

# Lead-free Solder Assembly: Impact and Opportunity

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## Abstract

There has been major interest in Lead-free soldering within the electronics assembly industry for the last several years, and this will continue with the agreement on the language and implementation dates of the WEEE/ROHS legislation in the EU. This paper will focus on several topics critical to the implementation of lead-free soldering. These topics include the impact of Tin-silver-copper as the alloy of choice for lead-free assembly both with respect to component and solder joint reliability, temperature exposure, and lead-free finishes. Results from the recently completed NEMI Lead-free Solder Project, the author's own work and other published data are discussed.

## Background

The recent history of lead-free solder for electronics assembly has been a tumultuous period of research on the technical merits of various candidate alloys as well as discussion of the actual benefits of eliminating lead from solder. Much of the initial push for lead-free came from Japanese electronics companies that perceived lead-free soldering as an opportunity to differentiate their product to consumers and increase sales [1]. Around the same time, the EU proposed legislation that are now known as WEEE (Waste from Electrical and Electronic Equipment) and ROHS (Restriction of Hazardous Substances Directive) [2,3]. The WEEE sets targets for take-back recycling while ROHS would severely limit the use of lead in electronics. The language of the legislation was finalized in late 2002, and if passed, the restrictions on lead would be enforced as of July 1, 2006. The bulk of electronic products are affected by the lead ban in ROHS, with only the following applications exempted at the present time:

- Lead in glass of cathode ray tubes, electronic components and fluorescent tubes.
- Lead as an alloying element in steel containing up to 0.35% lead by weight, aluminium containing up to 0.4% lead by weight, and as a copper alloy containing up to 4% lead by weight.
- Lead in high melting temperature type solders (i.e. tin-lead solder alloys containing more than 85% lead).
- Lead in solders for servers, storage and storage array systems (exemption granted until 2010).
- Lead in solders for network infrastructure equipment for switching, signaling, transmission as well as network management for telecommunication.
- Lead in electronic ceramic parts (e.g. piezoelectronic devices).

This has driven substantial interest in lead-free solder development around the world including within the US. Several industry consortia have investigated the Lead-free issue including those associated with NEMI [4], NCMS [5,6],

and IDEALS [7]. The NEMI Lead-free solder project was a three-year endeavor that focused on the technical challenges of lead-free implementation. A large number of companies including OEM, EMS, supply chain, and governmental agencies were active members and gave a broad perspective on what issues to focus on. There has also been work looking at the costs and to what extent there are environmental benefits of leaded solder elimination [8,9]. The legislative mandate of ROHS will push lead-free electronics assembly into the mainstream regardless of the scientific merits.

## Lead-free Alloys: Manufacturability and Reliability

The main issue with Lead-free soldering is to comparably replace the Sn-Pb solder with one that has the requisite processing and mechanical properties. The long supremacy of Sn-Pb owes itself to the relatively low processing temperature along with reasonable mechanical properties. Although Sn-Pb has some issues, such as with gold embrittlement, it is compatible with numerous metal finishes and has a reasonably low melting point of 183°C.

An initial study of lead-free alloys by NCMS [5] showed that of the numerous solder alloys examined, only a few met the initial baseline requirements of manufacturability, cost, availability, and reliability. The alloys recommended for further study included Sn-3.5Ag, Sn-58Bi, and Sn-3.5Ag-4.8Bi. However, the Sn-Ag eutectic melts at 221°C, (approx. 38°C above eutectic Sn-Pb) and much subsequent work has focused on alloying additions that lower the Sn-Ag melting temperature but preserve or enhance its mechanical properties. The two alloy groups that have received the most attention are Sn-Ag-Bi and Sn-Ag-Cu.

Japanese companies have heavily investigated Sn-Bi alloys for Sn-Pb replacement [10]. Bismuth is more effective in lowering the Sn melting temperature than Ag or Cu. However there are some issues that make Bi less than desirable as a general lead-free solder replacement. One concern is the potential of Bi alloying with Sn-Pb to form a low melting point eutectic [11] or peritectic as shown in Table 1. Anytime a lower melting point constituent forms in a solder joint it can greatly decrease reliability [12]. A couple of investigations have examined the interaction of Bi and Pb in Sn-Ag solders [13,14]. Figure 1 shows the first onset of melting for various Sn-Ag solders with and without Pb. The presence of Pb and Bi in Sn-Ag solders lowers the first onset of melting compared to Sn-Ag without Bi. An example of the reduced reliability of Sn-Ag-Bi solders as a function of Bi content when assembled to Sn-Pb plated TSOPs tested at -55 to 125°C is shown in Figure 2.

