Impact of Lead Contamination on Reliability of Lead Free Alloys

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Abstract
Meeting the RoHS directive will require the transition from the historical tin-lead based system of materials to one that does not contain lead. This is of course is not straight forward as it is impossible to control 100% component material compositions. It is therefore entirely possible that components with lead finishes will find their way into Lead Free processes. The concern is that lead contamination occurring in this way results in 1 to 10% level of lead, and that this lead is not uniformly distributed, but segregates to the grain boundaries and joint interfaces [1]. But what is the effect of this on thermal fatigue. The work reported here will describe experiments where the lead level in solder joints was controlled by altering the plating on component terminations and using controlled solder compositions. Microstructural examination verifies the segregation of lead. The built assemblies were then thermally cycled between –55 and 125ºC for 2000 cycles to assess this effect on reliability. Hot peel tests were also run to simulate problems that may occur is secondary wave operations where the fillet strength collapses and components can detach with little force at temperatures above 180ºC. The use of indicator test kits to detect lead were also evaluated on this set of reference samples. This paper will discuss these results and the likely impact on the industry and the necessary precautions.

Introduction
European legislation means that lead-containing solders will be eliminated from mainstream electronics manufacture, by 1st July 2006. The current preferred solder replacements are based on the Tin-Silver-Copper (SAC) system, which have melting points of 217 ^{o}C and above. T his 30+^{o}C increase in melting point from the established tin-lead solder alloys, necessitates a corresponding increase in processing temperature for both reflow and wave soldering.

The requirement to comply with these European regulations is driving the electronics manufacturing industry to the adoption of new component termination finishes and solder alloys. The first phase of this transition is already underway with many component suppliers offering Lead Free components, alongside conventional tin-lead terminations. There are concerns about the reliability of these new components during the interim period, when they will be used with tin-lead solders. Many manufacturers have reported reliability results for combinations of Lead Free components and both tin-lead and Lead Free solders [2, 3, 4 and 5], but few offer comparative studies with similar tin-lead terminated components.

Similarly, when users change to Lead Free solder alloys, there is concern that some tin-lead finished components will still be present in the supply chain and that these could constitute a reliability risk. Work at the Swedish Metals Research Institute (SMRI) [6] showed that lead-contamination in Lead Free joints segregated mainly to grain boundaries. After thermal cycling, micro-cracks were observed passing through the lead phases, which they felt might have a possible detrimental effect on reliability. Further work at the SMRI with plug and ring tensile test specimens, showed a reduction in strength for lead-contaminated samples of SAC alloy in the range 0 to 15% lead. AIM Solder USA has also reported reduced performance of Lead Free alloys in low cycle bulk solder fatigue testing when contaminated with lead [7]. Michigan State University have published work [8] showing the formation of a low melting point phase in lead-contaminated SnAg alloy and the Shanghai Institute of Metallurgy [9] have reported reduced hot shear strength in chip capacitors soldered with SnAg solder paste with additions of tin-lead paste. Counter to these examples, much anecdotal evidence exists that lead-contamination of SnAg solders is not a reliability risk. SnAg solders have been used extensively with tin-lead terminated components without reports of reliability problems.
To clarify the issues of solder joint reliability during the transition to Lead Free soldering, this study has investigated likely combinations of lead-containing and Lead Free materials by using accelerated ageing through thermal cycling to promote joint failures. Electronics assemblies are manufactured from a range of materials with different coefficients of thermal expansion (CTE) – see
Figure **1** for a cross-section of a typical joint. As these assemblies experience temperature/power changes during use (e.g. power consumption; switching equipment on/off; day/night temperature changes), the CTE mismatches place shear strains on the various components in the assembly. The properties of the materials used in assemblies mean that these strains are relieved in the solder joint, which become damaged as a consequence of continual thermal excursions. Such strains can result in crack initiation (usually in the solder joint under the component), subsequent crack propagation through the solder fillet, and finally failure of the joint. Thermal cycling, which accelerates the development of the cracks and structural changes that weaken the solder joint, can therefore be conveniently employed in accelerated testing of the joint, geared at assessing their reliability.

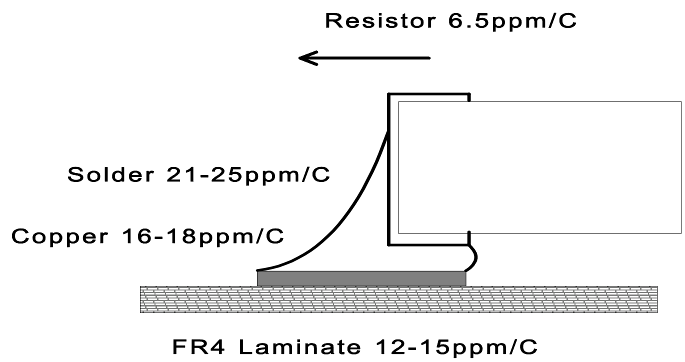

Figure 1 - Schematic Cross-Section of a SM assembly Highlighting The CTE (X-axis) Mismatches

Test Board Design

The test board (TB64) was specially designed to incorporate a range of common component styles currently in everyday use within the electronics assembly industry. A list of components is given in Table 1. Assemblies were populated with either tin-lead or Lead Free terminated components.

