Lead-Contamination in Lead-Free Electronics Assembly

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The question of what happens to a lead-free solder joint if it becomes contaminated with lead is important because during the transition to lead-free soldering it is very likely that tin/lead parts will still be used in a great deal of production. In other words, just because one implements a lead-free solder alloy does not mean that tin/lead coated components and boards will disappear immediately. In fact, exposure to lead from boards, components and repair operations could occur for years to come.

Unfortunately, in the past the presence of lead in lead-free alloys has been presumed to be acceptable. The logic behind this was that tin and lead are soluble in a lead-free system. However, what has been overlooked is that the intermetallic crystalline structures in lead-free systems are not soluble and will precipitate at lead boundaries. Thus, when using a lead-free alloy to solder to Sn/Pb coated component leads, Pb can actually create voids in the solder joint that can result in joint failure.

An example of what can also occur is with bismuth-bearing alloys, as bismuth and lead form pockets with a secondary eutectic of 96°C. This could have obvious negative effects on reliability if an assembly is exposed to any thermal stress. Of course, questions concerning the reliability of Sn/Cu and Sn/Ag/Cu alloys when exposed to lead also exist.

The Dynamics of Lead-Contaminated Solder Joint Failure

It is important to note that lead that contaminates a lead-free solder joint is not distributed uniformly through the joint; rather, the Pb localizes in the last point to cool. This is similar in dynamics to “zone refining”, a process utilized to refine high-purity elements. In zone refining, a heat source traverses across a billet. As this occurs, the elemental impurities are collected in the liquid phase and are condensed at the last point to cool (the end of the billet), which can then be removed (Fig. 1).

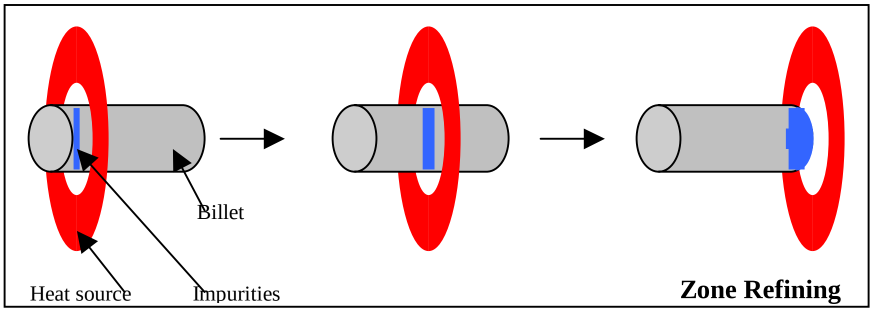

Fig. 1

Just as in zone refining, lead as an impurity in a solder joint migrates to the last area of the joint to cool. This occurs under the middle of the component lead at the solder joint-PCB interface (Fig. 2), which is inevitably the area of a solder joint that results in a failure. When this occurs, the joint forms pockets and the grain structure is disturbed. These Pb-rich regions are lower in melting temperature and may cause dewetting during soldering.