Table 1. Several Pb-based ternary constituents

| Composition, wt% | Type       | Melt Temp, °C |
|------------------|------------|---------------|
| Sn-18Bi-40Pb     | Peritectic | 137           |

|              |          |     |
|--------------|----------|-----|
| Sn-51Bi-32Pb | Eutectic | 96  |
| Sn-36Pb-2Ag  | Eutectic | 179 |

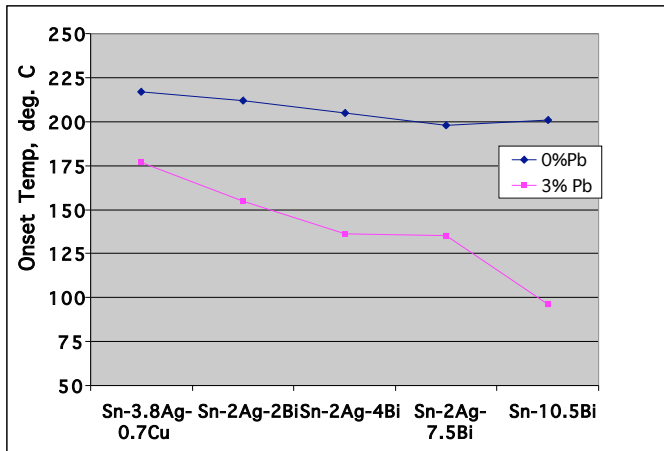


Figure 1. Minimum onset temperatures from DSC testing for various Sn-Ag alloys for 0% and 3% Pb.

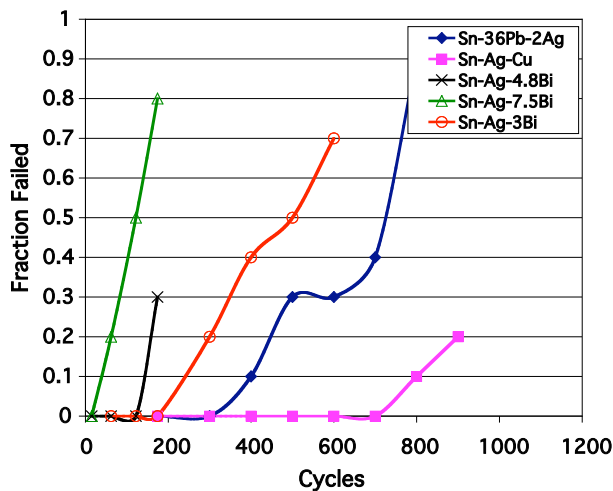


Figure 2. Reliability data for TSOPs assembled to electroless nickel immersion gold boards cycled from -55 to 125°C.

### Tin-Silver-Copper (Sn-Ag-Cu)

Sn-Ag-Cu alloys have emerged as the most promising lead-free alternative for reflow assembly. JEITA recommends Sn-3Ag-0.5Cu [15] while NEMI [16] and SOLDERTEC [17] have advocated Sn-3.9Ag-0.6Cu and Sn-(3.4-4.1)Ag-(0.45-0.9)Cu respectively. Ideally, one alloy would be the primary Pb-free alloy for electronics assembly, although there may always be niche applications that may require other alloy compositions. Realize that presently both Sn-37Pb and Sn-36Pb-2Ag are used in electronic assemblies, with the binary commanding a larger share of the market. The difference compositionally between Sn-3Ag-0.5Cu and Sn-3.9Ag-0.6Cu is less than that of Sn-37Pb and Sn-36Pb-2Ag. It is likely that general experience over time will determine which alloy emerges as the primary lead-free alloy going forward.

