Materials and Process Considerations for Lead-Free Electronics Assembly

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With the WEEE Directive in Europe potentially outlawing lead from some electronic devices produced and imported in the EU by 2006 and foreign competition driving the implementation of lead-free electronics assembly around the world, additional questions regarding the integrity and reliability of various alloy compositions continue to arise. In short, the issue of which alloy(s) to select continues to loom. This paper shall take an in-depth view of Sn/Ag, Sn/Ag/Cu and Sn/Cu alloys and compare the reliability testing results and process considerations for these.

Sn/Ag Alloy

The Sn/Ag3.5-4.0 alloy has a long history in the hybrid circuit and electronics assembly industry. For this reason, some in the industry feel comfortable utilizing Sn/Ag as a lead-free alternative. Unfortunately, there are several issues with this alloy. First of all, the melting temperature (221°C) and peak reflow temperature (240°-260°C) of this alloy are too high for many surface mount parts and processes. In addition, this alloy contains 3.5 to 4 percent silver, which makes it cost prohibitive for some applications. Most importantly, however, is the fact that this alloy has failed reliability tests due to silver phase change problems.

Note that during fatigue testing (results below[1]) Sn96/Ag4 failed one of the set cycles. Further investigation leads to the conclusion that this failure was due to a phase change. This is thought to be due to the various cooling rates at the different areas of the alloy.

Fatigue Test Set	# Cycles to Failure
1	10,003
2	6,267[2]
3	11,329

In order to study this matter further, a bar of Sn96/Ag4 was reflowed and force-cooled from the bottom in order to examine the alloy's microstructure when exposed to varying cooling rates. As is shown in Fig.1, the Sn96/Ag4 alloy went through three different phases, depending upon the cooling rate. This leads to concerns that structural weakness similar to these could occur in a solder interconnect, potentially leading to a field failure. It is for this reason that most OEMs and industry consortia have decided against the use of Sn/Ag as a mainstream lead-free alloy. This silver phase change problem

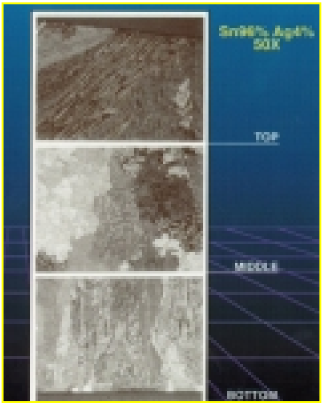

Fig. 1

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[1] According to ASTME 606, 1Hz triangular waveform oscillated between .15% strain and - .15% strain; 10,000 cycles constituted a passing mark.

[2] Failure, Load Amplitude dropped >20%

has also caused some concern regarding high-silver Sn/Ag/Cu alloys.

Sn/Ag/Cu Alloys

Despite concern regarding patent legislation, in general most of the world is settling in on the Sn/Ag/Cu family of alloys. But which exact alloy formulation should one select? This paper shall focus upon two Sn/Ag/Cu alloys: the Sn/Ag4/Cu0.5 alloy focused upon by various industry consortia and Sn/Ag2.5/Cu0.7/Sb0.5, which is used as a low-silver content comparative alloy.

Comparison of Sn/Ag/Cu Alloys

Before discussing the reliability testing performed on these systems, it is useful to compare these two alloys empirically. In general, the alloys are very similar: both offer very good fatigue characteristics, good overall joint strength, and sufficient supply of base materials. However, some minor differences do exist that are worth discussing.

Melting Points

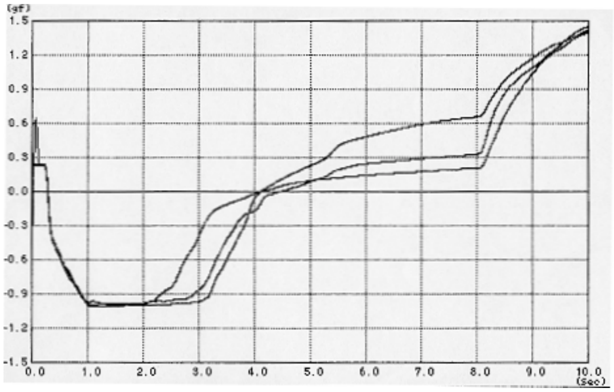
The melting points of these alloys are very similar: 218°C for Sn/Ag4/Cu0.5 and 217°C for Sn/Ag2.5/Cu0.7/Sb0.5. It is debatable as to whether this will have an impact in real-world applications. However, if one can control the reflow process strictly, this temperature reduction could have a positive effect in terms of reduced component exposure to high temperatures.