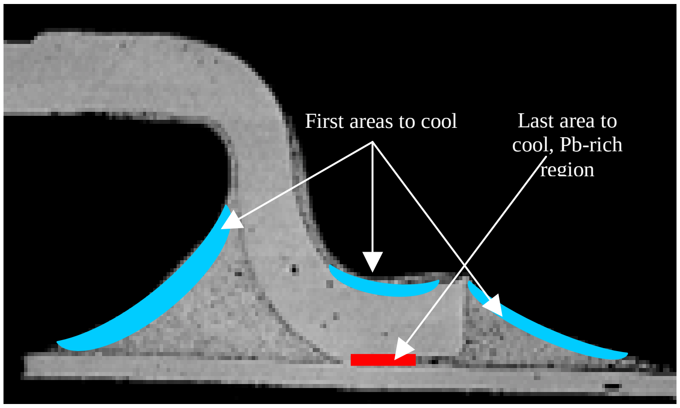

Fig. 2

Fig. 3 illustrates how much of a lead sphere dissolves into a Sn/Ag system during a normal reflow cycle. Fig. 4 is a close-up of Pb pockets that are dispersed through a Sn/Ag system. This dispersion is a common part of wetting: as the solder wets, the Pb dissolves into the joint. As the Pb starts concentrating in pockets, this starts forming a eutectic of Sn/Pb/Ag with a melting point of 179°C vs. 221°C for Sn/Ag or 217-218°C for Sn/Ag/Cu. This phase occurs during cooling, and the slower the cooling, the larger the pocket of this lower melting temperature alloy will form. In essence, this pocket of alloy acts as a void in the solder joint. As the component heats and cools during its product life, this void will eventually lead to joint failure. Failure rates related to this issue typically occur relatively quickly (in less than 400 thermal cycles).

Fig. 3

Fig. 4

Bulk Solder Testing

In order to determine Sn/Ag/Cu alloys' durability when exposed to lead, Sn/Ag4/Cu0.5 was tested for mechanical reliability with a 0.5% and 1% contamination of lead. The test methodology used in this study was simple: the mechanical strength of the Sn/Ag4/Cu0.5 bulk solder alloy without lead contamination was tested under Low Cycle Fatigue Testing in accordance with ASTM E606; then, the alloy was doped with 0.5% lead and tested; finally, the alloy was doped with 1% lead and tested. The samples tested were required to achieve 10,000 cycles without failure in order to pass the test. The results of this testing is summarized below.

Fatigue Test Results

Sample	Cycles to Failure	Result
Tin/Silver/Copper	13,400	Pass
0.5% Pb Contamination	6,320	Fail
1% Pb Contamination	3,252	Fail

As is seen above, Sn/Ag4/Cu0.5 passed the testing requirements. However, when contaminated with 0.5% lead, the alloy lasted only approximately 50% of the cycles as the alloy without lead contamination and failed the test. Furthermore, when contaminated with 1% lead, the cycles to failure were again reduced by 50%, which constituted another failure. The above results are contrary to the presupposition by many in the electronics industry that Sn/Ag/Cu alloys are not negatively affected by lead contamination.

The above reduction in bulk solder strength can impact solder joints as well. Fig. 5 is a magnified close-up of a fracture resulting from Pb contamination in a Sn/Ag/Cu solder joint. This occurred on an in-field assembly and resulted in a field failure. As discussed above, this fracture occurred at the middle of the component lead at the solder joint-PCB interface. Fig. 5 is a magnified view of the lead pockets found in the lead-free solder joint that led to this failure.