### Reliability of Sn-Ag-Cu Solders

One of the main issues with moving to a lead-free solder is to know and understand its effect on solder joint reliability. There have been innumerable studies published on Sn-Pb reliability, along with years of experience that give tremendous confidence of its field performance. Any alternative solder system suffers by comparison, but there has been much work recently to fill the gap of experimental results. The NEMI Lead-free solder project [18] evaluated the thermal cycling reliability of six different components: 256 PBGA, 256 CBGA, 48 TSOP, 2512 resistor, 169 CSP and 208 CSP and a summary of the results are shown in Table 2. The table indicates how either the lead-free (Sn-3.9Ag-0.6Cu paste + lead-free finish) or mixed (Sn-Ag-Cu paste + Sn-Pb finish) compared to the Sn-Pb standard assembly (Sn-Pb paste + finish) on immersion silver boards. Each test condition typically contained 32 components and was tested to at least 50% failure and the results were evaluated using Weibull analysis at a 95% confidence level. The ratio of the eta values (comparing Sn-Ag-Cu to Sn-Pb) from the Weibull analyses for -40 to 125C tests are plotted in Figure 3 and all are at or above 1. The results show that the Sn-3.9Ag-0.6Cu alloy compares favorably to the Sn-37Pb eutectic.

Table 2. Summary Results of the NEMI Thermal Cycling Evaluation

| Component     | Temp Cycle, °C | Lead-free vs. Sn-Pb | Mixed vs. Sn-Pb |
|---------------|----------------|---------------------|-----------------|
| 48 TSOP       | -40 to 125     | 0                   | -               |
| 2512 resistor | -40 to 125     | 0                   | 0               |
| 256 CBGA      | 0 to 100       | +                   | -               |
| 256 PBGA      | -40 to 125     | 0                   | 0               |
| 256 PBGA      | 0 to 100       | 0                   | 0               |
| 169 CSP       | -40 to 125     | +                   | +               |
| 169 CSP       | 0 to 100       | +                   | 0               |
| 208 CSP       | -40 to 125     | +                   | 0               |
| 208 CSP       | 0 to 100       | +                   | +               |

+ statistically better than Sn-Pb, - statistically worse, 0 = indeterminate

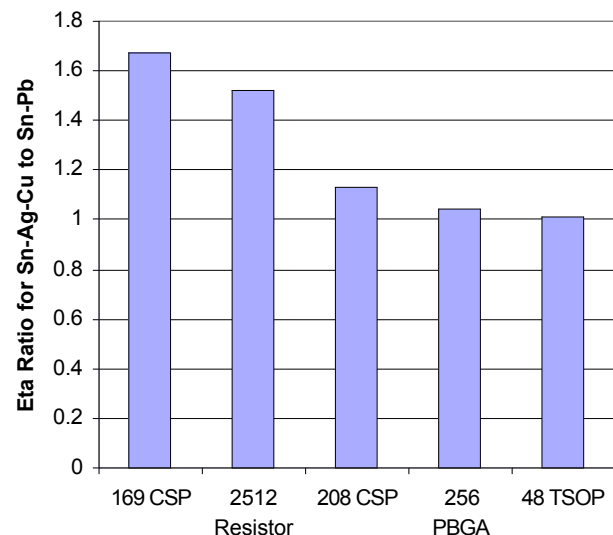


Figure 3. Calculated eta ratio from Weibull curves for Sn-3.9Ag-0.6Cu compared to Sn-37Pb for NEMI thermal cycling tests at -40 to 125°C.

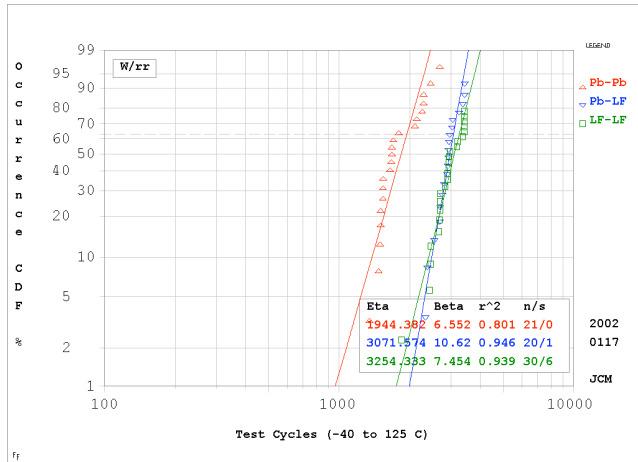


Figure 4. Weibull plot from NEMI testing of 169 CSPs cycled from -40 to 125°C. Green = Sn-3.9Ag-0.6Cu, Blue = Mixed, Red = Sn-37Pb.

