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Lead (Pb)-Free Solders for Electronic Packaging

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The harmful effects of lead on the environment and human health, coupled with the threat of legislation, have prompted a serious search for lead-free solders for electronic packaging applications. At present, Sn-Pb eutectic and other Pb-containing solders find widespread use in printed circuit board assembly. Several Pb-free solder alloys which appear to have the potential for replacing Sn-Pb solders are receiving increased attention from the electronic assembly community. Recently, numerous studies have been published detailing the wetting characteristics, tensile and shear strength, and creep and low-cycle fatigue properties of these alloys. It is the purpose of this paper to review these results and assess the suitability of the solders for electronic packaging from the viewpoints of process technology and reliability.

Key words: Lead-free, packaging, reliability, solder

INTRODUCTION

Soldering technology plays a key role in various levels of electronic packaging, such as flip-chip connection (or C4), solder-ball connection in ball-grid-arrays (BGA), or IC package assembly to a printed circuit board (PCB). Solder joints produced in the electronic packages serve critically as electrical interconnections as well as mechanical/physical connections. When either of the functions is out of service, the solder joint is considered to have failed, which can often threaten a shutdown of the whole electronic system. At present, Pb-Sn solders of various compositions are used in PCB assembly. Among them, the Pb-Sn eutectic is the most widely used, and its applications can be considered the "mainstream" applications. Our discussion will address these applications and ways of replacing Pb-Sn with Pb-free solders. The Pb-Sn eutectic solder has a composition of 62% Sn and 38% Pb (all alloy compositions are given in weight percent), with a melting point of 183°C.[1]

Currently, there are two soldering technologies employed for mass production: plated-through-hole (PTH) and surface mount technology (SMT) soldering. The basic difference between the two technologies originates from the difference in the PCB design and its interconnection scheme. In PTH soldering, solder joints are made by utilizing the plated-through-holes on a PCB. For example, in wave soldering, molten solder is directly applied to the area of the PTH and is further drawn in by a capillary force to fill the gap between the I/O pin and the wall of the plated-through hole. The current trend is toward surface mount technology, where a package having formed I/O leads is attached to the surface of a PCB. A major advantage of SMT is high packaging density, which is realized by eliminating most PTHs in the PCB as well as by utilizing both surfaces of the PCB to accommodate components. In addition, SMT packages have a finer lead pitch and a smaller package size compared to

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traditional PTH packages. Hence, SMT has contributed significantly in reducing the size of electronic packages and thereby the volume of the overall system.

Soldering in SMT is very different from that used for conventional PCBs with plated-through holes, in terms of solder materials, soldering process, mechanism, and joint reliability. In SMT soldering, solder paste is applied to a PCB by screen printing. Solder paste consists of fine solder powder, flux, and organic vehicles. The characteristics of solder paste in relation to soldering and solder joint reliability have been extensively studied.[2] During the reflow process, solder particles are melted, flux is activated, solvent materials are evaporated, and simultaneously molten solder coalesces and is eventually solidified. In contrast, in the wave soldering process, a PCB is first fluxed and components are mounted on it. Then, it is moved over a wave of molten solder.

The soldering process is usually completed by subjecting the solder joints to a cleaning step to remove residual flux materials. Due to environmental concerns, CFCs and other harmful cleaning agents are being eliminated and replaced by either water-soluble or no-clean flux materials.[3-5] Since the new flux chemistries change the surface tension of the solder-flux interface, the wettability or wetting action of the molten solder is affected. Another key factor determining the wetting characteristics of the molten solder is the surface chemistry and structure of the base metallization to which component leads are being soldered. The surface chemistry issue includes cleanliness, contamination, and oxidation of the metal surface, while metallizaton refers to the surface finish, for example, a gold- or nickel-plated layer. The purpose of the surface finish layer is manifold:

- to protect the underlying metal, usually copper, from oxidation,
- to prevent dissolution of the base metal, and
- to provide a good wettable surface for soldering.

Thin organic coatings, such as benzotriazole (BTA), are also used to protect the copper surface from oxidation temporarily.[6]

Table I. Melting Temperature of Selected Solder Alloys

Solder Composition (wt%)	Liquidus (°C)	Solidus (°C)	Phase
In-49Sn	120	120	eutectic
Bi-43Sn	139	139	eutectic
Sn-35In	162	120	hypoeutectic
Sn-38Pb	183	183	eutectic
Sn-3.5Ag	221	221	eutectic
100 Sn	232	232	pure metal
Sn-5Sb	238	232	peritectic
Bi-31Pb-19Sn	96	96	eutectic
Bi-34Sn-20Pb	100	100	eutectic

When molten solder is in contact with a clean metal surface to be joined, complex interfacial reactions are expected. These include dissolution of the base metal into the molten solder and formation of intermetallic compounds at the interface as well as in the interior of the solder joint. While the formation of a thin intermetallic layer is considered helpful in producing good metallic bonding, too thick an intermetallic is detrimental to solder joint reliability.

