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LEAD (Pb)-FREE SOLDER APPLICATIONS[1]

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Abstract: Legislative and marketing forces both abroad and in the US are causing the electronics industry to consider the use of Pb-free solders in place of traditional Sn-Pb alloys. Previous case studies have demonstrated the satisfactory manufacturability and reliability of several Pb-free compositions for printed circuit board applications. Those data, together with the results of fundamental studies on Pb-free solder materials, have indicated the general feasibility of their use in the broader range of present-day, electrical and electronic components.

I. INTRODUCTION

Lead (Pb), either in its elemental form or when alloyed with Sn to create so-called "soft solders," has had a role in joining together metal structures for nearly 5000 years. Those early applications included the construction of common utensils and light-duty tools as well as their use as a seal material to control leaks between the Pb liners of aqueducts built by the Roman Empire (first plumbing application).

The Industrial Revolution in the later 19th century and, in particular, the development of portable heat sources, expanded the use of soft-solders in structural applications, foremost, in the plumbing of conduit. In the early 20th century, soft-solders found an entirely new application with the development of electronics (radios). The low melting temperatures of soft-solders, in particular, the Sn-Pb alloys, caused them to be particularly well suited for the attachment of vacuum tubes, capacitors, etc. onto, what were then, very crude (and extremely flammable) circuit boards. And thus, from the 1920s up until the 1980s, the two principle applications of Pb-containing soft-solders have remained plumbing and electronics.

In the late 1970s and early 1980s, concerns were raised about the potential for Pb poisoning from solder joints used to assemble potable water (Cu) conduit and food containers. Mandates were subsequently issued by the US government, banning the use of Pb-bearing solders in the construction of food service equipment and, more importantly, the plumbing of potable water conduit. The latter case was embodied in Section 1417 of the Safe Drinking Water Act Amendments enacted in 1986[1]. At the time of this enactment, the availability of mechanical properties for soft-solder plumbing joints was limited to studies on the 50Sn-50Pb (wt.%) solder and the non-Pb containing 95Sn-5Sb alloy that were performed in the late 1930s[2,3]. Recently, more extensive mechanical properties studies have been completed by the International Tin Research Institute (ITRI, Ltd.) as well as by a collaborative program between the Copper Development Association (CDA) and the National Institute of Standards and Technology (NIST)[4,5]. These studies have greatly enhanced the properties databases for the now commonly used 95Sn-5Sb plumbing solder (ASTM "HB") as well as the newly developed 95.5Sn-4.0Cu-0.5Ag alloy (ASTM "E")[6].

The move to eliminate Pb from *electronic* solders was initiated in the early-1990s. The basis for the removal of Pb-bearing solders from electronic products was the contention that Pb leaching from an ever increasing amount of discarded electronics in landfills, would contaminate nearby ground water resources. Thus, a number of bills were introduced into the US. Congress that would either ban or heavily tax the use of Pb in manufactured products, including electronics that used Pb-bearing solders[7,8]. Interestingly enough, at the same time, there was very little activity along these lines occurring in European or in the Pacific rim countries. Ultimately, these bills were defeated in their respective governing bodies as lawmakers were made aware of the potential consequences to the US electronics industry in terms of lost market-share both domestic and abroad.

The current impetus to remove Pb-bearing solders from electronic components and assemblies remains based upon reducing potential ground water contamination from discarded electronic products. Now, however, the drivers for Pb elimination have come almost entirely from abroad - primarily Europe and Japan. Moreover, while the European initiative is based largely upon legislative actions, the case in Japan stems from the initiatives of individual corporations to remove Pb-containing solder from their respective electronic products. First, the case of Europe will be examined. The primary legislative action targeting the European

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Union (EU) is the Waste from Electrical and Electronic Equipment or *WEEE* directive. This directive, which remains in draft form at the time of this writing (July 2000), has the following stipulations pertinent to solders in electronics:

- The recycling of end-of-life equipment is the producers responsibility, and there being no take-back fees to the user.
- Ban on the use of certain heavy metals in manufactured equipment, namely Pb, Hg, Cd, and Cr.

This directive would apply to products manufactured in the EU *and* imported items. The original implementation date for the WEEE directive was January 1, 2004; however, upon release of the fourth draft of the directive in May 2000, a new implementation date of January 1, 2008 was proposed. Separate legislative actions are also being considered within individual European nations. Denmark is considering a ban on the sale of imported or domestically produced metallic Pb or products containing Pb (>50 ppm)[9]. Sweden, through the Swedish Environmental Quality Objectives, is seeking to have all new products be "largely" Pb-free by the year 2020[9]. Because the Swedish-based company, Nokia, has a leading role in the world-wide cellular telephone industry, it can significantly impact future trends in electronics assembly.

Lead-free solder research and development activities in Europe began with an exhaustive study in the UK during the mid-1990s. The work was performed by a consortium of European companies and spearheaded by the International Tin Research Institute[10]. Today, a larger consortium of companies have formed SOLDERTEC, a Lead-Free Solder Technology Center which acts as a clearing house of current technological issues dealing with Pb-free soldering implementation[11]. In addition, individual companies and academic institutions in the UK and throughout Europe are conducting both fundamental materials research as well as process optimization and reliability studies on Pb-free solders (for primarily electronics assembly); the results of those investigations have been presented at conferences held in the US.