The Weibull curves for the lead-free 169 CSP (Figure 4) are substantially better than Sn-Pb both in mean time to failure as well as early failure. Overall, the NEMI results agree with other published reports that the Sn-Ag-Cu alloys, when assembled to lead-free terminations, are typically as reliable as Sn-Pb eutectic in accelerated testing.

Sn-Ag-Cu has been shown to outperform high-Pb C4 joints in CBGA assemblies [19]. Syed [20] showed consistently better results in thermal cycling for Pb-free alloys. The findings also show that Sn-Ag-Cu alloys are proportionately better in thermal fatigue as the thermal cycling range decreases. Figure 5 shows the ratio of mean fatigue life for the two accelerated test conditions (0 to 100°C and -40 to 125°C) comparing Sn-Ag-Cu to Sn-Pb for the Syed and NEMI results. A higher ratio indicates improved thermal cycling performance at the more benign test condition relative to the more extreme condition. Sn-Ag-Cu performs better relative to Sn-Pb at the less extreme cycling conditions.

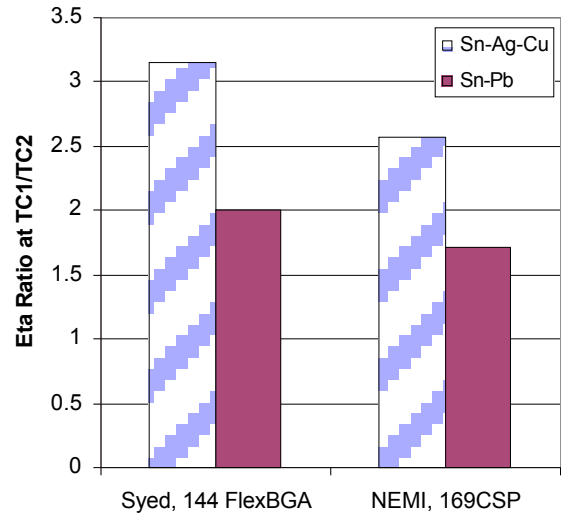


Figure 5. Eta ratio at two different thermal cycling conditions demonstrating the higher acceleration factor for Sn-Ag-Cu compared to Sn-Pb. TC1 = 0 to 100°C, TC2 = -40 to 125°C.

There is limited published data for lead-free solders subjected to vibration or other isothermal cyclic fatigue conditions. Kanchanomai [21] performed isothermal strain-controlled fatigue tests and found that Sn-3.5Ag exhibited twice the cycles to failure for a given plastic strain range than Sn-37Pb at room temperature.

As shown in Table 2 and Figure 2, Pb contamination in lead-free solder joints can adversely affect reliability of lead-free alloys. There are two ways a lead-free solder joint can contain more than trace amounts of lead: (1) lead-free finishes assembled with Sn-Pb solder and (2) Sn-Pb finishes assembled with lead-free solder. For type 1 assemblies there are substantial data and experience assembling non-BGA style components with lead-free finishes such as gold, Ni-Pd, and matte tin using Sn-Pb solder, but little information with lead-free BGAs and Sn-Pb paste. Type 2 was expected by the NEMI project to be the more common manufacturing scenario and was chosen for testing. As shown in Table 3, type 2 mixed cells are richer in Pb for BGAs compared to leadframe or leadless components, and so care must be taken if extrapolating mixed cell results to other component types. Table 4 shows the nominal composition of the three types of assemblies for two components tested by NEMI.

In the NEMI study, the mixed cell is statistically lower than the corresponding Sn-Pb cell for two of the nine test conditions, and is statistically higher for two as well [22]. Analysis of the microstructure of the mixed assembly BGA components did not show any macroscopic Pb or Ag compositional gradients within the solder joints, and the fatigue crack path is similar in both cases. Greater detailed analysis is needed to understand the root cause of the variation and determine the relative importance of composition versus assembly process.