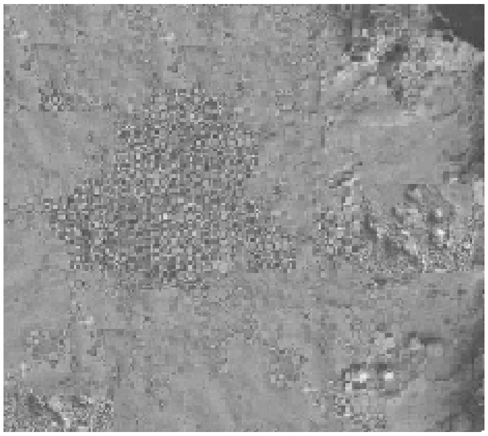

Fig. 5

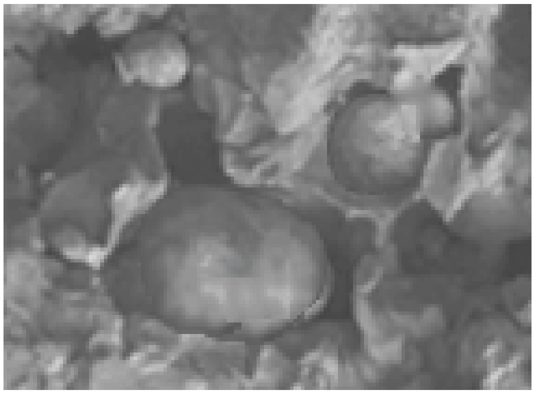

Fig. 6

BGA Thermal Cycling Data

As previous testing has demonstrated[1], potential reliability issues exist when mixing Sn/Pb parts with lead-free solders during BGA assembly. 35 x 35mm 388ld PBGA packages with both Sn/Pb and Sn/Ag/Cu balls were assembled using Sn/Pb and Sn/Ag/Cu pastes. Several failures did occur in -40° to +125°C testing. As indicated in the chart below, the most reliable of these assemblies were those produced with Sn/Ag/Cu balls and paste. (As an aside, this superior thermal fatigue resistance is one reason that the automotive industry has been pursuing lead-free soldering irrespective of legislative or marketing concerns.) However, it is important to note that assemblies that mixed Sn/Pb balls with Sn/Ag/Cu paste fared significantly worse than either the all lead-free or all Sn/Pb assemblies. This data reiterates to potential reduced reliability of mixing lead parts with lead-free solders.

BGA Thermal Cycling Results Summary

Ball	Paste	% Cum Failures
Sn/Pb	Sn/Pb	47%
Sn/Pb	Sn/Ag/Cu	56%
Sn/Ag/Cu	Sn/Ag/Cu	3%

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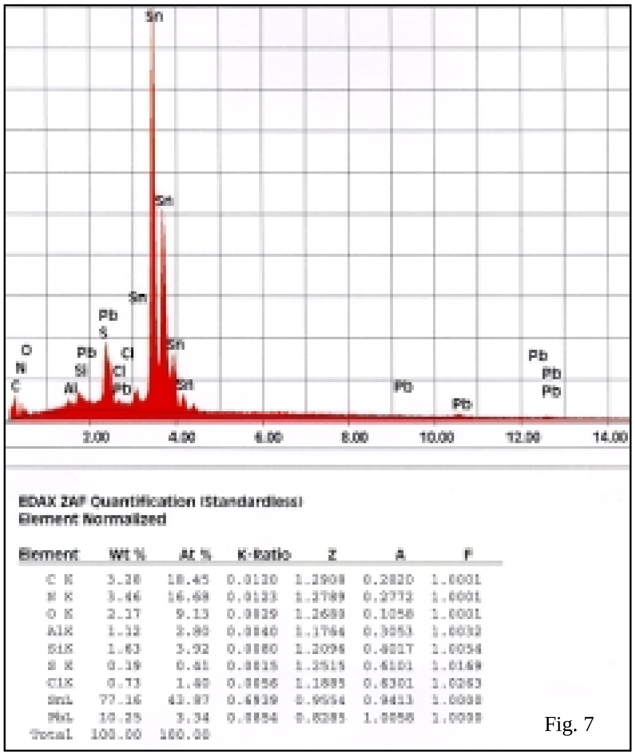
[1] MEPTEC Summit on Lead-Free Solder Implementation, January 10, 2001, “Lead-Free: An Overview of Temperature Cycling, Aging, Bend Testing and Plating Chemical Evaluation Results”, Swaminath Prasad et al.

Field Failures From Lead-Contamination

A leading multinational electronics manufacturing company recently experienced field failures in a product assembled with a tin/silver/copper alloy, and tin/lead coated components and leads. Samples of the failed solder joints were viewed using SEM to determine the possibility of lead or other contamination that could have lead to the failure. EDS was used to determine if there was contamination in the solder joint. As shown in Fig.7, the EDS revealed lead contamination levels ranging from 3% to 10%. In Fig. 8 the mating area of the lead-free alloy and tin-lead parts is shown. The Sn/Ag/Cu alloy is seen in the lighter areas and the darker Sn/Pb areas surround it.