Table 1 - Component List for TB64

Component	Pitch	Finish	No.
PBGA256	1.0 mm	SAC or SnPb	4
SOIC14/16W	1.27 mm	Sn or SnPb	4
	1.27 mm	SnCu	4
	1.27 mm	SnBi	4
	1.27 mm	PdNi	4
LQFP100	0.65 mm	Sn or SnPb	2
R1206		Sn or SnPb	20 + 20
R0603		Sn or SnPb	20 + 20
MELF		Sn or SnPb	20
DIP16/20	2.54 mm	Sn or SnPb	4
	2.54 mm	SnBi	4
	2.54 mm	PdNi	4
CCGA	1.0 mm	PbSn	2

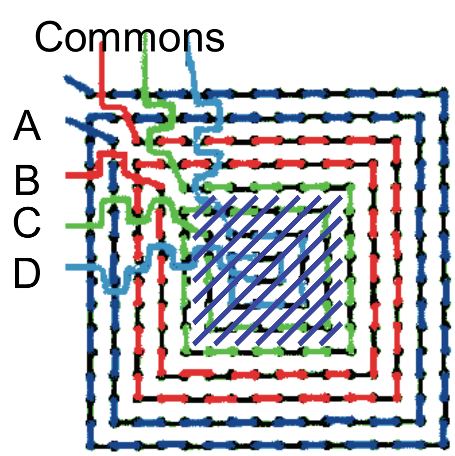

Figure 2 - Diagram of Daisy-Chaining within BGAs Showing Four Concentric Interconnected Rings (A, B, C and D), and a Hatched Area Representing The Location of The Component Eie

All components were interconnected to edge fingers for insertion into an edge connector. As components were internally daisy-chained or were low resistance, this enabled electrical resistance of the components to be periodically monitored to determine electrical failures. Each BGA has four separate, concentric interconnected rings as shown in Figure 2.

The test board design is shown in Figure 3. The PCB was 264 x 162 mm, FR4 (IPC4101/21, Tg=140 ºC), ENIG finish, 1.6 mm, 1oz/sq foot Cu

The controlled lead content section on the left side of the design was utilised for assembling specially manufactured SOIC16W components which had termination platings of 100%Sn, 90Sn10Pb, 80Sn20Pb, 70Sn30Pb and 60Sn40Pb. When assembled with SAC solder paste, these assemblies were pull tested to determine the effect of lead-contamination of joint strength. The resultant joints were also analyzed using energy dispersive X-ray analysis (EDX) to determine lead content.