In Japan, reducing the extent to which Pb enters the environment has encompassed two approaches, each with a different champion[12]. The first approach pertains to the elimination of Pb-bearing solders from electronic products. This effort has been undertaken largely by Japanese industry; some of the individual initiatives are listed below:

- Matsushita (Panasonic): Eliminate Pb from their four major electronic product lines by 2001.
- Sony: Eliminate Pb from all products except HDEP by 2001.
- NEC: Cut the levels of Pb use by 1/2 from those in 1997, by 2002.
- Toshiba: Eliminate Pb from mobile phones by 2000.
- Hitachi: Cut the levels of Pb by 1/2 from those in 1997, by 1999; eliminate Pb entirely by 2001.
- Mitsubishi: Cut the levels of Pb by 1/2, by 2004; eliminate Pb entirely by 2005.
- Automobile manufacturers (except the battery): Cut the levels of Pb by 1/2, by 2000 and by 1/3, by 2005.

Data obtained by several of these companies have demonstrated a preference by Japanese consumers for environmentally friendly products; similar studies have confirmed like attitudes amongst consumers in Western markets. These studies have suggested that market share is as important a factor in the Japanese Pb-free electronics roadmap as are the environmental drivers.

A second approach toward reducing the quantity of Pb entering the environment, which has been spearheaded by the Japanese government (MITI and Ministry of Health and Welfare), is to develop *recycling* legislation. The Appliance Recycling bill is targeted for implementation in April 2001; it will introduce mandatory recycling of both large appliances (TVs, refrigerators, washers, etc.) as well as smaller electronic products (PCs, audio equipment, etc.). The consumer will bear some of the cost for dealing with returned products from manufacturers that are no longer in business, likely by means of a product tax paid to the government.

Research and development activities in Japan have increased significantly over the past three to five years. Those efforts have taken place either within the individual companies or as company sponsored research activities at the universities. Technical data have been released at conferences in the US and overseas, as well as in archived journals.

In the US, there have been no new bills before the Congress to ban or tax the use of elemental Pb or Pb-bearing materials in manufactured products. On the other hand, state and municipal governments retain the options to pressure local industries to reduce the disposal of Pb-bearing products into landfills by introducing regulations that impose an increasingly heavier cost burden on the Pb producer/user. The resulting economic impact would ultimately force those companies to change materials or to cease operations altogether.

Therefore, it appears that the US electronics industry will be forced into Pb-free soldering technology. However, this time, the primary driver may be market share rather than specific, domestic legislation (at least in the foreseeable future). Globalization of the US economy has caused a large number of electronics manufacturers (OEMs), contract manufactures, and secondary (user) industries to have developed significant markets in both Europe and in Pacific rim countries. Import/export restrictions based upon Pb content in items such as computers, radios, CD players, etc. would significantly cripple the marketing of those US products abroad. As a result, companies such as Motorola and Ford have established benchmarks for reducing or eliminating Pb from one or more product lines, much like their Japanese counterparts. It is certain that other corporations will likewise follow suit.

Although the US appears to be in a somewhat reactionary mode in terms of implementing Pb-free soldering technology into electrical and electronic products, in fact, the US still has the upper hand in terms of both fundamental and engineering data on Pb-free solder alloys, processing, and reliability. This database stems, not only from the extensive studies currently underway by consortia, individual companies, and academia, but also from the vast amount of information that was collected in work performed in the early to mid-1990s. Referred journals (e.g., *Journal of Electronic Materials, Journal of Electronic Packaging,* etc.) as well as conference proceedings (*NEPCON, Surface Mount International, Electronic Components and Technology Conference,* etc.) contain much of that information, including solder properties as well as process development and reliability data.

II. DISCUSSION

A. Melting properties

Elemental metals (Sn, Pb, In, etc.) melt at a single temperature called the "melting point." Alloys, which are a combination of more than one elemental metal, can either melt at a single temperature or melt over a temperature range. In the former case, the melting point is referred to as the "eutectic temperature," T_{eut}. In the latter case, the temperature range is identified by the lower temperature value at which melting begins, the "solidus temperature," T_s, and the upper temperature value at which melting is complete and the alloy is 100% liquid, the "liquidus temperature," T_l. In nearly all electronics applications, soldering is performed at a temperature that is 20 - 40°C above the eutectic or liquidus temperature of the alloy; that is, the solder is entirely liquid when a joint is being made.

The Pb-free solders presently on the market represent both cases described above. In addition, most Pb-free solders are categorized as "high-temperature" alloys because their liquidus temperatures exceed the eutectic temperature of 63Sn-37Pb solder which is 183°C. Some Pb-free solder compositions include:

- 91Sn-9Zn T_{eut} = 199°C[13]
- 91.84Sn-3.33Ag-4.83Bi T_{onset} = 212°C[14]
- 95.5Sn-3.8Ag-0.7Cu T_{eut} = 217°C[15]
- 96.5Sn-3.5Ag T_{eut} = 221°C[16]
- 99.1Sn-0.9Cu T_{eut} = 227°C[17]
- 95Sn-5Sb T_s = 233°C; T_l = 240°C[18]

The higher processing temperatures required by these solders necessitate more stringent process control in order to realize proper solderability of the faying surfaces while avoiding overheating ("charring") the flux or causing thermal damage to the base materials.

Two low-temperature, Pb-free solders that are available off-the-shelf are the 58Bi-42Sn alloy with T_{eut} = 138°C and the 52In-48Sn alloy with T_{eut} = 118°C. Although having an advantage of reducing thermal damage to the parts, the low melting points limit the service temperature to which the product may be exposed. Also, solderability may be degraded because the reduced process temperatures are unable to fully "activate" the flux for the proper removal of surface tarnish. Raising the process temperature to accommodate the flux behavior countermands some of the advantage of using a low-temperature solder.

