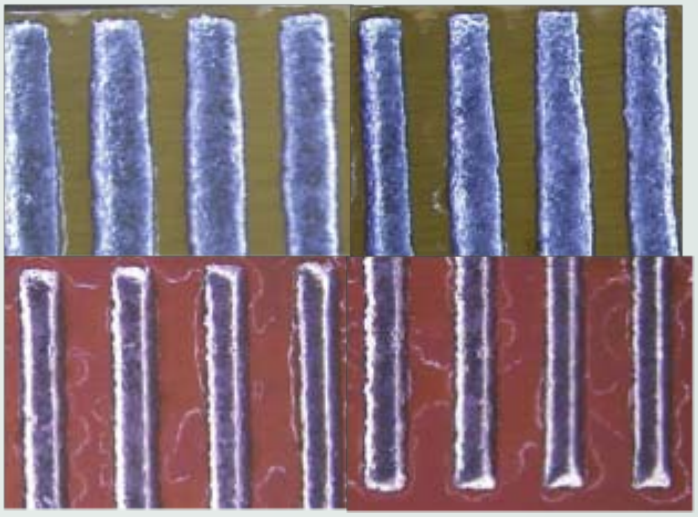

Figure 10. ENIG on Top, CuOSP on Bottom - 3hrs. 76%RH, 3hrs. 90%RH, 3hrs. 76%RH, 3hrs. 90%RH.

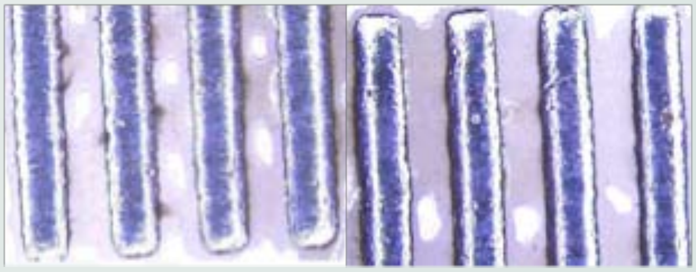

Figure 11. ImAg - 3hrs. 76%RH,3hrs. 90%RH.

Solder Ball

A test vehicle with 100mm CuOSP pads was selected. Solder balls are typically increased if the printed solder paste deposit infringes onto the solder mask. To challenge the solder paste, stencil apertures were also incorporated to purposely overprint onto the solder mask. Stencil apertures for the experiment were 75, 100, 125, 175, 225, and 275mm so that the later aperture openings overprinted the 100mm pads (Figure 12).

The results were very favorable with only 1 solder ball at 225mm stencil aperture (ratio 1.0/2.25) and 2 solder balls on the largest overprint 275mm stencil aperture (ratio 1.0/2.75).

Figure 12. 100mm (1.0/1.0) on Left, 175mm (1.0/1.75) in Middle, 225mm (1.0/2.75) on Right..

Voiding

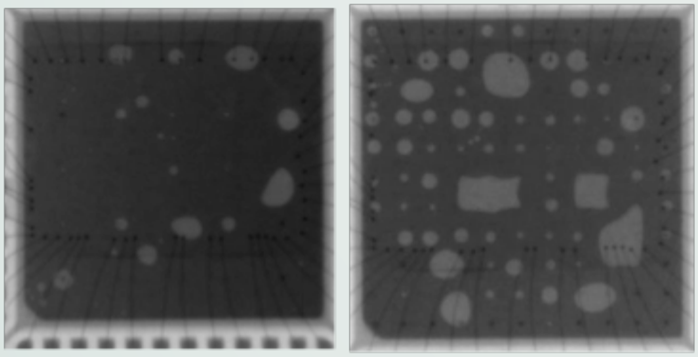

Figure 13. Pattern 1: 5 x 5 via pattern on left, pattern 2: 11 x 11 via pattern on right.

The test vehicle utilized 6mm x 6mm QFNs, ImAg finish, with via-on-pad. The solder paste was printed 1:1 to observe the worst case scenario in regards to voiding. The components were then reflowed and x-rayed to observe the voiding. Examples of the results are shown in figure 13. The results were actually quite good on the 5 x 5 pattern of vias, the 11 x 11, though not as good, was typical compared to lead-free SAC alloys.

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2) 57Bi-42Sn-1Ag: A Lead Free, Low Temperature Solder for the Electronic Industry, Ernesto Ferrer, Helen Holder.
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4) Strength and Fatigue Behavior of Joints Made With Bi-42Sn-1Ag Solder Paste: an Alternative to Sn-3.5Ag-0.7Cu for Low Cost Consumer Products, Valeska Schroeder, Fay Hua and J. Gleason.
5) Fine Powder Solder Pastes: Stencil Printing and Reflow in Lead-Free Assembly, Chris Anglin, Ed Briggs, Tim Jensen, and Ron Lasky.

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