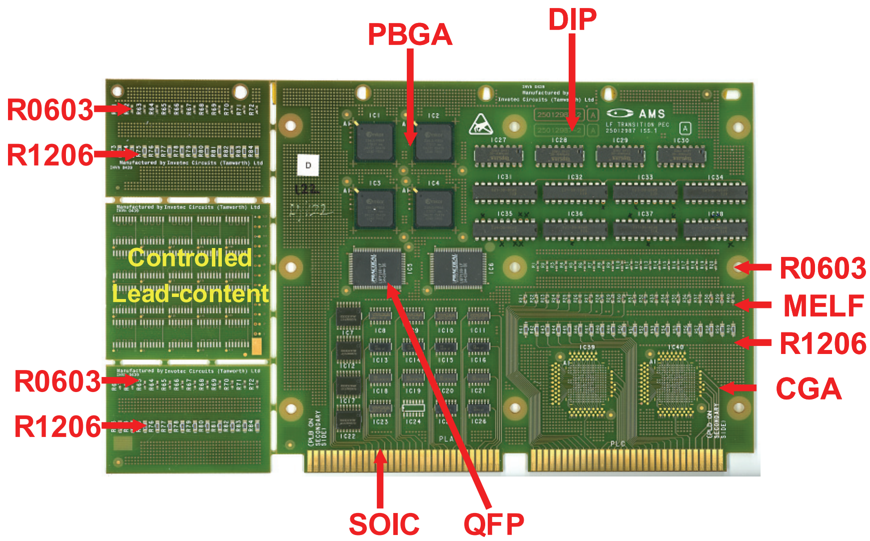

Figure 3 - TB64 Test Board

Experimental Test Vehicle Manufacture

A total of 125 assemblies in 10 batch variants were manufactured by an experienced surface mount assembly contract manufacturer. The combinations for the component finishes and solder paste alloys for each batch of assemblies are given in Table 2. Batch C had been intended to cover variations in lead plating on PCBs, but this was dropped for manufacturing reasons. The lead-containing paste used was a tin-lead-silver, no-clean paste (62%Sn36%Pb2%Ag, Henkel-Multicore Sn62CR36AGS89.5). The Lead Free paste was no-clean paste (95.5%Sn3.5%Ag0.7%Cu, Henkel-Multicore 96SCCR35AGS88.5). The solder pastes for batches E2, E3, E4 and E5 were mixed from both these pastes. The resultant joints were analysed using energy dispersive X-ray analysis (EDX) to determine lead content.

These combinations represented the full range of combinations likely to occur before, during and after the transition to Lead Free soldering.

Table 2 - Manufacturing Batch Variants

Batch	Components	Paste
A	SnPb	SAC
B	SnPb	Sn62
D	Lead Free	Sn62
E1	Lead Free	SAC
E2	Lead Free	SAC/1%Sn62
E3	Lead Free	SAC/2%Sn62
E4	Lead Free	SAC/5%Sn62
E5	Lead Free	SAC/10%Sn62

Solder paste was screen printed using a standard 150µm thick stencil, and the SM components were placed using a automatic placement system. Boards were exclusively populated with either tin-lead or Lead Free components.

Thermal Cycling

Assemblies were thermally cycled between –55 and 125ºC, with a 50 min cycle. One assembly from each batch was removed after 0, 500, 1000, 1500 and 2000 thermal cycles. These assemblies were subjected to shear testing and micro-sectioning. Five assemblies from each batch were subjected to the full 2000 thermal cycles with periodic electrical measurement using an automatic switching system and digital ohmmeter at 0, 500, 1000, 1250, 1500, 1750 and 2000 cycles.

Pull Testing

SOICs were pull tested from a routed section of the assembly, which could be easily removed to allow mounting in the pull-test equipment. During each test, the pull tool was moved upwards at a defined speed of 200μm/s, and the force was monitored until the solder joint broke. For some SOIC components, where there was little clearance between the lead and the component body, a wire loop was placed under the lead and the pull tester attached to the loop. The pull tester was a Dage Series 4000, with a WP10 10Kg testing head. The four corner joints on each of two SOIC components were tested for each condition. All pull testing was undertaken at room temperature. Further experimental conditions can be found in [10].

Results - Composition Analysis of Mixed Solder Pastes

The EDX analysis of the R1206 components manufactured with mixed pastes is given in **Table 3**. Figures 4 to 8 show micro-sections of the joints. In these sections the lead-rich phase appears as white areas within the solder. Both the table and the images, clearly show increasing lead-content within the joints. The lead-rich areas also appear to have segregated to the grain boundaries.

When lead-content is very low, the segregation of the lead-rich phases to the grain boundaries means that the position where the EDX sample is taken can be important. The analysis of sample E2 registers no lead, but a limited number of lead-rich phases can be clearly seen in
Figure 5.

Table 3 - EDX Analysis Composition of Mixed Solder Paste Joints

Assembly	Nominal Pb	%Sn	%Ag	%Cu	%Pb	%Ni
E1	0%	94.9	1.5	0.4	0	3.3
E2	1%	97	3	0	0	0
E3	2%	94.7	3.2	0	2.1	0
E4	5%	93.7	2.1	0	4.2	0
E5	10%	90.6	1.7	0	7.3	0.4