B. Solderability and processing

Solderability describes the ability of a molten solder to wet and spread spontaneously over an open surface. A metric of solderability is the contact angle, θ_c, formed at the edge of the spreading solder; the lower the value of θ_c, better is the solderability. The value of θ_c can be measured directly by sessile drop experiments or computed from experimental data obtained by the meniscometer/wetting balance technique[19]. Shown in Table I are the contact angles determined for several Pb-free alloys on Cu using a rosin-based, mildly activate (RMA) flux[20]. It is clear that the solderability of the Pb-free solders is not as good as that of the traditional 63Sn-37Pb alloy; however, numerous prototyping experiments have confirmed that the Pb-free solders have adequate solderability (i.e., sufficiently low contact angles) to support cost-effective assembly processes for electronic components and printed circuit boards.

Table I. Contact Angles of Several Pb-Free Solders (Substrate: Cu; Flux RMA)

Solder (wt.%)	Test Temperature (°C)	θ_c (°)
96.5Sn-3.5Ag	260	36±3
95Sn-5Sb	268	42±7
91.84Sn-3.33Ag 4.83Bi	260	31±4
58Bi-42Sn	215	37±7
50Sn-50In	215	63±3
63Sn-37Pb	*260*	*17±4*

Capillary action will often assist the wetting and spreading action of a molten solder in the case of confined geometries such as gaps and holes. Shown in Figure 1 is a graph of capillary rise between two parallel, Cu plates as a function of gap thickness. The solder alloy compositions (wt.%), abbreviations, and test temperatures were: (1) 95Sn-5Sb, SnSb, 280°C; (2) 63Sn-37Pb, SnPb, 260°C; (3) 96.5Sn-3.5Ag, SnAg, 260°C; (4) 91.84Sn-3.33Ag-4.83Bi, SnAgBi, 260°C; and (5) 95.5Sn-4.0Cu-0.5Ag, SnCuAg, 267°C. All tests were performed with an RMA flux. The SnAgBi solder showed the highest capillary rise and sensitivity to gap thickness amongst the Pb-free alloys.

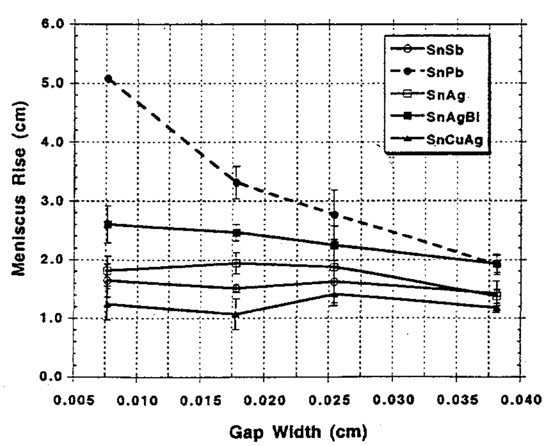


Figure 1. Capillary rise between two parallel, Cu plates as a function of gap thickness.

The extent of capillary flow was significantly less with the Pb-free alloys as compared to the baseline SnPb solder. Also, fundamental fluid mechanics would predict that a smaller gap would increase the flow distance of the solder[21]. However, the effect of gap thickness was not well pronounced with the Pb-free solders, including no significant effect had by SnSb, SnAg, and SnAgCu solders. The overall limited capillary flow behavior exhibited by the Pb-free solders was attributed directly to the inherently high surface tension of these particular alloys[22]. One method to modify (decrease) the surface tension of a Pb-free solder is to change the brand of flux. Proprietary additions to basic flux chemicals can lessen the surface tension of the molten solder. Also, the use of Au plating on the faying surfaces, with due precaution against excessive Au that will embrittle the joints, can help to reduce the surface tension of the solder[23].

A second characteristic of capillary flow is the propensity for voids to become entrapped in the newly formed joint. Void formation is strongly dependent on the particular flux type. Per a given flux brand, void formation increases as the gap thickness decreases; a smaller gap raises the difficulty with which flux volatiles and air can escape during solder flow. The extent of voiding, as determined by x-ray radiography of the capillary flow test samples, is summarized by the graph in Fig. 2. The expected trend of more voids with smaller gaps was observed. The behaviors of the individual solders became less distinguishable when the gap was equal to, or greater than, 0.025 cm. Finally, the solders SnAg and Sn-Pb (baseline) gave consistently more voids than the other solders, particularly at the smaller gaps.

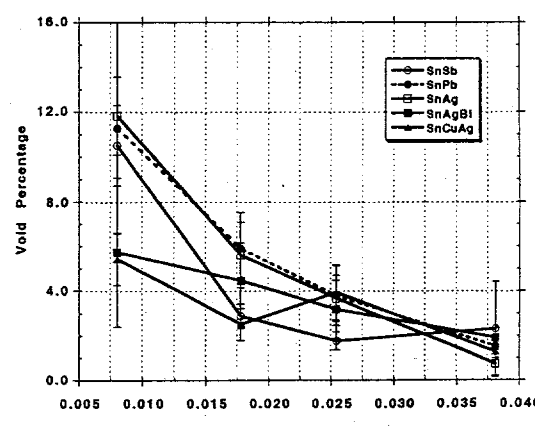


Figure 2. Void formation in solder joints between two parallel, Cu plates as a function of gap thickness.

The SnAgBi and SnAgCu consistently resulted in the least number of voids. Therefore, there appears to be a value, or range of values, of one or more parameters (e.g., surface tension) that minimizes the presence of voids in the gap. These void data, as well as the capillary rise results, can be generalized for other joint configurations for the purpose of relative comparisons.

C. Surface finishes

Surface finishes can be used to enhance a Pb-free soldering processes. Coatings can provide an alternative surface to which the joint is made; they can also cause small changes to the solder composition. These concepts are better understood with the assistance of Fig. 3 which illustrates the two-coating approach.

