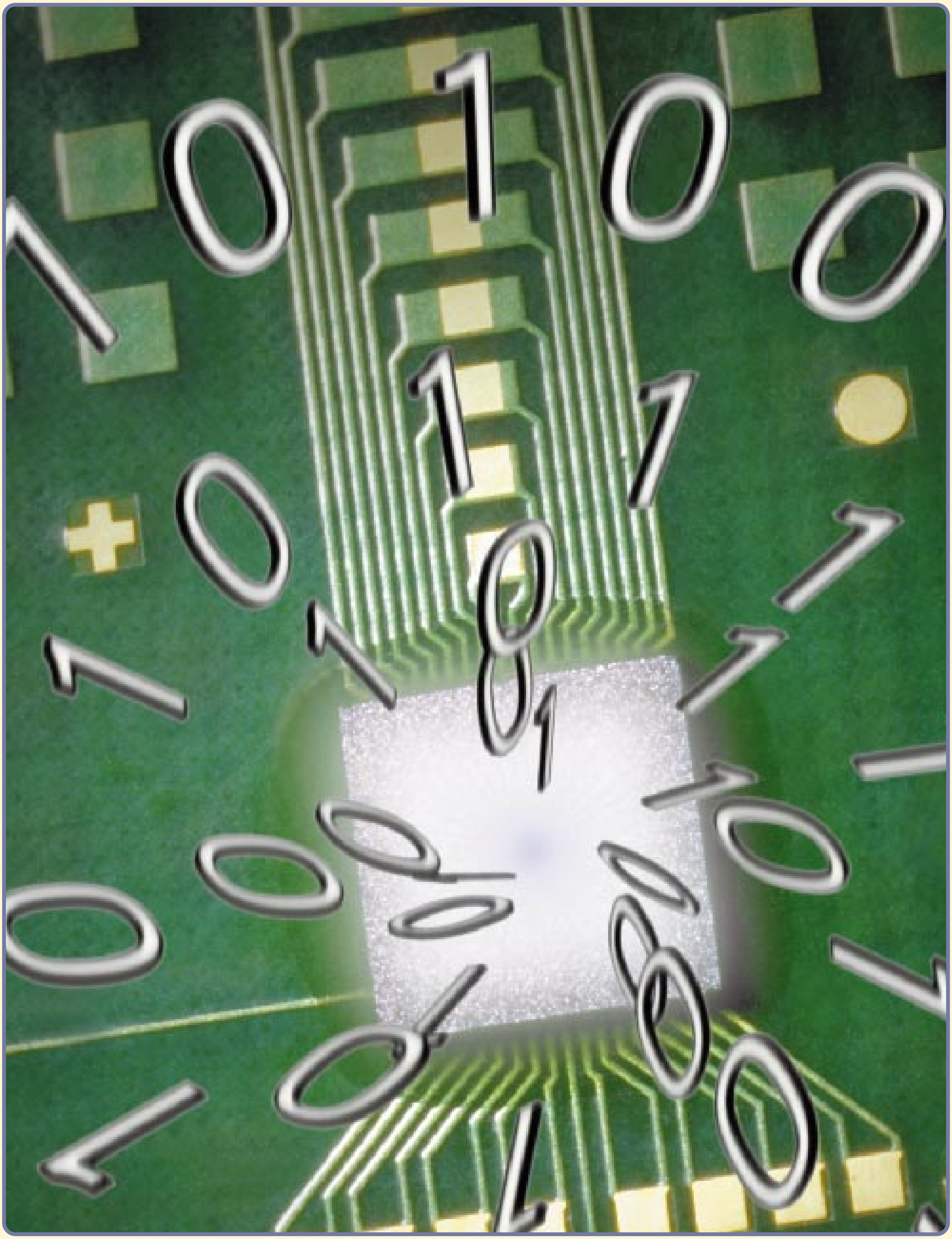

Mark Teague Photography, Smyrna, GA.

Research Update: Lead-Free Solder Alternatives

Jasbir Bath, Carol Handwerker and Edwin Bradley

The NEMI Lead-Free Assembly Project makes its recommendation for standardized alternatives to tin/lead solder.

Increasing global concern about the environment is bringing regulatory and consumer pressure on the electronics industry in Europe and Japan to reduce or completely eliminate the use of lead in products. As Europe and Japan move toward lead-free electronics, North American electronics manufacturers must prepare to do the same.