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	3.28	18.45	0.0120	1.2908	0.2820	1.0001
N K	3.46	16.68	0.0123	1.2789	0.2772	1.0001
O K	2.17	9.13	0.0029	1.2680	0.1058	1.0001
AlK	1.12	2.80	0.0040	1.1766	0.3053	1.0032
SiK	1.63	3.92	0.0080	1.2096	0.4017	1.0054
S K	0.19	0.41	0.0015	1.2515	0.6101	1.0169
ClK	0.73	1.40	0.0056	1.1885	0.6301	1.0263
SnL	77.16	43.87	0.6939	0.9554	0.9413	1.0008
PbL	10.25	3.34	0.0854	0.8285	1.0058	1.0008
Total	100.00	100.00				

Fig. 7

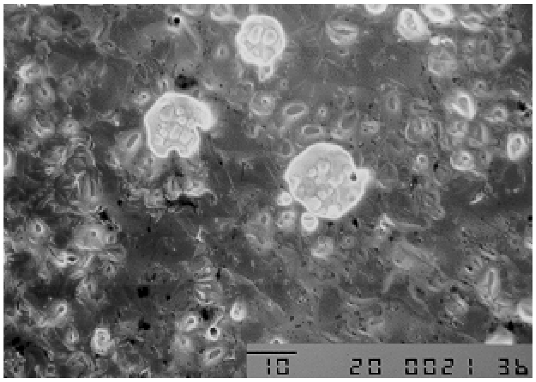


Fig. 8

The failure is an intergranular separation and is being driven by lead in the solder. Figure 9 is a 3500X photo that shows a distinct phase between the normal grains that causes the grains to separate easily. The lead forms a ternary alloy of tin/lead/silver that is trying to go to the eutectic at 179°C. This alloy is surrounding the grains of the lead-free alloy. This intergranular phase exhibits poor adhesion to the lead-free alloy, thus causing the grain separation.

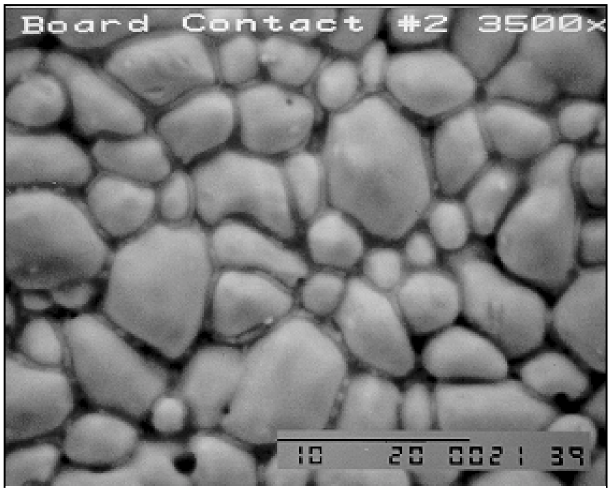


Fig. 9

This particular grain boundary interface that led to the failure could be the result of a specific heat cycle being utilized. In other words, utilizing different heating profiles during assembly may minimize, but not eliminate, this problem. To determine this, more joints, processed using different thermal profiles, would need to be investigated.

Conclusion

A tremendous amount of interest exists in lead-free soldering. Much of this is derived from a fear of legislation and marketing activities. This has spurred a great deal of committee and consortia activity, some of which has been valuable to the industry.

One of the most pressing questions in lead-free soldering pertains to the lead-contamination of lead-free solders and its effects. As the above evidence demonstrates, lead-free alloys can suffer decreased reliability when contaminated with lead. To avoid problems related to this, the most prudent course of action is to reduce the lead-free transition period to as short as possible. In other words, when a company implements a lead-free solder alloy, it should also implement lead-free component terminations and circuit board coatings. If these above guidelines are not followed, the reliability of the solder joint is risked.

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