Wetting

In comparing these two alloys, it is necessary to question why one would select an alloy with a higher silver-content, as this will increase costs. Some have theorized that this higher silver content will aid in wetting. However, as the wetting tests below demonstrate (Figs. 2 & 3), alloys with lower silver contents actually wet stronger and faster than those with higher silver contents.

Sn/Ag2.5/Cu0.7/Sb0.5

Fig. 2



Sn/Ag4/Cu0.5

Fig. 3

Patent Situation

It is desirable for the industry to find an alloy that is widely available. Therefore, patented alloys have been viewed as undesirable. Although the Sn/Ag4/Cu0.5 alloy is patent-free and the Sn/Ag2.5/Cu0.7/Sb0.5 alloy is patented, a more circumspect view needs to be taken to understand the impact of patents and the true number of sources available for these alloys.

As stated above, the Sn/Ag2.5/Cu0.7/Sb0.5 alloy is patented. However, it has been licensed to solder manufacturers with an unlimited number of licensees and no sign-on costs. Currently, the alloy is globally available through several North American, Japanese, and European-based solder manufacturers. Although the Sn/Ag4/Cu0.5 alloy is not patented, the users of this alloy should be aware that solder *joints* produced while using this alloy may be patented and the number of electronic-grade solder manufacturers able to sell this product under license in the U.S. is extremely limited.

Alloys such as Sn/Ag4/Cu0.5 have been recommended to the industry despite the fact that solder joints produced from these may infringe existing patents; it has been assumed that since prior art exists on these systems that they are exempt from the patent. This is wrong, as most of the patents written have both alloy composition and application (solder joint) coverage. In other words, if prior art can be proven, it may be possible to beat the alloy composition section of the patent; however, if the patent is properly written it will also be necessary to challenge the application side that claims a unique use for soldering electronics assemblies. This is the section of the Ames Lab/Iowa State patent (# US05527628) that is probably enforceable and could potentially result in patent infringement. Basically, this means that even if a manufacturer is using an alloy outside of a patent range (such as Sn/Ag4/Cu0.5), if during manufacturing the alloy "picks up" base metals (normally copper) and forms an intermetallic that contains the elements covered under a patent, *the manufacturer has violated that patent and may be subject to legal action.*

Cost of Metals

The Iowa State patent claims a silver content of 3.5 to 7.7 percent. This high silver content results in a costly alloy in bulk solder form; to fill a wave soldering pot every 1% silver in solder is approximately an additional $.66/lb. (see table below). To combat this expense, some have suggested lead-free alloys that do not contain silver for wave soldering applications and a silver-containing alloy for surface mount applications. As discussed below, this is an approach likely to lead to failure due to the drawbacks of Sn/Cu and a dual alloy process.

Raw Cost of Metals

Alloy	Price[3] Per Pound
Sn/Ag2.5/Cu0.7/Sb0.5	$4.01
Sn/Ag4/Cu0.5	$4.99
Sn/Ag4.7/Cu1.7	$5.40

Sn/Cu Process Drawbacks

While it is logical to try to contain costs, there are several issues with Sn/Cu that must be considered. First, the melting temperature of this alloy is 227°C, which prohibits its use for many temperature-sensitive applications. In addition, as widely proven, this is a poorer wetting alloy as compared to other lead-free solders, which may mandate the use of nitrogen and aggressive fluxes for many applications and could result in wetting-related defects. Furthermore, Sn/Cu typically has lower capillary action to draw it into

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[3] U.S. Dollars, based upon cost of metals March 9, 2001

barrels during PTH technology and lacks the fatigue resistance needed for surface mount assembly. Finally, the poor fatigue characteristics of this alloy may result in field failures, which clearly negate any initial cost savings provided by this less-expensive alloy[4].