Among the materials targeted for elimination is lead-containing solder. In 1999, the National Electronics Manufacturing Initiative (NEMI, Herndon, VA) formed its Lead-Free Assembly Project to help the North American electronics industry develop the capability to produce lead-free products by 2001. The group's first task was to recommend a standardized lead-free solder alternative. Industry can benefit by focusing on one standard alloy for replacing lead in solder. By cooperatively developing one solution, a replacement may be implemented sooner, multiple manufacturing processes may be avoided and understanding of the material may be enhanced while ensuring its reliability.

Earlier this year, NEMI announced its recommendations for lead-free solder. For reflow applications, representing at least 70 percent of all board assembly production, NEMI is recommending a predominantly tin (Sn)-rich alloy with 3.9 percent silver (Ag) and 0.6 percent copper (Cu): Sn3.9Ag0.6Cu. For wave solder production, requiring more solder than reflow processes, the group is recommending a less expensive tin/copper alloy (tin with 0.7 percent copper, Sn0.7Cu) or, as an alternative standard, tin with 3.5 percent silver (Sn3.5Ag).

Selection Criteria

The goal of the task group responsible for alloy selection was to choose a single alloy for reflow applications and, if necessary, a second alloy for wave soldering. The task force used eutectic tin/lead solder as the model to evaluate the new alloys for reliability, melting point and other pertinent properties.

The group began with a literature search to use as much existing data as possible to minimize duplication of effort. Group members also obtained a patent search, sought the advice of six North American solder manufacturers, and sought opinions from experts in the field such as the National Institute of Standards and Technology (NIST, Gaithersburg, MD) and the International Tin Research Institute (ITRI, Uxbridge, England).

Based on its initial findings, the industrial members of the alloy selection group defined the following criteria for selection:

- If possible, stay with ternary alloys or less. Quartenary alloys can present control difficulties.
- The new alloy should be near eutectic. For example, it should not have a large pasty range during cooldown.
- Avoid using a patented alloy, if possible, so industry freedom of action is guaranteed.
- Using the best knowledge available, choose an alloy with no possible environmental issues.

A key report used by the NEMI selection group in identifying potential alloy replacements came from a three-year study by the National Center for Manufacturing Sciences (NCMS, Ann Arbor, MI), which evaluated over 79 solder alloys.[1] Based on this study, input from the alloy selection group, and other information including oral and written reports from the European IDEALS consortium, a short list of solders was chosen. All were predominantly high tin-based except for tin/58bismuth (Sn58Bi). These solders were:

- tin/58bismuth (Sn58Bi)
- tin/zinc/bismuth (SnZnBi)
- tin/silver/bismuth (SnAgBi)
- tin/silver/copper (SnAgCu)
- tin/silver (SnAg)
- tin/copper (SnCu).

These solders were evaluated by the selection group to determine the relative advantages and disadvantages of each, as discussed below.[1-6]

Potential Alloys

Sn58Bi

The alloy Sn58Bi has a melting temperature of

138°C (eutectic temperature) and has been shown to be resistant to fillet lifting and to outperform eutectic tin/lead in thermal cycling tests undertaken by NCMS.[1] However, it has a lower melting temperature than Sn37Pb, which will preclude it from applications where the upper use temperature is close to 138°C. For example, most automotive assemblers are looking for a higher melting point alloy than eutectic tin/lead for under-the-hood applications at 150°C to 175°C.

During any transition to lead-free solders, components will still be used that contain lead from the tin/lead surface finishes. The Sn58Bi solder will react with the lead to form some fraction of the tin/bismuth/lead ternary eutectic phases with a melting temperature of 96°C. This possible result is considered a manufacturing process issue and potential reliability exposure.

Cost and continued availability of bismuth and other alloying elements for use in such high concentrations are also issues. Approximately 60,000 tonnes of tin/lead solder are used in electronics per year (1 tonne = 1,000 kg = 2,200 lbs). Up to 50,000 tonnes are used in wave soldering per year, and up to 10,000 tonnes are used in solder paste applications per year. Considering current production and spare capacity, a solder containing up to 6 percent (weight) bismuth could supply the whole electronics solder market. When additional sources of bismuth are considered, the NCMS lead-free project estimated that the bismuth composition of a solder completely replacing eutectic tin/lead could be as high as 20 percent (weight) bismuth, which is still lower than Sn58Bi. The alloy Sn58Bi will probably be used for consumer products with low-use temperatures and for temperature-sensitive components and substrates. The issues regarding consumption and availability, and its low melting phase formation with lead, will limit the widespread adoption of Sn58Bi.