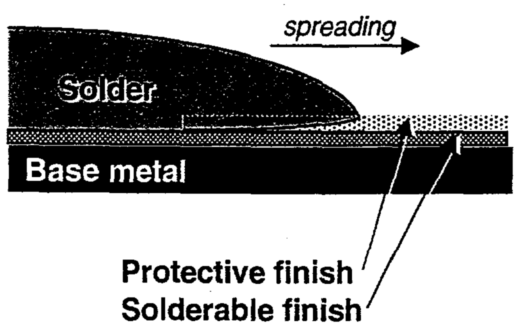


Figure 3. Schematic illustration of the role of the "protective finish" and "solderable finish" on the solder wetting/spreading process.

The layer placed directly on the base metal is the "solderable finish" and, as the term implies, forms the surface to which the joint will ultimately be made. The top-most layer is the "protective finish." The protective finish protects the solderability of the surface of the solderable finish. During the assembly process, the molten solders first wets the protective finish. Then, the protective finish dissolves into the solder. The molten solder then wets the surface of the solderable layer and bonds to it upon solidification. Some of the solderable surface will dissolve into the molten solder.

As noted, protective and solderable coatings not only impact solder wetting and spreading behavior over their respective surfaces, but also change the solder composition. The protective finish has the greater effect on solder composition. For example, Au has been used widely as a protective finish. Numerous studies have clearly demonstrated the potential for the embrittlement of 63Sn-37Pb solder by Au dissolved in it[24,25]. Similar concerns must be addressed with the effect of Au on the performance of Pb-free solders. For example, work by Jacobson and Humpston showed that Au concentrations of 10 wt.% were required to embrittle 96.5Sn-3.5Ag solder as compared to 4-5 wt.% for 63Sn-37Pb alloy. On the other hand, only 0.8 wt.% would embrittle 58Bi-42Sn solder[26]. The amount of Sn in the solder is one factor determining the alloy's propensity for embrittlement; however, the inherent strength/ductility of the solder is an equally important factor. For example, the relatively high strength of the 58Bi-42Sn solder is also believed to cause its high sensitivity to dissolved Au (above). Similarly the ductility of the very strong 91.84Sn-3.33Ag-4.83Bi solder appears to be further degraded by Au dissolved in it[27]. Conversely, the relatively soft 52In-48Sn solder is not readily embrittled by Au [26].

A number of alternative protective finishes are becoming popular for solderability requirements of electronic components. Those finishes include Pd, Pd (protective finish)-Ni (solderable finish), and Ag[28]. A number of studies have shown that the current Pb-free solder compositions are compatible with the new finishes in terms of solderability and mechanical properties requirements[29]. Of course, these compatibility issues must be re-addressed with any new Pb-free solders through the use of solderability tests (e.g., the meniscometer/wetting balance technique) and mechanical properties measurements.

At the present time, several popular protective finishes may include Pb, such as electroplated Sn-Pb finishes or hot Sn-Pb solder dipped coatings. Some concerns have been raised as to the compatibility between Pb in the coatings and Bi contained in several Pb-free solder(s). Specifically, the issue being raised is that of the possible formation of the low melting temperature ternary eutectic phase, 53Bi-30Pb-17Sn (T_{eut} = 95°C). A study performed by Vianco and Rejent examined the properties and microstructural changes that take place to the 91.84Sn-3.33Ag-4.83Bi solder by Pb contamination[30]. The levels of Pb contamination that were commensurate with protective coatings observed on typical electronic components and printed circuit boards, were found to be between 0 and 5 wt.% Pb. Differential thermal analysis showed no indication of the formation of the ternary Bi-Pb-Sn ternary phase. A nominal 15% loss of shear strength exhibited by the Sn-Ag-Bi alloy at the maximum Pb contamination level was attributed to the formation of a 64Pb-33Bi-3Sn particle phase that depleted Bi from the Sn-rich matrix, thereby curtailing the solution strengthening role of the Bi; the strength decrease was not caused by the formation of the low-temperature ternary phase.

D. Monotonic strength

A study by K. Stone, et al. demonstrated that the bulk mechanical properties of solders (constant displacement rate and creep) are not necessarily reflected in the mechanical performance of soldered joints[31]. Therefore, a comparative evaluation of the strength of Pb-free solders against traditional 63Sn-37Pb alloy was made using the ring-and-plug shear test (Fig. 4)[14]. A

Cu plug was soldered to a Cu ring; then, the plug was pushed through the ring using a mechanical test frame. The shear strength (stress) was computed from the maximum load divided by the solder joint area.

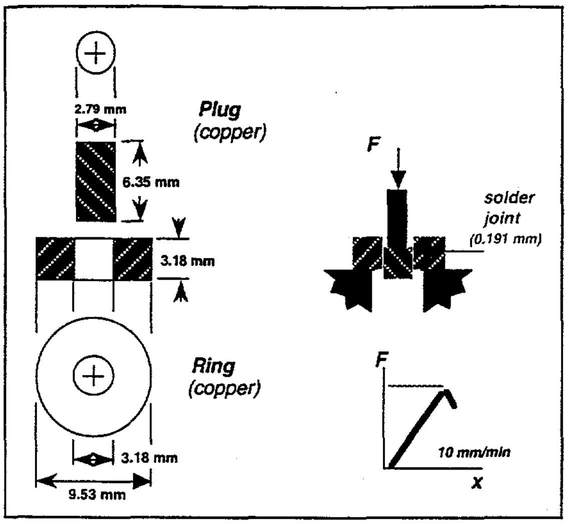


Figure 4. Schematic diagram of the ring-and-plug sample configuration and shear test procedure.

A list of shear strengths (25°C, 10 mm/min displacement rate) for several Pb-free solders as well as that representing the 63Sn-37Pb alloy is provided in Table II.