Replacing Pb-Sn solders with the Pb-free solders for the electronic applications has implications for the technical issues discussed above, and also on economic issues such as materials/assembly cost, material availability, and capital investment for new processes and equipment. In addition, the accumulated investment on research/development spent by the electronic industry over the last 40 years to produce the reliability data base for Pb-containing solders is enormous. A new investment on development has to be made prior to safely replacing the conventional solders with the Pb-free ones.

In the present paper, the existing data base for Pb-free solders and their applications in electronic packaging are reviewed and an attempt is made to identify the areas where further research and development are needed to assess the possible replacement of the Pb-Sn solders with Pb-free solders.

CANDIDATE SOLDERS

An acceptable Pb-free solder must satisfy both process requirements and reliability objectives. Ideally, it should be suitable for mass production applications of both SMT and PTH soldering. Furthermore, the process technologies currently in use for Pb-

Table II. Comparison of Properties of Bulk Solder Alloys

Properties	Sn-51In	Sn-57Bi	Sn-38Pb	Sn-3.5Ag	Sn-5Sb
Melting Point (°C)	120	139	183	221	238
UTS (MPa)	11.9[54]	45–80[7]	31–46[55]	55[44]	36.6[32]
Elongation (%)	83[54]	40–200[7]	35–176[55]	35[44]	38[32]
Shear Strength (MPa)*	11.2[54]	48.3[56]	28.4[57]	32.1[57]	31.8[57]
Stress-rupture life (min)					
at 0.69 MPa (24°C)	—	16.7[13]	8.3[13]	—	—
at 0.62 MPa (60°C)	—	1.1[13]	0.4[13]	—	—
Low cycle fatigue life† cycles	—	8500[9]	1900[9]	—	—
Cu dissolution‡ (µm/5 min)	—	1.02[8]	7.87[8]	—	—

*Tests conducted at a cross-head speed of 1.27 mm/min; †4 cycles/h, 3% strain, –4 to +24°C; ‡Tests at 50°K above solder alloy melting point

Sn eutectic or other Pb-bearing solders must be adaptable to the new solder without major changes, or significant capital investments. The wettability of the new solder should be better or equivalent to that of the Pb-Sn solder, and accordingly a better or equivalent defect rate in the assembly line should be achievable. It should be workable with water-washable or no-clean fluxes. The melting point of the new solder is desired to be lower than those of the current solders in order to reduce the magnitude of thermal stresses or thermal shock experienced during soldering. The new solder must be able to produce solder joints with acceptable joint strength, and at the same time must withstand thermal fatigue over the projected operating life of the assembly and meet other reliability requirements, such as corrosion or oxidation. Lastly, the material cost of the new solder should not be so high that it may overwhelm the assembly cost.

With the above guidelines in mind, several Pb-free solders used currently in some electronic applications are discussed in the following sections. These include Bi-Sn eutectic solder, Sn-rich Sn-Sb alloys, Sn-rich Sn-Ag alloys, and In-Sn alloys. Some of the typical solders in this category are listed in Table I, with composition and melting point information.

Bi-Sn Eutectic Solder

Bi-Sn eutectic solder (57% Bi-43% Sn) has the melting point of 139°C, which is significantly lower than that of Pb-Sn eutectic solder, 183°C. The mechanical/physical properties of the bulk Bi-Sn eutectic solder compare favorably with those of eutectic Pb-Sn. Table II compares some of these properties among a few candidate solders. The mechanical properties of the solder alloys are strongly influenced by both the strain rate of deformation and their microstructure.[7] This strong strain-rate sensitivity of these materials is recognized by noting the wide ranges of tensile strength and elongation data of Pb-Sn and Bi-Sn solders listed in Table II. At a given strain-rate (possibly with an equivalent microstructure), Bi-Sn solder has a higher tensile strength, but less ductility than Pb-Sn solder does. However, the mechanical properties of bulk solders cannot be directly applied to those of the solder joints, simply because a solder joint consists of more than the solder itself. Moreover, a soldering process can cause a complicated interfacial reaction between the molten solder and the base metal, and thus can yield a different microstructure in the solder joint. Table III displays shear strength and elongation data obtained at different strain rates from different solder joints. Considering this factor, it is not surprising that a large discrepancy exists between the elongation data of the bulk solders and those of the solder joints even when tested under equivalent conditions.