Tin/Zinc/Bismuth

The tin/zinc/bismuth alloy has a melting range of 189°C to 199°C (Sn8Zn3Bi), thus having a higher melting temperature than Sn37Pb (183°C). The term *melting range* means that the alloy begins to melt at 189°C (solidus temperature) and finishes melting at 199°C (liquidus temperature). This temperature range is an obvious advantage over other high tin alloys with maximum temperatures as high as 221°C. However, zinc-containing alloys oxidize easily, showing severe drossing in wave solder pots; are prone to corrosion; and have a paste shelf life that is measured in days or weeks as compared to months for tin/lead.

The bismuth is added to improve the wettability, reduce the liquidus temperature and reduce corrosion as compared with binary tin/zinc alloys. The presence of bismuth may also result in the formation of low melting point phases in contact with tin/lead-coated components and boards associated with tin/bismuth/lead that would affect the reliability of the assembly as in the case of Sn58Bi. Due to the manufacturing control difficulties, all six of the solder suppliers consulted recommended strongly against adoption of a zinc alloy. Given these drawbacks, its utility as a replacement for eutectic tin/lead is small.

Tin/Silver/Bismuth

The melting range of the tin/silver/bismuth alloy family is 210°C to 217°C, with bismuth compositions ranging from 3 to 5 percent (weight) and silver compositions from 2 to 4 percent (weight). The alloy Sn3.4Ag4.8Bi outperformed eutectic tin/lead in thermal cycling tests undertaken by NCMS[1] and by Sandia National Laboratory, (Albuquerque, NM) which conducted 0°C to 100°C thermal cycling experiments for up to 10,000 cycles on chip capacitors, small outline integrated circuits (SOIC) gull-wings and plastic leaded chip carrier (PLCC)-J-lead solder joints.[4]

Despite its excellent performance in surface-mount applications, several issues exist with this alloy. One is the possibility of the low melting points of tin/lead/bismuth eutectic phases when combined with tin/lead-coated components.[7] Although Panasonic/Matsushita has manufactured a consumer product with this type of alloy paste and lead-containing component finishes, the presence of a lower melting point did not arise in the company's testing.[8]

Alloys of tin/silver/bismuth have also been found to have a severe problem with fillet lifting in through-hole joints; cracking occurs in the solder joint between the solder and the land at the end of wave soldering (Figure 1). This tendency toward fillet lifting increases with bismuth concentration to a maximum in the range of 5 to 10 percent bismuth.[1] When these alloys are used with tin/lead-coated components and boards, the tendency toward fillet lifting can be increased. All of the other issues noted above for bismuth-containing solders also apply to these alloys.

Tin/Silver/Copper

Alloys in this family with melting ranges near 217°C to 222°C have the most promise as the main replacement for tin/lead solder. The alloys Sn3.5Ag, Sn2.6Ag0.8Cu0.5Sb and other high-tin alloys containing silver and copper with small additions of other elements such as antimony (Sb) were shown to perform as well as eutectic tin/lead for bumpered quad flat pack (BQFP), PLCC, and 1206 capacitors in thermal cycling tests by NCMS.[1]

The Sn3.8Ag0.7Cu alloy was recommended by the European IDEALS consortium as the best lead-free alloy for reflow as a result of reliability testing from –20°C to 125°C for up to 3,000 cycles and power cycling from 25°C to 110°C for 5,000 cycles.[3,6] In these tests, reliability of Sn3.8Ag0.7Cu was equivalent to or better than tin/lead and tin/lead/silver. No low melting point phases occurred with lead. The 7°C higher temperature compared to tin/lead/bismuth alloys may be a small price to pay to ensure good reliability of through-hole joints. These alloys have an approximately 4°C lower melting temperature than the Sn3.5Ag eutectic alloy (221°C), with a potential improvement in solderability and reliability.

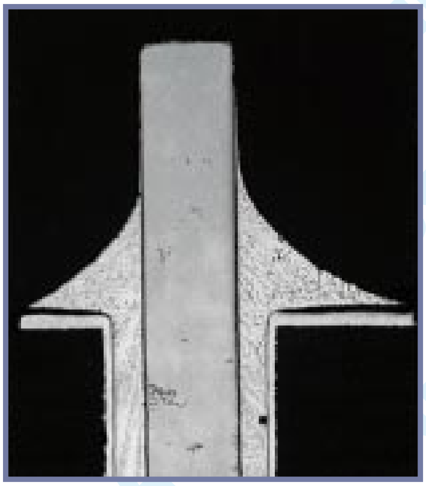

FIGURE 1: Fillet lifting of Sn3.4Ag4.8Bi solder in a through-hole joint.