Table II. Shear Strength of Several Pb-Free Solders (25°C, 10 mm/min)

Solder (wt.%)	Shear Strength (MPa)
96.5Sn-3.5Ag	55±1
100Sn	40±2
91.84Sn-3.33Ag 4.83Bi	81±5
58Bi-42Sn	63±2
63Sn-37Pb	*40±2*

It is observed that the Pb-free solders generally have higher strengths than the 63Sn-37Pb alloy. In fact, the strength of the 91.84Sn-3.33Ag-4.83Bi alloy is twice that of the Sn-Pb solder. Generally, higher strengths are accompanied by reduced ductility.

The very high strength of some Pb-free solders can cause damage to through-hole solder joints, as exemplified by the case of a printed circuit board. This defect is referred to as "fillet lifting" (Fig. 5) Fillet lifting occurs upon solidification of the joint. Residual stresses within the solder place a large tensile load on the fillet edge, causing fracture at the solder/base metal (Cu) interface. Although reportedly seen on only circuit board products, this defect may be generalized to any similar solder joint configuration; its occurrence will depend upon the exact joint dimensions, solder and base materials, as well as the process techniques.

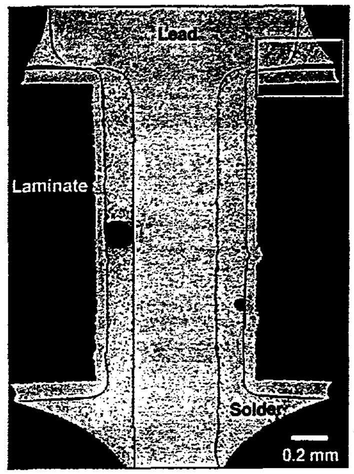


Figure 5. Fillet lifting of a printed circuit board through-hole made with the 91.84Sn-3.33Ag-4.83Bi solder.

E. Fatigue strength

As in the case of monotonic strength, the fatigue resistance of soldered joints is not necessarily well represented by the bulk fatigue properties of the solder alloy. Besides simple mechanical fatigue, solder joints may also be subjected to thermal mechanical fatigue in which the thermal expansion mismatch between joined materials causes a cyclic deformation in the solder under conditions of temperature fluctuations. This latter scenario has been particularly well illustrated in case studies of surface mount circuit boards products. Several evaluations of the thermal mechanical fatigue resistance of Pb-free solders have been performed on circuit board test vehicles. Those data provide some performance generalizations which can be extended to other applications. One such case study is described below:

Surface mount circuit boards assembled with 96.5Sn-3.5Ag, 58Bi-42Sn, 96.2Sn-2.5Ag-0.8Cu-0.5Sb, and 91.84Sn-3.33Ag-4.83Bi were thermal cycled under the following conditions: 0-100°C; 10°C/min ramps; and 5 min hold times. Units were exposed for 1000, 2500, 5000, and in the case of the 91.84Sn-3.33Ag-4.83Bi, 10000 cycles. The components were 1206 chip capacitors, 24 I/O (gull wing) SOICs, and 68 I/O (J-lead) PLCCs. Electrical failures were not recorded with any of the solders. The 96.5Sn-3.5Ag and 91.84Sn-3.33Ag-4.83Bi solders did not exhibit any general deformation after all cycling levels. Relatively small cracks were observed in the solder fillets; however, they were not of a magnitude that would significantly impact the integrity of the interconnects. The 58Bi-42Sn solder showed some phase boundary sliding and a few isolated cracks. The resistance to thermal mechanical fatigue was further substantiated by only a nominal decrease in the shear strength of the chip capacitor solder joints upon mechanical testing (10 mm/min).

The results of this study suggest that the fatigue performance of those Pb-free solders is equal or, most likely, superior to that of 63Sn-37Pb solder. More important, there does not appear to be an inherent, catastrophic failure mode for these solder under cyclic temperature environments.

F. Intermetallic compound layer formation

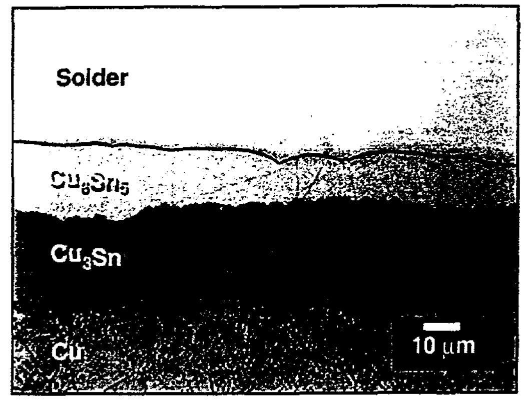
An extensive, long-term accelerated aging study was performed on Pb-free solder/Cu couples[32]. The goal of the experiments was to determine both the reaction chemistry and growth kinetics of intermetallic compound layers formed between the solder and Cu substrate. The type of data obtained from the study are illustrated in Fig. 6. The optical micrograph in Fig. 6a shows the 95.5Sn-4.0Cu-0.5Ag/Cu interface after aging at 205°C for 200 days. An electron microprobe analysis (EMPA) trace made across that interface is shown in Fig. 6b and confirmed that Cu_3Sn and Cu_6Sn_5 sub-layers comprised the intermetallic compound layer.