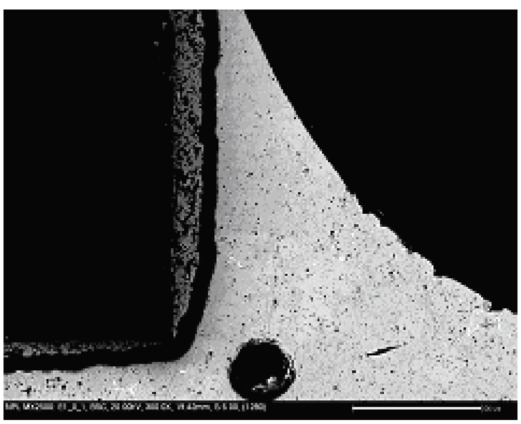

Figure 4 - Micro-section of E1 Composition

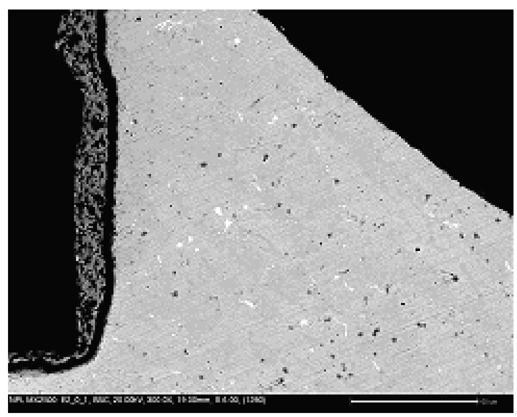

Figure 5 - Micro-section of E2 Composition

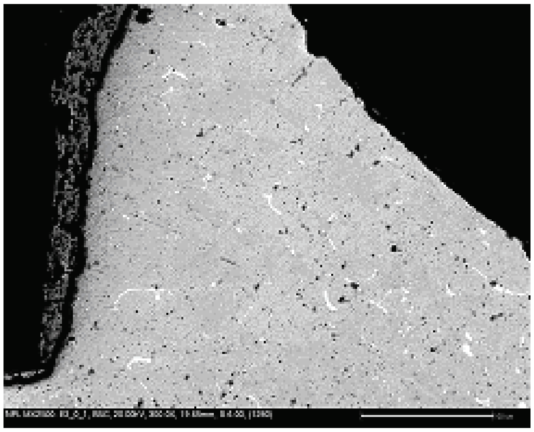

Figure 6 - Micro-section of E3 Composition

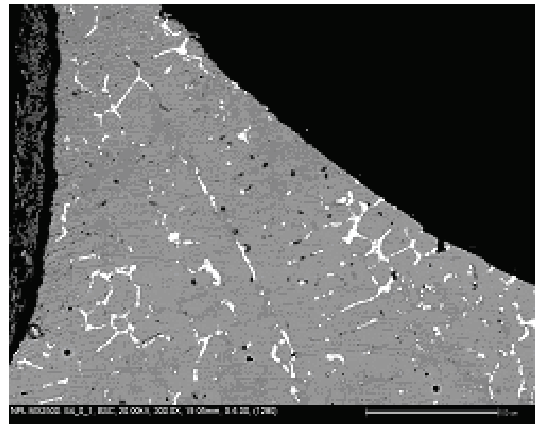

Figure 7 - Micro-section of E4 Composition

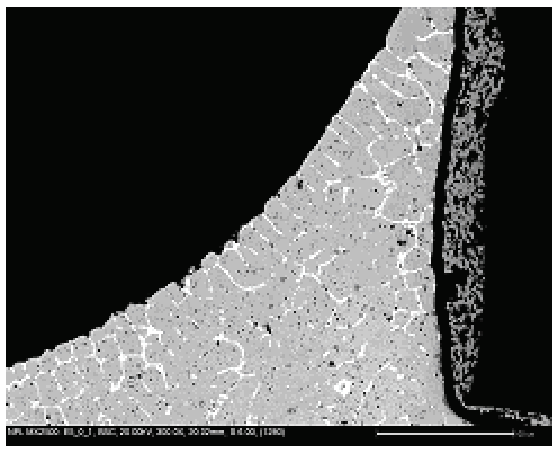

Figure 8 - Micro-section of E5 Composition

Electrical Test Failures

For the purposes of this report, an electrical failure was defined as an interconnect loop resistance greater than 100Ω. The electrical faults detected at 2000 thermal cycles by the automated switch system, were confirmed manually with a digital ohmmeter. Where possible the location of failure was more accurately determined by probing with the ohmmeter between individual pins. This was not possible with QFP joints as probe pressures caused the joints to return to the closed circuit state. Confirmed joint failures are detailed in Table 4, with further details given below.

Table 4 - Electrical Failure Summary after 2000 Thermal Cycles

Component (All types, SnPb, LF, Pb contaminated)	% Failures at 2000 cycles for all types	Comments
SOIC	0%	No failures on any assembly
R0603	0.24%	1 failure @ 1000 cycles for 2% Pb contamination
R1206	0%	No failures on any assembly
DIP	0%	No failures on any assembly
MELF	1.5%	3 failures SnPb comp/SAC paste 1 failure each, 1%Pb, 2%Pb, 10%Pb
CCGA	?	Similar failures for SnPb and SAC pastes
QFP	2.5%	4 failures Sn comps/SAC paste (1000-2000 cycles)
BGA	10%	Mostly (84%) SnPb components with SnPbAg or SAC paste.

SOIC, R1206 and DIP Electrical Testing

- No electrical test failures occurred at all.