Three readily available tin/silver/copper solders have melting temperatures near 217°C. These are Sn3.5Ag0.7Cu, which is available in Japan, and Sn3.8Ag0.7Cu and Sn4Ag0.5Cu, which are available in North America and Europe. All have similar solderability, mechanical properties and melting behaviors. The NEMI lead-free group decided on Sn3.9Ag0.6Cu—a composition midway between Sn3.8Ag0.7Cu and Sn4Ag0.5Cu—as the alloy to recommend to the industry. The ANSI J-STD-006 specifies that an alloying element less than 5 percent (weight) can vary in composition by ±0.2 percent (weight), so the Sn3.9Ag0.6Cu alloy would cover both these compositions. A solder manufacturer usually gives a ±0.2 percent (weight) tolerance when manufacturing a particular solder alloy.

NIST melting point data using several tin/silver/copper alloys were compared to data from Marquette University[9] and Northwestern University[10] to determine that the ternary eutectic alloy had a melting temperature of 216°C to 217°C with a composition of approximately Sn3.6Ag0.9Cu (Figure 2). Alloys with compositions within the range of Sn/3.5 to 4 percent (weight) Ag/0.5 to 1 percent (weight) Cu are close enough to the eutectic to have a liquidus temperature of around 220°C with similar microstructures and mechanical properties. The literature indicates that the solderability of tin/silver/copper is adequate. Note that results from the literature and from solder vendors indicate that the solderability of all lead-free solders is worse than eutectic tin/lead.

The patented alloy Sn2.6Ag0.8Cu0.5Sb (CASTIN™) is in the same tin/silver/copper family, with similar melting temperature, solderability and reliability as the alloys above.[11] Additions of less than 1 percent antimony do not degrade solderability and only slightly change the melting point. Antimony is considered to be toxic by some companies, but, at this low concentration, it may or may not be problematic.

NEMI's patent review found many patents in the tin/silver/copper phase system (Table 1) but with considerable overlap. The alloy Sn4Ag0.5Cu was reported in a German thesis and a corresponding paper[12] as the ternary peritectic/eutectic, and some solder companies are producing this alloy without any licensing. In the United States, both Sn3.8Ag0.7Cu and Sn4Ag0.5Cu formulations are available from the main solder manufacturers.

Sn3.5Ag

The alloy Sn3.5Ag has been used for many years in module assembly. Ford (Visteon Automotive Systems) has reported using Sn3.5Ag solder successfully in production for wave soldering since 1989.[13] No patent issues exist regarding its use, and it is already available from most solder manufacturers in bar, wire and paste form. The alloy's reliability is similar

TABLE 1: Relevant lead-free solder patents.

SnAgCu	Patent No.	Assigned to:	Sn	Ag	Cu	Bi	Sb	Zn	In	Other
USA	4,879,096	Oatey Company	88-99.35	0.05-3	0.5-6	0.1-3				
USA	Pending	Kester Solder	90-93.5	2.0-5	0.3-2	0.5-7				
Japan	08-132277	Ishikawa Kinzoku	Balance	1.0-3	0.5-2	1.0-10				
Japan	08-206874	Matsushita	Balance	0.1-20		0.1-25 *			0.1-20 *	*Add Cu 0.1-3 or Zn 0.1-15
USA	4,778,733	Engelhard Corporation	92-99	0.05-3	0.7-6					
USA	5,527,628	Iowa State University; Sandia	Balance	3.5-7.7	1.0-4.0	0.0-10.0		0.0-1.0		
Japan	08-215880	Ishikawa Kinzoku	Balance	0.5-3.5	0.5-2.0					
Japan	05-050286	Senju/ Matsushita	Balance	3.0-5	0.5-3		0-5			

or better than Sn37Pb.[1,14,15] The primary difference between the Sn3.5Ag and the tin/silver/copper alloys is the addition of the copper, which lowers the melting temperature by 4°C.