The total layer growth kinetics are represented by the following equation:

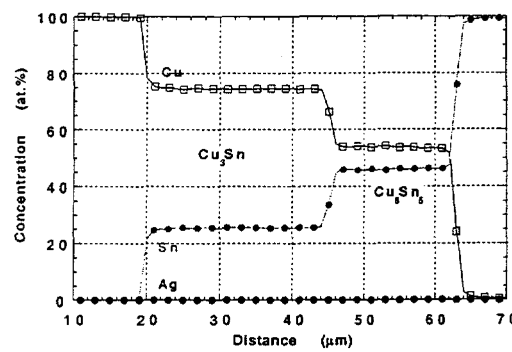
$$x = 1.7 \times 10^{-6} + 1.78 \times 10^{-2}\, t^{0.52} \exp(-57700/RT) \qquad (1)$$

where x is the layer thickness expressed in meters (m); t is time in seconds (s); R is the universal gas constant, 8.314 J/mol-°K; and T is the temperature expressed in °K.

Two generalized conclusions were drawn from these and similar studies on other alloys. First, the compositions of the sub-layers comprising the intermetallic compound layer were sensitive to the composition of the solders. On the other hand, the total layer thickness differed very little between the different solder compositions, including the baseline 63Sn-37Pb alloy, in spite of modestly different growth kinetics. Also, Cu ring-and-plug shear tests were performed on aged samples made with 91.84Sn-3.33Ag-4.83Bi, 96.5Sn-3.5Ag, and 100Sn. Although the aging treatments caused the intermetallic compound layer to thicken, there was no significant impact on the shear strength of the respective solder joints.



(a)



(b)

Figure 6. (a) Optical micrograph of the intermetallic compound layer which developed between the 95.5Sn-4.0Cu-0.5Ag solder and Cu after aging at 205°C for 200 days. (b) Electron microprobe analysis trace across the same interface, showing the Cu_3Sn and Cu_6Sn_5 sub-layers.

G. Advanced alloy concepts

The present list of available Pb-free alloys is comprised largely of Sn-based solders originally used to replace the Sn-Pb materials in plumbing applications. The Sn-based solders have been modified to realize lower melting temperature(s) or improve other properties (e.g., higher monotonic or fatigue strengths). New alloy designs are being developed which use the same concepts as those applied to the development of advanced superalloys for jet engines. The desired properties of these new alloys remain the same: lower melting temperature and/or improved service performance[33]. The alloy composition, 86.85Sn-3.15Ag-5.00Bi-5.00Au, has a solidus temperature of 194°C; the liquidus temperature was not clearly discernable but was bounded at less than 199°C. The lowest solids temperature realized with a high-Sn, Pb-free solder was measured for the composition: 62Sn-5Ag-10Bi-10In-4Au-4Cu-5Ga; the T_s was 159°C with no discernable liquidus temperature (T_l < 164°C). Similar approaches based upon lessons-learned from studies such as this one, can provide the necessary background with which to develop other alloy design concepts that meet particular design and/or service requirements.

H. Modeling approaches for reliability predictions

The reliability of solder interconnects is generally concerned with thermal mechanical fatigue (TMF) failure. Thermal mechanical fatigue is caused by strains generated in the solders as a result of thermal expansion mismatch between the substrate material(s) and the solder, under cyclic temperature conditions. Inelastic deformation builds up in the solder until small cracks are formed; these cracks develop into a single fracture that is ultimately responsible for failure of the interconnect.

In the case of Sn-Pb solders, TMF reliability databases have been developed for the vast number of electronic package configurations. The development of these databases required large-scale empirical studies using accelerated aging techniques. Today, a similar approach for developing the fatigue behavior of Pb-free solders is not viable for two reasons: (1) The necessary resources for this level of "R and D" effort, including test vehicle builds, temperature cycling, and failure mode analysis, are no longer available. (2) Such an empirical program today would be hard-pressed to accommodate the wide variety of solder joint designs and sizes within the electrical and electronics component industries. Therefore, the development of critical TMF reliability data for Pb-free solders will rely heavily upon computational models.

The computational modeling approach is comprised of three tasks: (1) Materials properties measurements; (2) the development of actual computational model and codes; and (3) validation of the model predictions through limited (empirical) accelerated testing activities. Accurate reliability predictions by any computational model requires that said model have the necessary material properties of the solder and substrate materials. Those properties include elastic modulus, yield strength, and Poisson's ratio. The modulus and Poisson's ratio parameters are best obtained from speed-of-sound wave measurements using ultrasonic techniques. The yield strength data can be obtained from tensile or compression stress-strain tests; the latter technique is depicted in Fig. 7 for 97In-3Ag (wt.%) solder tested at 125°C under a strain rate of 4.2 x 10^{-5} s^{-1}. The temperature dependencies of these properties must also be measured over the pertinent use and/or accelerated test regimes.

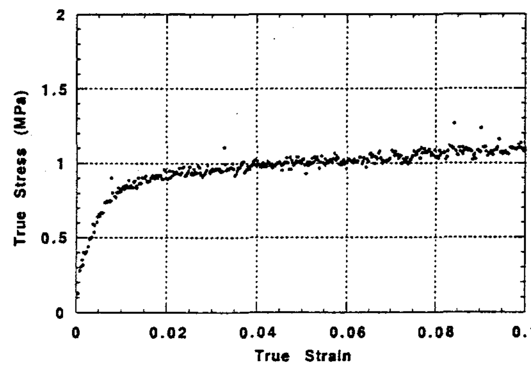


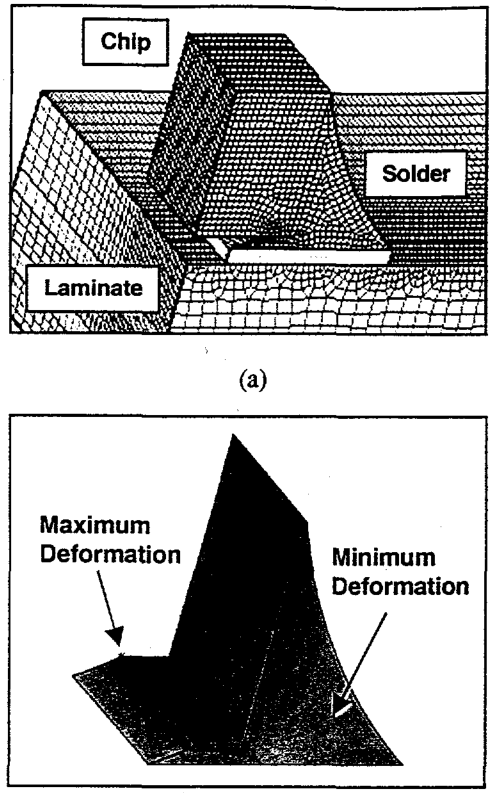
Figure 7. Compression stress-strain test: 97In-3Ag; 125°C; $4.2x10^{-5}$ s^{-1}