Dual Alloy Assembly

It should also be noted that, in addition to the problems associated with Sn/Cu, the use of two solder alloys (i.e., Sn/Ag/Cu for SMT and Sn/Cu for wave soldering) could result in problems as well. It is undesirable to intermix Sn/Ag/Cu and Sn/Cu because this could result in non-uniformly alloyed solder joints. If this occurs the joint may be susceptible to fatigue failure due to its inability to stress and strain relieve. Because of these potential intermix problems, when repairs or touch-ups are required two inventories of alloys are needed and specific instructions need to be given and policed so as to not mix these alloys. Unfortunately, experience demonstrates that no mater how well this situation is policed, operators will tend to use the solder that is easiest to use, i.e., flows the best and has the lower melting temperature. Thus, it is likely that many joints will be touched up with the Sn/Ag/Cu alloy, even if these were originally assembled with Sn/Cu. This is analogous to no-clean and RA core wires; if these are both on the production floor the RA often gets used when it should not for the simple reason that it is easier to use. The bottom-line is that a dual alloy assembly process results in potential reliability problems and can be very difficult to police effectively.

Solder Joint Reliability Testing

In order to analyze the reliability of Sn/Cu and Sn/Ag/Cu alloys, these were subjected to various thermal and mechanical fatigue tests. The descriptions and results of these tests are below.

Thermal Cycling Test Results

Test boards were built using Sn/Cu0.7, Sn/Ag4/Cu0.5, and Sn/Ag2.5/Cu0.7/Sb0.5 in conjunction with 1206 thin film resistors. The boards were then thermal shocked from -40° to +125°C for 300, 400 and 500 15 minute cycles. Solder joints were then cross-sectioned and inspected for cracks.

Post-test inspection shows that the Sn/Cu alloy exhibited some cracked solder joints as a result of poor wetting (Fig. 4). In addition, well-formed solder joints made from the Sn/Cu alloy also showed cracks on the third set of boards cycled to 500 repetitions (Fig. 5).

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[4] Major OEMs have reported Sn/Cu joint failures due to both poor wetting and the alloy itself.

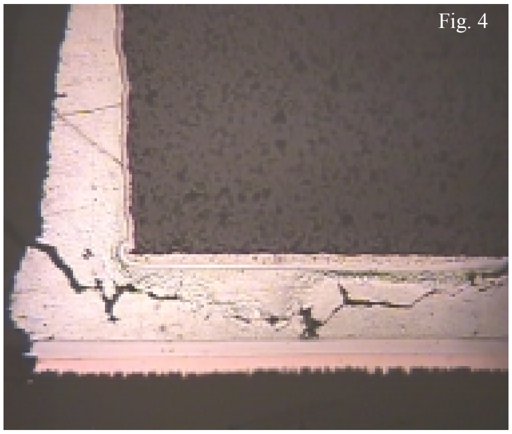
Fig. 4


Fig. 5

It is interesting to note that the Sn/Ag4/Cu0.5 (Fig. 6) and Sn/Ag2.5/Cu0.7/Sb0.5 (Fig. 7) alloys did not show any cracks during testing up to 500 repetitions. As this demonstrates, the Sn/Ag/Cu alloys have significantly superior thermal fatigue resistance as compared to Sn/Cu. However, as is apparent in Fig. 7, it should be noted that the Sn/Ag4/Cu0.5 alloy did exhibit some change in grain structure throughout the joint after thermal cycling.