Sn0.7Cu

The eutectic alloy Sn0.7Cu with a melting temperature of 227°C was another alloy evaluated for reflow and wave soldering. The available reliability data for Sn0.7Cu indicates it is similar to Sn37Pb for surface-mount use.[14] However, its melting temperature, which is 10°C higher than tin/silver/copper, makes it undesirable for reflow applications. In wave soldering applications, the temperatures that the boards and components reach are much lower than in reflow soldering.

A problem does exist with using tin/silver, tin/copper or tin/silver/copper alloys for wave soldering with lead-containing surface finishes. The alloys themselves show good resistance to fillet lifting; however, additions of lead cause an increase in the tendency for fillet lifting, as reported by NCMS and others.[1]

The most significant advantage of Sn0.7Cu for wave soldering is the cost of bar solder. Because it does not contain silver or bismuth, Sn0.7Cu is one of the cheapest lead-free solder alloys available, as indicated in Table 2. Pricing is a key criterion for wave solder pots that have capacities as large as 1,600 lbs.

In contrast to wave soldering, the price of the various alloying elements for paste is less of a consideration compared with solder bar because the metal costs account for much less than 50 percent of the cost of the paste. So, the differences in cost among tin/silver/copper, tin/copper, tin/silver and Sn37Pb pastes will be small.

NEMI Alloy Choices

With the alloy review completed, Sn3.9Ag0.6Cu was identified as the number-one choice for reflow soldering. This alloy is being subjected to further trials along with Sn37Pb as a control. The Sn3.9Ag0.6Cu alloy also fits into the alloy range recommended by the International Tin Research Institute, which bodes well for the acceptance of international standards.[2]

The number one and two choices for wave soldering are Sn0.7Cu and Sn3.5Ag. They are also being investigated in further work by NEMI.

Reflow Characteristics

With tin/silver/copper's melting point of 217°C, past experience indicates that worst-case temperatures will reach 260°C at the component level and to act as a margin for repair, which is a much more variable process. Other papers have reported lower peak reflow temperatures in prototype applications,[6,8] and variations in profiles are to be expected. A reflow profile recommended for use by component manufacturers has a peak temperature of 260°C, with a time above the melting point of up to 90 seconds for the full range of temperatures likely to be encoun-

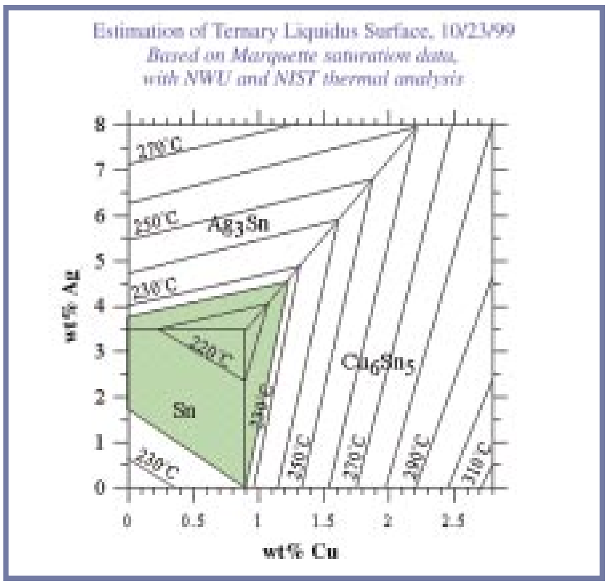

FIGURE 2: Tin/silver/copper phase diagram.[9,10]

tered during manufacturing. This profile is going to cause much development work to qualify current and emerging components to these temperatures. New material sets may need to be introduced with more precautions used to safeguard against moisture intake in component packages that will be subjected to the higher reflow temperatures. This work is currently underway.

The use of these higher temperatures will affect the type of reflow ovens used now and in the future. Specifically, convection reflow ovens will be more effective than infrared reflow ovens in terms of ensuring a lower temperature gradient (ΔT) across the board during the higher temperature lead-free soldering.

Test and Inspection Implications

The use of tin/silver/copper is at too early a stage of development to give any specific guide into its behavior for test and inspection. The NEMI process group will be assembling boards soldered with tin/silver/copper for reliability evaluation. The board manufacturers will report on their assembly compared with tin/lead assembly.

Alloy	Metal Cost
63Sn37Pb	$1.61/lb
96.5Sn3.5Ag	$4.90/lb
Sn3.5Ag5Bi	$4.96/lb
Sn3Ag3Bi	$4.58/lb
Sn4Ag0.5Cu	$5.24/lb
Sn0.7Cu	$2.41/lb
Sn2Ag0.8Cu0.5Sb (Castin)	$3.82/lb
Sn8Zn3Bi	$2.32/lb
Sn58Bi	$3.11/lb

TABLE 2: Estimated costs of lead-free solder alloys based on metal prices alone.