Table III. Shear Strength of Solder Joints to Copper Substrate[*]

Solder Comp. (wt%)	Strain Rate (mm/min)	Shear Strength (MPa)	Elongation (%)	Ref.
Sn-52In	0.13	10.4	—	46[†]
Sn-52In	0.51	12.9	38	8[‡]
Sn-57Bi	0.05	25.3	4.8	39
Sn-57Bi	50.0	19.6	3.2	39
Sn-58Bi	50.0	23.7	—	58
Sn-58Bi	0.51	48.0	30	8[‡]
Sn-40Pb	50.0	18.0	—	58
Sn-37Pb	0.51	41.8	35	8[‡]
Sn-3.5Ag	0.05	26.8	10.2	39
Sn-3.5Ag	50.0	36.6	7.8	39
100 Sn	0.05	15.4	6.7	39
100 Sn	50.0	31.7	7.6	39
Sn-5Sb	0.05	21.8	5.7	39
Sn-5Sb	50.0	29.6	7.2	39
Sn-5Sb	0.51	43.1	38	8[‡]

[*] at room temperature; [†] Si substrate was used with thin film layers of Nb/Pd/Au; [‡] Cu-plated steel substrate used.

The eutectic Bi-Sn solder has been used for quite a long time in the electronic applications where low temperature soldering is required.[8,9] However, when decreasing the soldering temperature, there is often an adverse impact on flux activation, thus changing the wetting characteristics of the molten solder. A special soldering process must be developed for the application of this solder, such as immersion wave soldering.[9] The immersion wave soldering process was developed for PTH soldering of advanced multilayer PCBs. In this process, an assembled and fixtured PCB is immersed in a fluxing fluid and preheated to the soldering temperature. After preheating and while still immersed in the fluxing fluid, the PCB is passed over a Bi-Sn eutectic solder wave to form the solder joints. The fluxing fluid is gylcerine activated with ethylenediamine tetra-acetic acid (EDTA). This flux is water-soluble.[9,10] Another application of Bi-Sn in a conventional wave soldering process has been recently reported.[11] Furthermore, a two-step soldering process has been demonstrated by using both Pb-Sn and Bi-Sn solders in sequence.[12] In this process, SMT components are attached to one side of a PCB by using Pb-Sn solder, while through-hole or SMT components are attached to the second side by using the Bi-Sn solder wave. However, caution should be exercised in this process in terms of possible Pb-contamination. It has been reported that a low level of Pb-contamination of Bi-Sn solder joints can seriously degrade both the joint strength and the thermal fatigue life.[8,13] The deterioration of the mechanical properties is attributed to the formation of a low melting point ternary phase in the Bi-Sn-Pb system, as listed in Table I.

However, mainstream SMT soldering applications using Bi-Sn solder and conventional fluxes and surface finishes have not been reported. This may be due to the fact that the wetting characteristics of the Bi-Sn solder is generally not as favorable as the Pb-Sn solder with the existing flux materials and surface metallization. A detailed study on the wetting characteristics of Bi-Sn eutectic solder has been reported in terms of impurity effects, fluxes, base metals, and soldering temperature.[13] It was found that the Bi-Sn eutectic solder is far less tolerant of impurities than the Pb-Sn eutectic.[14] In particular, impurity elements which form intermetallic compounds with this solder, such as Cu, Ni, Fe, and Pd, are especially critical, while Sb and Pb appear to be beneficial in terms of the wetting characteristics. Table IV shows another report on the solderability of several low melting point solders investigated for different surface metallizations.[15] Only the Au/Ni-plated metallization is considered acceptable for the Bi-Sn solder, while the Cu, Ni, and Au/Ni metallizations are all acceptable for the Pb-Sn solder when a rosin-base flux is used. A recent investigation has also confirmed that the Bi-Sn solder does not wet Cu-base metallizations as well as the Pb-Sn solder does when a rosin-base flux is used.[16] However, a pre-tinned Cu surface was found acceptable even with a rosin-base flux.[17] Based on the wettability studies, it is evident that the Bi-Sn solder can be considered a successful candidate only when an acceptable flux system and surface metallization are concurrently developed.

Table IV. Solderability of Selected Solder Alloys[15]

Solder Alloy (wt%)	Cu-Clad	Spread Factor* (%)		Solid
		Au/Ni-Plate	Ni-Plate	Ni200
Sn-52In	76	67	62	66
Sn-58Bi	72	89	69	69
Sn-35In	73	82	48	67
Sn-37Pb	91	86	99+	81
Sn-40Pb	89	89	99+	81
Sn-3.5Ag	71	80	74	72
100 Sn	73	79	71	73
Sn-5Sb	66	78	68	68

Note: Test conditions: temperature, 260°C, flux type RMA, hold time, 5 s after preform melted.