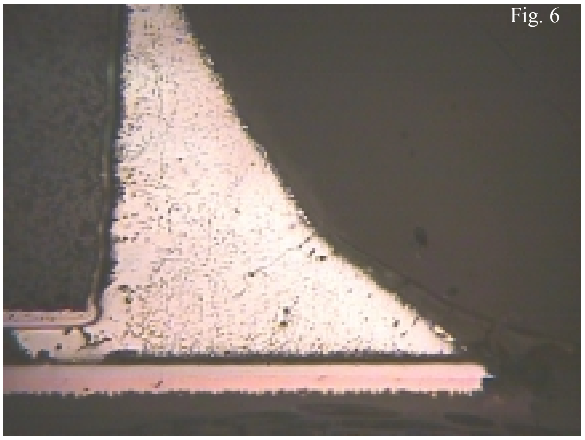
Fig. 6

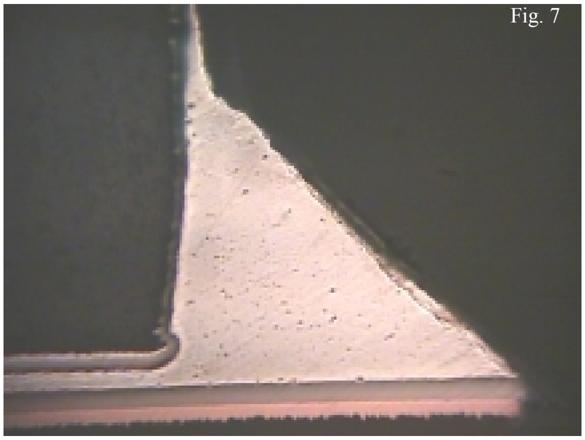
Fig. 7

Mechanical Strength- Flex Testing

Test boards were built using Sn/Cu0.7, Sn/Ag4/Cu0.5, and Sn/Ag2.5/Cu0.7/Sb0.5 in conjunction with 1206 thin film resistors and were subjected to flex testing. As is shown in the images below, solder joints produced from Sn/Cu0.7 (Fig. 8) cracked during flex testing, which is indicative of a joint that cannot withstand a wide range of mechanical stresses. Contrarily, solder joints produced from Sn/Ag4/Cu0.5 (Fig. 9) and Sn/Ag2.5/Cu0.7/Sb0.5 (Fig. 10) passed all flex test requirements.


Fig. 8

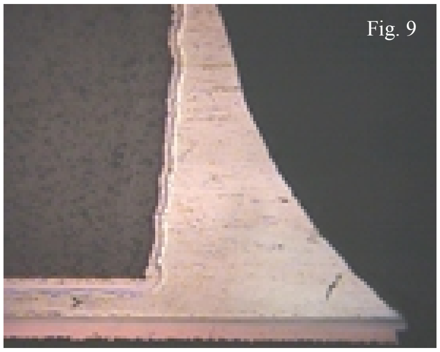
Fig. 9

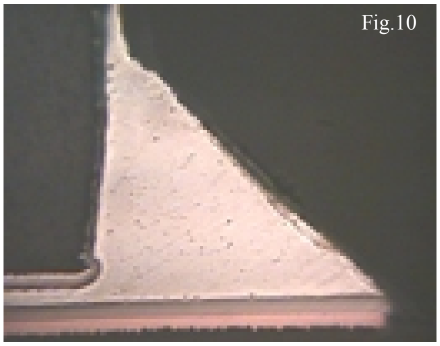
Fig.10

Drop-In Solution?

Bance Hom[5] is an independent consultant with Consultech International specializing in the semiconductor industry. To assuage fears within the electronics industry, Ms. Hom has developed a drop-in solution for complete lead-free assembly. In implementing a system using matte tin lead finishes (QFP 208 ICs), organic surface protectant PWBs, and a solder paste alloy of Sn/Ag2.5/Cu0.7/Sb0.5, Ms. Hom was able to produce completely lead-free assemblies without a dramatic increase in complexity or expense. Key to this success was that Ms. Hom was able to reflow these assemblies with a peak temperature of 234°C. It should be noted that these assemblies were processed in an inert environment. Of course, not all assemblies will be able to be processed as the above due to component availability issues and the fact that a 234°C peak board temperature may not be achievable on all assemblies due to varying ΔT's resulting from component mass, fixturing devices, etc. However, it is important to note that in certain cases lead-free soldering may be painlessly achieved now with the implementation of certain materials.

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.

Several problems related to processing and reliability are associated with Sn/Cu alloys. In addition, difficulties arise when using two alloys to assemble a circuit board. As pointed out earlier, silver is the cost element in the Sn/Ag/Cu alloys. Since there are no advantages in terms of processing, reliability, or availability for the high-silver alloys as compared to the low-silver alloys, it is only logical to utilize the less expensive of these for use in all soldering applications. In fact, the low-silver alloys eliminate the potential for silver phase change problems with high-silver alloys and offer improved wetting and a slightly lower melting temperature. These alloys are available from several solder manufacturers throughout the world and have been recommended for widespread use in Japan by the JEIDA industry organization. Most importantly, the low-silver Sn/Ag/Cu alloys provides users with the advantages of the Sn/Ag/Cu family of alloys, are less cost-prohibitive and therefore may be utilized in all solder operations, and thus eliminate the problems associated with Sn/Cu alloys and a dual-alloy process.

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