The IDEALS group reports that the visual appearances of the lead-free solder joints seem to be duller than those made with tin/lead. The wetting angles are also different, with tin/silver = 30° as compared to tin/lead = 10°.[18] Numerous JEDEC/IPC standards will have to be revised for lead-free solders.

X-ray inspection of the joints is an area that also needs to be investigated. The IDEALS report, among others, indicates an increase in the occurrence of voids using lead-free solders, which needs to be understood. A typical cross section comparing a tin/lead-soldered and tin/silver/copper-soldered QFP components is shown in Figure 3.

Rework

For Sn3.9Ag0.6Cu, Sn0.7Cu and Sn3.5Ag, an appropriate rework material is Sn3.5Ag. This rework wire has a history of use in the industry, has similar reliability to Sn37Pb, and is readily available from the major solder suppliers. For ball grid array (BGA) rework, tin/silver/copper paste is recommended.

Reliability

Reliability data for the tin/silver/copper lead-free alloys indicate they have better or equal reliability than Sn37Pb, but more extensive measurements are needed with a larger component set. The NEMI Lead-Free Task Force will be investigating the reliability of the tin/silver/copper-soldered lead-free chip resistors, BGA, chip-scale package (CSP), ceramic BGA (CERBGA) and thin small outline package (TSOP) components. Additional data should be available soon from the IDEALS project. A NCMS consortium on high temperature, high fatigue-resistant solders is currently conducting reliability testing of tin/silver/copper-soldered BGA components.

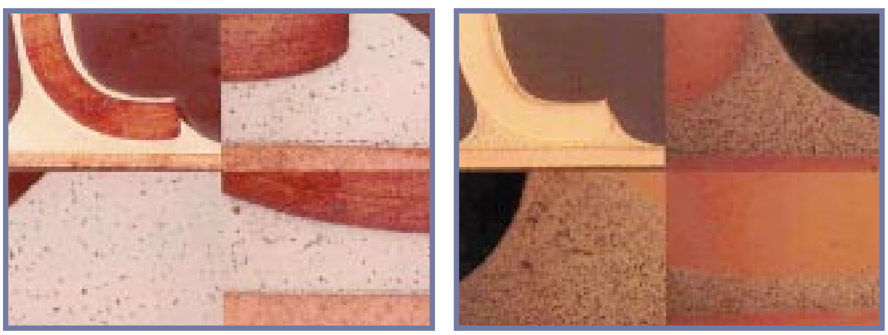

FIGURE 3: Comparison of cross sections of Sn37Pb-soldered (left) and Sn3.8Ag0.7Cu-soldered (right) tin-lead-coated 16-mil pitch QFP component on OSP-coated board.

Modeling Behavior/Mechanical Characterization

The mechanical/materials property database on the chosen alloys is limited and must be expanded to allow modeling of the package/assembly field performance of these new alloys. The NEMI alloy group is currently reviewing data from the NCMS lead-free project to determine what data exist for these alloys and what remaining data are needed.[1] The various properties that need to be measured include microstructure evolution during use and mechanical characterization of the solder joints, both in bulk and solder joint form.

As part of the work of the NEMI alloy group, the materials/mechanical property requirements are being compiled for release to all interested parties. This document also includes a list of properties required to be determined for lead-free tin and tin alloy surface finishes for PCBs and components, and for combinations of these surface finishes with tin/silver/copper. Updated information on the materials property database can be found on the NEMI web page: www.nemi.org/PbFreePUBLIC/.

Conclusions

In North America, Sn3.9Ag0.6Cu is the favored alloy for reflow applications, and Sn0.7Cu and Sn3.5Ag alloys are favored for wave soldering applications. NEMI's Lead-Free Task Force is developing the necessary database to allow member companies to implement these alloys. Efforts are also underway to develop additional reliability data, determine component and board tolerance for the higher reflow temperatures, and assemble the necessary mechanical database for model development.

The movement toward a single lead-free alloy will be beneficial to all in the industry so that a global solution can be reached in the same way that eutectic Sn37Pb solder is used in the industry today. The component, board, solder and equipment manufacturers can then efficiently focus their efforts and resources toward developing products to cater to the manufacturing requirements of the alloy. ■

Acknowledgments

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