Table 3. Comparison of Pb content for different mixed assembly types

|  | BGA style       | Leadframe / leadless style |
|--|-----------------|----------------------------|
| Lead-free finish + Sn-Pb solder (type 1) | Low Pb content  | High Pb content            |
| Sn-Pb finish + lead-free paste (type 2)  | High Pb content | Low Pb content             |

Table 4. Nominal Pb content (wt %) of 2512 resistor and 169 CSP in from NEMI testing

|                               | 169 CSP                 | 2512 Resistor        |
|-------------------------------|-------------------------|----------------------|
| Sn-Ag-Cu assembly             | Sn-3.9Ag-0.6Cu          | Sn-3.7Ag-0.6Cu       |
| Sn-Pb finish + Sn-Ag-Cu paste | Sn-32.7Pb-0.45Ag-0.07Cu | Sn-0.6Pb-3.7Ag-0.6Cu |
| Sn-Pb assembly                | Sn-37.0Pb               | Sn-35.7Pb            |

### Effect of Gold in Sn-Ag-Cu Solders

Another positive result with Sn-Ag-Cu is that it appears to be more resistant to gold embrittlement than Sn-Pb. In Figure 6 are the bend test results of Ni-Au finish LCCCs assembled to OSP finish PCBs. The strength of the joints is substantially higher for the Sn-Ag-Cu versus Sn-Pb, and the failure mode is changed from a partially brittle joint separation at the AuSn<sub>4</sub> plates with the Sn-Pb to a ductile tearing with the Sn-Ag-Cu. The microstructure of the Sn-Pb joints has numerous plates of AuSn<sub>4</sub> intermetallic (Figure 7) that contributed to the failure while the lead-free joint shows no such AuSn<sub>4</sub> plate morphology.

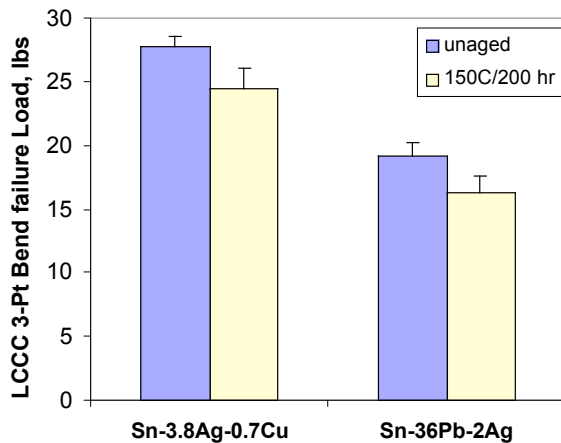
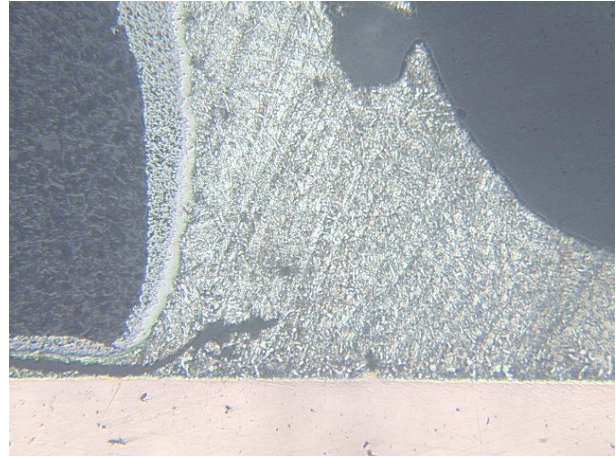
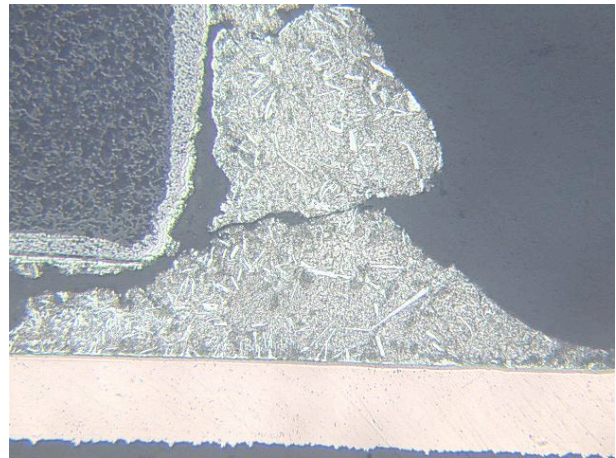


Figure 6. LCCC bend tests results.