R0603 Electrical Testing

- The only electrical failure occurred with E3, a single component failed at 1000 cycles in the

MELF Electrical Testing

- No electrical test failures occurred for: Batch B, D, E1, & E4
- Electrical failures occurred at or before 2000 thermal cycles for the following: Batch A, 3 failures; Batches E2, 1 failure; Batches E3, 1 failure; Batches E5, 1 failure

CCGA Electrical Testing

- Electrical failures occurred at similar levels in both batches of boards containing CCGAs as follows: Batch A, 9 failures; Batch B, 6 failures

QFP Electrical Testing

- The only electrical failures occurred with Batch E1 with 4 failures between 1000 and 2000 thermal cycles

BGA Electrical Testing

- Only Batch D survived 2000 thermal cycles with no electrical test failures
- Electrical failures occurred only in the following:
    - Batch A, 19 failures in the C-rings between 1000 and 2000 cycles
    - Batch B,
        - 3 failures in A-rings between 1500 and 2000 cycles
        - 7 failures in B-rings at 2000 cycles
        - 22 failures in C-rings between 1000 and 2000 cycles
        - 7 failures in D-rings between 1500 and 2000 cycles
    - Batch E1, 3 failures in C-rings between 1750 and 2000 cycles
    - Batches E2, 1 failure in C-rings at 2000 cycles
    - Batches E3, 2 failures in C-rings at 2000 cycles
    - Batches E4, 3 failures in C-rings between 1500 and 2000 cycles
    - Batches E5, 2 failures in C-rings between 1500 and 2000 cycles

4.1.1 Hot peel testing of controlled lead-content SOIC components

Figure 9 shows the results for the peel testing of SOIC leads at elevated temperatures. As the test temperature increases, the peel strengths for all samples reduce. The values for SOIC joints not containing lead are consistently higher than for lead-contaminated joints. Indeed at the higher temperatures, the Lead Free joints continue to remain intact, with pads failing rather than joints. At 190°C (above the melting point of eutectic tin-lead), all the lead-contaminated joints failed at the minimum force required to bend the lead, indicating that the joint strength is minimal. There appeared to be no difference in the required force between 1 and 10% lead content in the solder joint.

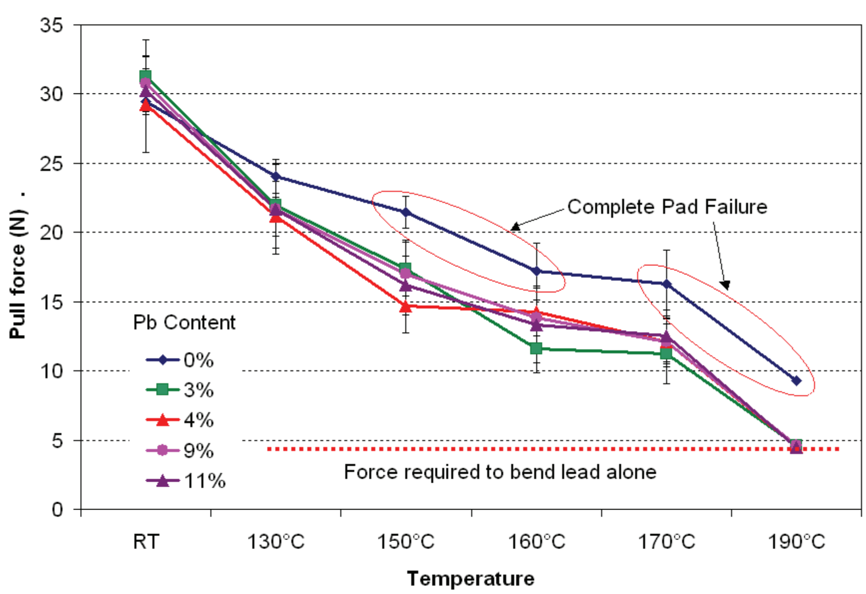

Figure 9 - Hot Peel Testing Results for Controlled Lead-Content SOICs

Discussion

The principal purpose of this work was determine if either lead-contamination of SAC soldered joints, or Lead Free surface finishes contamination tin-lead solder joints, presented any issues with solder joint reliability. To this end, a range of assemblies has been manufactured using both tin-lead and Lead Free components and tin-lead and Lead Free solder pastes. In addition, joints have been seeded with known quantities of lead to produce joints in the range of 0 to 10% lead-contamination. This was achieved over a range of SM components by mixing SAC and tin-lead solder pastes. It was also achieved with SOIC components by altering the composition of the plating of the leads to contain different amounts of lead, and soldering with Lead Free paste.