A successful computational modeling technique of solders is that of the constitutive model. The *constitutive equation* predicts the extent of inelastic deformation (ε) in a material, typically expressed as an inelastic strain rate ($d\varepsilon/dt$) as a function of the applied stress (σ), temperature (T), and the material properties of elastic modulus (E) and yield strength (σ_y). A constitutive equation of the solder includes both time-independent (or plastic) deformation and time-dependent (or creep) deformation behaviors; one format is shown in Equation 2[34]

$$d\varepsilon_{11}/dt = \mathrm{sgn}(\sigma_{11}-B_{11}) f_o \exp(-Q/RT) \sinh^p[(/\sigma_{11}-B_{11}/)\alpha D] \qquad (2)$$

where the parameters, B_{11}, α, and D are derived from the time-independent deformation (stress-strain) experiments and the parameters f_o, Q, and p are computed from the time-dependent deformation (creep) experiments. The latter parameters are determined from compression creep tests. The constitutive equation is then coupled into a finite element mesh of the joint; the latter provides the geometric distribution of stress(s) throughout the joint, and in particular, within solder fillet (Fig. 8). Thus, the value of $d\varepsilon_{11}/dt$ can be computed at each location (or node) in the solder, using equation (2).

Finally, the model must be validated; that is, the extent of TMF degradation predicted by the model must be correlated to that observed in actual hardware exposed to similar accelerated aging conditions. The hardware must be assembled under tightly controlled conditions to



(b)

Figure 8. (a)Finite element mesh and (b) deformation contours of a 63Sn-37Pb chip capacitor solder joint (-40°C to 85°C; 6 cycles).

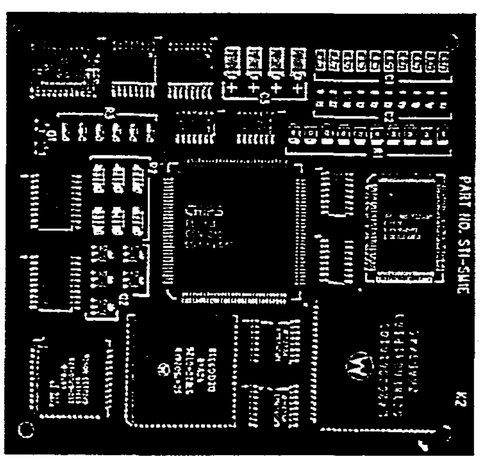


Figure 9. Surface mount test vehicle.

Assure the formation of uniform, defect-free solder joints. Specially designed circuit board test vehicles (Fig. 9) have provided important validation data to support computational model development and implementation. Cross sections of the modeled interconnects, electrical continuity monitoring, or even solder joint shear strength can be used to establish physical metrics of TMF degradation. The validation hardware can also establish the uncertainty or variability with which each solder joint succumbs to TMF degradation.

III. CONCLUSION

1. Legislative and marketing forces both abroad and in the US are causing the electronics and electrical industries to consider the use of Pb-free solders in place of traditional Sn-Pb alloys. Innovative approaches towards alloy design can provide Pb-free solders with melting and strength properties that are optimized for particular applications.

2. Solderability performance as well as the monotonic and cyclic mechanical strength properties provide first-screening protocols to determine the appropriateness of a Pb-free alloy for particular assembly processes and service environments, respectively.

3. The results of previous circuit board case studies that evaluated the assembly and reliability performance of Pb-free solders, have demonstrated the viability of these compositions for other electronic and electrical applications.

4. The characterization of intermetallic compound layer development (chemistries and kinetics) provides the design engineer with reliability data pertaining to the aging behavior of the solder/Cu interface.

5. Computational models will replace extensive, empirically-derived databases describing the TMF performance of the non-Pb bearing solders. However, the implementation of computational model will require (a) the measurement of materials properties per each solder, (b) development of the specific code(s), and (c) performing a limited empirical study on prototype test vehicles to validate the computational models.

IV. REFERENCES

[1] Safe Drinking Water Act, 1986 Amendment, PL99-329, June 19, 1986.

[2] A. Maupin and W. Swanger, "Strength of Soft-Solder Joints in Copper Tubing, Building Materials, and Structures," *Report BMS 58,* National Bureau of Standards, US. Dept. of Commerce, Washington, DC, 1940, pp. 1-25.

[3] A. Maupin and W. Swanger, "Strength of Sleeve Joints in Copper Tubing Made with Various Lead-Base Solders, Building Materials, and Structures," *Report BMS 83,* National Bureau of Standards, US. Dept. of Commerce, Washington, DC, 1942, pp. 1-9.

[4] *Solder Alloy Data, Publication 656*, International Tin Research Institute, Uxbridge, Middlesex, UK. 1986

[5] R. Fields, D. Shepherd, A. Cohen, and A. Kireta, Jr., "Stress Rupture of Lead-Free Soldered Joints Used to Assemble Copper Plumbing Systems," *Proc. Inter. Brazing and Soldering Conference 2000,* April 2-5, 2000, Albuquerque, NM (American Welding Society, Miami, FL), pp. 501-506.