Table V. Thermal Fatigue Failure Rate of Plated-Through-Hole Solder Joints Encapsulated with Epoxy (Percent Failures vs Thermal Cycles)[15]

Solder Alloy (wt%)	Thermal Cycles*					
	1	25	50	75	100	150†
Sn-52In	0.0	0.0	0.0	0.0	0.0	10.0
Sn-58Bi	0.0	100	100	100	100	100
Sn-35In	8.3	91.6	100	100	100	100
Sn-37Pb	0.0	100	100	100	100	100
Sn-40Pb	0.0	100	100	100	100	100
Sn-3.5Ag	0.0	0.0	0.0	0.0	0.0	0.0
100 Sn	0.0	0.0	18.2	27.3	27.3	27.3
Sn-5Sb	0.0	0.0	0.0	0.0	0.0	0.0

*Test conditons: temperature cycling between −54% and 75°C, soak time of 2 h in each chamber; †thermal fatigue failure rate (in percent) was determined by detecting a 360°C crack around the solder fillet at a magnification of 40X at the first cycle and every 25 cycles thereafter.

Several investigations on thermal and mechanical fatigue behavior of the Bi-Sn solder joints were conducted in comparison with those of the Pb-Sn.[8,15,18,19] Table V summarizes a comprehensive study of PTH solder joints made of various low melting point solders. It is shown that under a severe thermal cycling condition both Bi-Sn and Pb-Sn exhibit poor fatigue resistance compared to joints made of Sn-3.5% Ag, Sn-5% Sb, or Sn-52% In solders.[15] In a recent investigation, thermal fatigue resistance of PTH Bi-Sn solder joints is reported to be comparable to that of the Pb-Sn.[19] Table VI and Table VII show low cycle fatigue data of lap-shear joints made of several low-melting point solders. At low cycle testing (1/15 cpm), Pb-Sn solder joints show a superior fatigue life for a wide range of shear strains to that of Bi-Sn, while at a high cycle (5 cpm) and/or at a high temperature (100°C), Bi-Sn solder joints show a much longer life. In addition, at high strains (between 8 and 20%), Pb-Sn solder joints again exhibit a longer life than the Bi-Sn joints do. This can be understood by the fact that Pb-Sn solder joints usually possess a larger ductility or elongation than the Bi-Sn joints do when tested under similar conditions.

Creep behavior of the low-melting point solders has been carefully investigated only in very recent years.[18,20,21] Table VIII lists the steady-state creep parameters of a few solders. It is noticeable that the steady-state creep rate of the Bi-Sn solder joints is smaller than that of Pb-Sn, even though Bi-Sn solder has a significantly lower melting point than the Pb-Sn solder does.

No corrosion and oxidation data on the Bi-Sn solder (and joints) are available. However, Bi-Sn eutectic solder has been used for many years on a family of large circuit boards by at least one user without any problem.[9]

Finally, a concern is raised with regard to the

Table VI. Fatigue Life Comparison of Lap Shear Solder Joints* (at Different Strain, Temperature, and Frequency)[53]

	Percent Shear Strain vs. Cycles to Failure†								
	1/15 CPM at 25°C			5 CPM at 25°C			5 CPM at 100°C		
Solders	20%	8.0%	3.0%	20%	8.0%	3.0%	20%	8.0%	3.0%
Sn-52In	200	1800	17000	130	300	6700	700	150000	—
Sn-58Bi	1.6	110	8500	3.3	100	6300	9.3	250	8500
Sn-37Pb	30	630	16000	13	180	3000	13	160	1900
Sn-5Sb	65	600	6300	28	290	3600	15	200	3000

*10 mil solder joint thickness; †failure point was established by the 0.03 milliohm resistance change.

replacement of Pb with Bi metal in the current Pb-Sn solder. Since the major source of Bi metal is as a by-product of Pb refining,[22] the replacement of Pb with Bi would lead to the dilemma of drastically increasing the amount of refined Pb metal.

Sn-5%Sb Solder

Since many Sn-rich solder alloys, including Sn-5%Sb and Sn-3.5%Ag, generally have a higher melting point than that of Pb-Sn eutectic, they may not be suitable as replacement for Pb-Sn eutectic. However, they can be candidates for the replacement of the Pb-rich solder alloys, such as Pb-20%Sn, Pb-10%Sn, and Pb-5%Sn, which have a liquidus temperature higher than 280°C. The Pb-rich solders have been extensively used for flip chip connection,[23] and solder ball connection,[24,25] where either Si chips or modules are mounted onto a ceramic substrate.