Reliability of Mixed Alloy Systems

Assemblies with different mixtures of tin-lead and Lead Free solder pastes were subsequently thermal cycled with electrical continuity measurement and periodic shear testing of chip resistors. The majority of the combinations did not show any weak links with little differential between the reliability of tin-lead and SAC alloy joints up to 2000 thermal cycles over a wide range of components and component termination materials, including R0603 chip resistors, MELFs, SOICs, ceramic column grid arrays and dual-in-line packages. Performance was also similar for special lead-contaminated joints over this number of thermal excursions. R1206 resistors did show the pure Lead Free, batch E1, and batch A (tin-lead component and SAC alloy), did yield poorer reliability than any of the alloys containing lead. Two other component types did exhibit reliability differences between alloy combinations and these are discussed below.

Sn-plated QFPs with SAC Solder

Sn plated QFP components soldered with SAC alloy pasted did reveal reliability issues. This combination showed 4 component failures between 1000 and 2000 thermal cycles. None of the other combinations (Sn components with tin-lead solder and lead-contaminated solder, and tin-lead components with either tin-lead or SAC solder) showed any electrical failures over 2000 cycles.

Figure **10** shows a typical failure of a Sn-plated component with SAC alloy. The failure occurs close to the interface between the component and the joint. No similar failures were noted for Sn-plated SOIC components with SAC alloy joints.

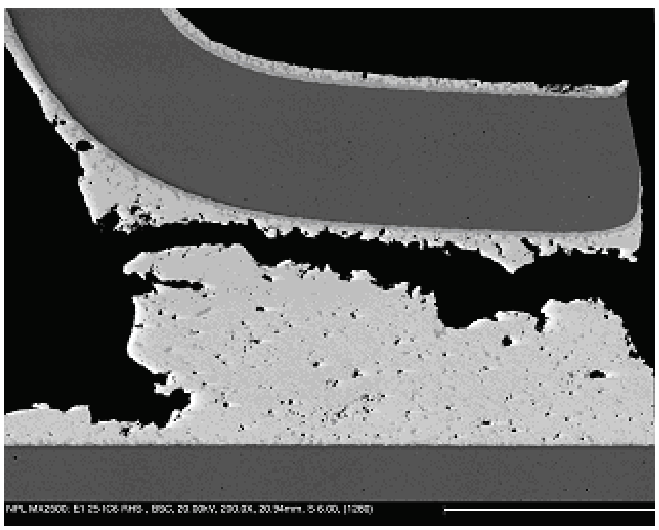

Figure 10 - SEM Image of Micro-sectioned Sn-Plated QFP with SAC Alloy Joint after 2000 Thermal Cycles

Solderability testing of samples from both the Sn-plated and tin-lead plated batches was undertaken and the wetting time was 1.02 and 0.17seconds. It may be that this difference is sufficient to account for the reliability differences. The process window for SAC alloy soldering is narrower than for equivalent tin-lead processing. Small additions of lead may also help widen the process window. It is therefore considered that these differences in QFP component reliability are probably batch related.

BGA Component Joint Reliability

The other component system to show significant failures during the 2000 thermal cycles, were the BGA components. Figure 11 shows the development of failures within the C-rings of the various BGA/solder alloy combinations. It is clear that the two batches with tin-lead-terminated components, and either tin-lead solder (Batch B) or SAC solder (Batch A) are consistently out-performed by the SAC alloy dominated systems (batches D and E1 to E5).

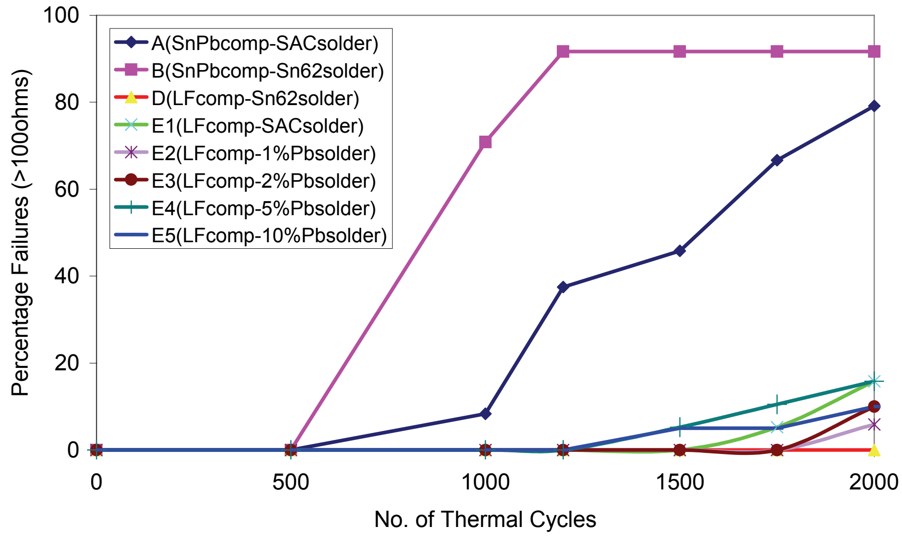

Figure 11 - Development of BGA C-Ring Failures During Thermal Cycling

Other workers [11] have reported reliability problems with SAC components soldered using tin-lead alloys, where the SAC ball has not reflowed during assembly. However the samples tested here, the tin-lead reflow profile was sufficiently hot to ensure that the BGA balls did reflow. This can be seen in
Figure **12**, where the lighter Pb-rich phases can be seen distributed throughout the joint.