[6] "Solder Specification for Solder Metal," *ASTM B32-96*, American Society for Testing and Materials, West Conshohoken, PA.

[7] H. Reid, "Lead Exposure Reduction Act of 1993," *S-729.* 1993

[8] B. Cardin and H. Waxman, "Lead-Based Paint Hazard Abatement Act or 1991", *HR-2922.* 1991.

[9] K. Nimmo, "Worldwide Environmental Issues in Electronics and the Transition to Lead Free," *Proc. IPC Works 99*, October 23-28, 1999, Minneapolis, MN, (IPC, Northbrook, IL) pp. S-01-2-1 to S-01-2-6.

[10] "Alternative Solders for Electronic Assemblies," *Final Report MS/20073,* DTI Sponsorship, 1993.

[11] K. Nimmo, "Environmental Issues in Electronics and the Transition to Lead-Free Soldering," *Proc. of SMTA Inter.* Sept. 14-16, 1999, San Jose, CA (SMTA, Edina, MN), pp. 377.

[12] K. Suganuma, "Research and Development for Lead-Free Soldering in Japan," *Proc. IPC Works 99*, October 23-28, 1999, Minneapolis, MN, (IPC, Northbrook, IL) pp. S-01-5-1 to S-01-5-4.

[13] P. Vianco, *Soldering Handbook* 3rd edition, (Amer. Welding Society, Miami, FL: 2000), pp. 215-216.

[14] P. Vianco and J. Rejent, "Properties of Ternary Sn-Ag-Bi Solder Alloys: Pt. I, Thermal and Microstructural Analysis," *J. Electronic Materials* 28, 1999, pp. 1120 - 1138.

[15]K. Feldmann and M. Reichenberger, "Assessment of Lead-Free Solders for SMT," *Proc. APEX 2000*, Mar. 12-16, 2000, Long Beach, CA (IPC, Northbrook, IL) pp. P-MT2/2-1 to /2-12.

[16] P. Vianco, *op. cit.* p. 211.

[17] *Binary Alloy Phase Diagrams - Volume 2* ed. by T. Massalski, (ASM, Inter., Materials Park, OH: 1986), p. 2086.

[18] P. Vianco, *op. cit.* p. 212.

[19] P. Vianco, *op. cit.* pp. 163-165.

[20] A. Jackson, I. Artaki, and P. Vianco, "Manufacturing Feasibility of Several Lead-Free Solders for Electronic Assembly," *Proc. 7th Inter. SAMPE Electronics Conf.* June 20-23, 1994, Parsipanny, NJ, pp. 381-393.

[21] J. Bickerman, *Surface Chemistry for Industrial Research* (Academic Press, New York, NY: 1947), p. 19.

[22] P. Vianco and J. Rejent, "Capillary Flow Solder Wettability Test," *Soldering and Surface Mount Technology* No. 25, February 1997, pp. 4-7.

[23] P. Vianco and A. Claghorn, "Effect of Substrate Preheating on Solderability Performance as a Guideline for Assembly Development," *Soldering and Surface Mount Technology,* No 24, October 1996, pp. 12-18.

[24] M. Bester, "Metallurgical Aspects of Soldering Gold and Gold Plating," *Proc. Inter/NEPCON* Brighton, UK, 1969, pp. 211-231.

[25] R. Duckett and M. Ackroyd, "The Influence of Solder Composition the Embrittlement of Soft-Soldered Gold Coatings," *Electroplat. Met. Finish,* 29, 1976, pp. 13-20.

[26] D. Jacobson and G. Humpston, "Gold Coatings for Fluxless Soldering," *Gold Bulletin* 22 1989, pp. 9-18.

[27] P. Vianco and C. May, "An Evaluation of Prototype Surface Mount Circuit Boards Assembled with Three Non-Lead Bearing Solder," *Proc. Surface Mount Inter.* Aug. 29-31, 1995, San Jose, CA: 1995, 481-494.

[28] P. Vianco, "An Overview of Surface Finishes and Their Role in Printed Circuit Board Solderability and Solder Joint Performance," *Circuit World* 25 1998, pp. 6-24.

[29] C. Hunt and D. Lea, "Solderability of Lead-Free Alloys," *Proc. of APEX 2000*, March 12-16, 2000; Long Beach, CA; pp. P-MT2/3-1 to 3-4.

[30] P. Vianco and J. Rejent, "Properties and Performance of Sn-Ag-Bi Solder for Electronics Applications," presentation at the TMS Fall Meeting '99, November 2, 1999; Cincinnati, OH.

[31] K. Stone, R. Duckett, S. Muckett, and M. Warwick, "Mechanical Properties of Solders and Soldered Joints," *Brazing and Soldering* No. 4 Spring 1983, pp. 20-27.

[32] P. Vianco, "Solid State Intermetallic Compound Layer Growth Between Cu and Selected Pb-Free Solders-Interface Reaction Compositions and Growth Kinetics," *Environmentally Friendly Electronics Manufacturing* ed. J. Hwang, to be published, 2000.

[33] P. Vianco, J. Rejent, and R. Grant, "Development of Multicomponent Alloys as Pb-Free, Low-Melting Temperature Solders," presentation at TMF Fall Meeting '97, Indianapolis, IN; 1997.

[34] M. Neilsen, S. Burchett, C. Stone, and J. Stephens, "A Viscoplastic Theory for Braze Alloys," SAND96-0984, Sandia National Laboratories, Albuquerque, NM 1996.

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Key words: Pb-free, solder, processing, reliability, intermetallic compound, thermal mechanical fatigue