(a)



(b)

Figure 7. Etched microstructures of unaged LCCC solder joints after bend loading. The assemblies were made with a) Sn-Ag-Cu and b) Sn-Pb solder paste. Note that the Sn-Pb has numerous plates of AuSn<sub>4</sub> intermetallic that contributed to the failure while the lead-free solder joint does not have a similar microstructure.

### Effect of Lead-free Assembly Temperatures on Components

Given that the vast majority of companies have migrated to Sn-Ag-Cu, the major roadblock for implementation is that some components have trouble meeting the higher processing temperatures. Applying the typical reflow temperature process delta used with Sn-Pb to Sn-Ag-Cu, one can quickly calculate that a similar reflow peak for Sn-Ag-Cu would be around 260°C, and this was proposed by NEMI as a good target for development efforts. [23,24] Initial characterization has shown that certain parts are more robust than others with respect to the higher temperatures [25]. Swan [26] evaluated a number of component types and found many were capable of higher temperature reflow at MSL levels of 3 and higher.

Some of the components that are susceptible to the Sn-Ag-Cu assembly temperatures are electrolytic capacitors, connectors, opto-electronics, and older style plastic components. Recently, a number of companies have been issued press releases stating the availability of lead-free components that meet 260°C, and this shows that the

development efforts are making progress. The pressure on component suppliers is developing components that work at the higher temperatures while adding minimal cost.

### Component Leadframe Composition

The vast majority of component leadframes are Sn-Pb plated, and BGAs typically use Sn-37Pb or Sn-36Pb-2Ag spheres. Therefore, a major issue is the conversion of component terminations to lead-free alternatives. There are many existing types of lead-free component finishes (e.g. nickel-palladium, gold, and matte tin) that are lead-free. However, the cost of palladium is quite high and in recent years has often surpassed that of gold, reaching spot prices over \$1000 (US) per ounce. As a result, most recent efforts are focused on tin-based plating alternatives including tin, tin-copper, tin-silver, and tin-bismuth.

The two most popular choices are tin (US/Europe) and tin-bismuth (Japan). There is also concern with the propensity of tin whisker formation for these tin-based chemistries that is the focus of two NEMI projects [27]. An additional issue with tin-bismuth plating includes backward compatibility with Sn-Pb assembly. The levels of Bi deposited are nominally low (approx. 2-3%), so the risk of Sn-Pb-Bi eutectic formation is low, but process variations could possibly allow for microstructures that contain that. However, the author is not aware of any papers to date reporting reliability problems with Sn-Bi plating assembled with Sn-Pb solder. [28]

### Lead-free Assembly Experience

Only a few articles have been published on lead-free manufacturing of actual products [29,30] and not many products have been identified as being lead-free. Japanese manufacturers has been much more active and have published roadmaps showing conversion to lead-free for many products within the next few years.



Figure 8. Motorola i85 handset assembled with Sn-Ag-Cu solder paste.

Motorola has published some details on the evaluation and qualification of the iDEN i85 handset (Figure 8) assembled with lead-free solder paste using the higher silver Sn-Ag-Cu alloy [31]. All indications are that Pb-free did not introduce any major issues as compared to conventional Sn-Pb.

### Summary

Lead-free soldering of electronic assemblies is becoming a reality with the passage of the WEEE and ROHS directives in Europe and continuing pressure from Japanese manufacturers, even in the face of conflicting information on its environmental benefits. The bulk of data indicates that Pb-free soldering is a process that, although not a direct drop in replacement, can be applied with minimal reliability risk. Many components are compatible with lead-free assembly, and the biggest roadblock is to have all components compatible with the assembly process as well as the composition limits. As more companies gain experience in designing and building lead-free products, this will raise the maturity of lead-free technology into the mainstream.

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