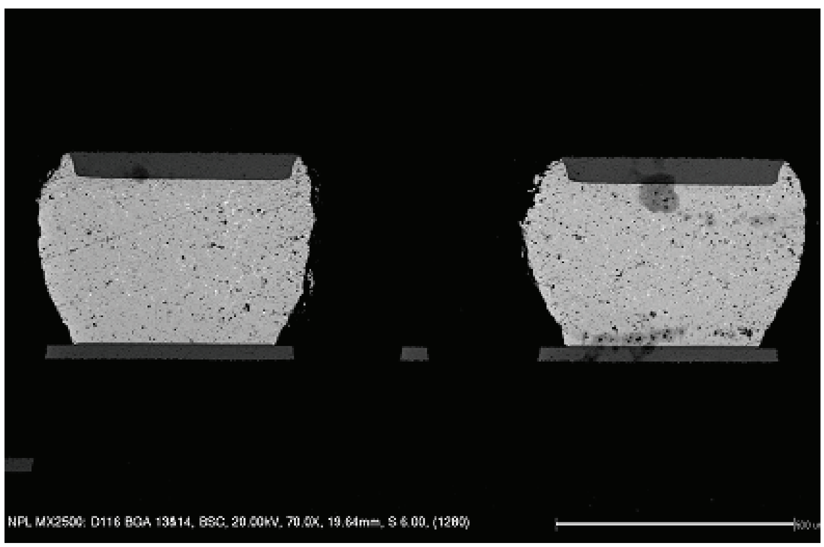

Figure 12 - Section of Two Joints as Manufactured from SAC BGA Soldered with SnPbAg Solder Paste Showing Reflow of SAC Ball (PCB Uppermost) as Manufactured

Sections of typical tin-lead dominated BGA joints after 2000 cycles are shown in
Figure **13**. Both systems show fatigue cracking adjacent to the component/solder interface. Batch A (tin-lead BGA with SAC solder) also show fatigue cracking at component/PCB interface. Similar fatigue cracking was seen in SAC dominated systems but such cracks are less advanced than in the tin-lead dominated systems.

Clearly, SAC solder in BGA joints provides better fatigue resistance than tin-lead solder. Small levels of lead-contamination can be tolerated, provided that the BGA ball has been fully reflowed. Results here indicate that tin-lead BGAs soldered with SAC alloy, have a reduced reliability compared to SAC dominated system. However, this systems' reliability would still be greater than tin-lead BGAs with tin-lead solder alloy,

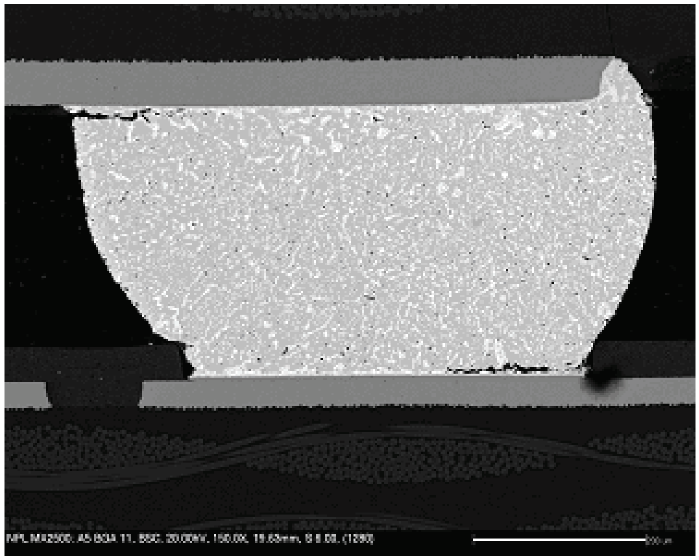

Figure 13 - Section from Batch A (Tin-Lead BGA with SAC Solder) after 2000 Cycles Showing Fatigue Cracks at Both BGA/Solder and Solder/PCB Interfaces (PCB Uppermost)

Testing of Mixed Alloy Systems at Elevated Temperatures
Hot shear testing of resistors showed little differentiation between uncontaminated and lead-contaminated systems up to 170 °C. Above this temperature, the PCB failed due to pad shear before joints fail.

Hot peel testing of lead-contaminated SOIC joints provided more interesting results. Joints contaminated with lead failed at lower pull forces than pure Lead Free systems between 130 °C and 170 ºC. At 190 ºC contaminated joints failed at the minimum pull force required to bend an SOIC lead. This phenomena can be further illustrated by heating a test sample containing SOIC joints with 0, 1, 2 5 and 10% lead-contamination to 190 °C and holding it inverted. When given a sharp tap, the lead contaminated components fall from the assembly (with the exception of the 1% lead-contaminated components), whilst the pure Lead Free system components remain in place. The results of such a test can be seen in Figure **14**.

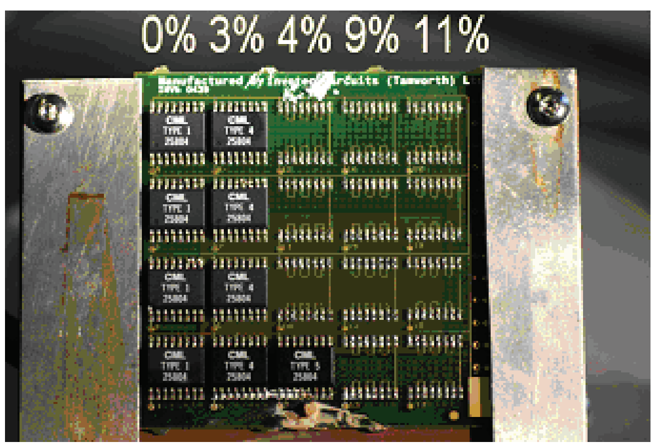

Figure 14 - Lead-Contaminated Assembly after Inversion at 190ºC Showing Loss of Lead-Xontaminated Components after Sharp Tap (Annotated % Refers to Lead in Joint)

Thermal Cycling Reliability
Thermal cycling has shown that lead-contamination has no effect on reliability up to 2000 cycles but this lowering of pull forces for lead-contaminated systems at elevated temperatures may be a significant issue. One clear scenario where this problem is likely to manifest itself is during assembly. If components with lead-containing finishes are used on initial assembly side, during second side reflow and wave soldering, if the assembly is bowed or twisted, lead-contaminated joints may be separated or deformed, leading to open joints or joint with poor reliability.

Conclusions

A wide-ranging study of lead-contamination of Lead Free solder joints has been undertaken. Over 200,000 solder joints on assemblies incorporating the main types of surface mount and through components, have been manufactured with tin-lead and Lead Free terminated components using tin-lead, Lead Free and mixed alloy systems. The work has included manufacture of joints with specifically controlled levels of lead-contamination between 1 and 10%. All these assemblies have subsequently been thermally cycled (-55 to 125 ^{o}C) to 2000 cycles, continuity tested, shear tested, pull tested and vibration tested.

The work has indicated that there should be few solder joint reliability problems when mixing tin-lead and Lead Free components and solder alloys (with lead contamination in the range 1 to 10%). Very few thermal cycle fatigue failures were experienced other than within two component groups.

Two groups of components did show significant thermal cycle failures. Ball grid array components did fail generally, in the rings of balls adjacent to the edge of the silicon die within the package. In this area the TCE of the package is constrained by the die, creating a maximum strain in these joints. However, the failures in these devices were largely restricted to tin-lead alloy dominated systems, i.e. tin-lead terminated components soldered with tin-lead or SAC alloy solder pastes. Uncontaminated SAC systems or those systems contaminated with low levels of lead showed fewer failures and thus must be considered more reliable. Indeed, the system showing greatest thermal cycle fatigue in BGA components was the tin-lead terminated BGAs with tin-lead solder. All other systems were shown to perform better.

The other component type to show significant failures, were the QFP components where failures were confined to Sn-plated components with SAC solder. Solderability testing of these components showed that they were slower to wet than the tin-lead counterpart and it may be that this difference is sufficient to account for the reliability differences. The process window for SAC alloy soldering is narrower than for equivalent tin-lead processing and small additions of lead may help widen the process window, improving the reliability for these soldering batches. It is therefore probable that these differences in QFP component reliability are batch related.

Work with hot peel testing of SOIC components has indicated that lead-contamination may cause end-users some problems during processing. The addition of small quantities of lead (<10%) to a Lead Free joint will increase the pasty range of the alloy. If the initial side of a double sided assembly reaches temperatures above 180ºC during second side assembly, stress on the joint (such as those that occur if the assembly is warped), may cause the first side solder joint to separate or deform. This could produce an open joint or perhaps worst, produce an electrically conducting joint, but one with low resistance to low cycle or mechanical fatigue. Such a joint would be a reliability “time bomb”. However, it should be reiterated that there are no indications in this work that lead-contamination of well formed joints, has any effect on low cycle fatigue resistance.

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