Several electronic applications of Sn-5% Sb solder have been reported, including hermetic sealband of multichip modules,[26] bonding a semiconductor device onto a substrate,[27] and joining of I/O pins to multilayer ceramic substrates.[28] In the joining I/O pins, Au-20%Sn braze alloy was replaced by Sn-5%Sb solder, thus realizing several advantages, such as lowering the joining temperature by about 50°C, and reducing the stress induced due to the joining process. In addition, Sn-5%Sb solder joints offer good strength and creep properties for the application. In another application, Sn-5%Sb solder was used as corrosion protection coating to a steel plate, as well as an electrically conductive area which could be used for subsequent grounding.[29]

A small addition of Sb to the Pb-Sn eutectic solder has been recognized for a long time to impart several beneficial effects, such as prevention of tin pest,[30,31] strength improvements,[32,33] and creep resistance.[34] Antimony addition to the pure Sn metal generally confirms the same beneficial effects observed with the Pb-Sn eutectic solder. In Table III, a significant increase in shear strength is noted for solder joints made of Sn-5% Sb solder in comparison with those made of the pure Sn. Table V also shows a better thermal fatigue life of PTH joints made with Sn-5%Sb than those of pure Sn. However, one drawback is recognized with Sn-5%Sb solder in terms of solderability as shown in Table IV. The solderability of Sn-5%Sb, as measured by the percent spread of a wetting area, is lower than that of the Pb-Sn eutectic, and it is also reduced by adding Sb to pure Sn. The addition of Sb into pure Sn can be harmful to the mechanical properties when the Sb level approaches the solubility limit in Sn, which is about 10% by weight at 250°C.[35] This is attributed to an excessive formation of the cubic intermetallic phase, SnSb.[36] Unlike the Pb-Sn system, the Sn-Sb system exhibits a peritectic reaction whereby the Sn-rich primary solid solution is formed at 250°C.[37] The microstructure of the Sn-5%Sb solder joints is, therefore, expected to be highly dependent upon the soldering process and the thermal exposure afterward.

Table VII. Low Cycle Fatigue Life of Solder Joints

	Percent Shear Strain vs Cycles to Failure	
Solders	**10%**	**8%**
Sn-52In	20*	1800†
Sn-58Bi	50*	110†
Sn-37Pb	150*	630†

*Fatigue life is established as the cycle of 50% reduction in the initial load amplitude. Mechanical fatigue testing at 1/10 CPM, 10% strain/cycles, at 20°C;[18]

†LCF at 1/15 CPM, 25°C; failure point established by the resistance increase of 0.03 milliohm.[53]

Table VIII. Creep Properties of Solder Joints

Solder (wt%)	A* (1/s)	n*	ΔH* (Kcal/mole)	Ref.
Sn-52In	1.9492 × 10E +4	3.2205	22.862	21
Sn-58Bi	5.5403 × 10E–7	4.0514	16.852	18
Sn-40Pb	1.0927 × 10E–12	6.3	20.0	20

*Steady state creep rate, $d\gamma/dt = A\ \tau^n \exp(-\Delta H/RT)$, where τ = applied stress, A = pre-exponential factor ΔH = activation energy, R = gas constant, and T = temperature in Kelvin scale.

A serious concern in using the Sn-rich solders is the excessive dissolution of the base metal into the molten solder. The dissolution rate of Cu into molten Sn-5%Sb solder is not available in the literature, but is expected to be about twice of that observed in the Pb-Sn eutectic solder, (refer to Table II). The high dissolution rates of Ni in pure Sn are reported: 1.5 µm/min at 270°C, and 2.9 µm/min at 350°C.[38] This suggests that the Sn-rich solders require a very good dissolution barrier layer, such as Pt, underneath a good wetting surface. Otherwise, there would be excessive dissolution of the base metal as well as intermetallic formation.

Sn-3.5%Ag Solder

The Sn-rich Sn-Ag solder in consideration is the eutectic composition of Sn-3.5%Ag, having the melting of 221°C. Because of the high melting point, it may not be suitable for the replacement of Pb-Sn eutectic. However, it can be a candidate for the high temperature Pb-containing solders as mentioned earlier. The mechanical properties of the Sn-Ag eutectic solder compare favorably to those of the Pb-Sn eutectic. However, the comparison should be made with a high temperature Pb solder to be replaced, not with the Pb-Sn eutectic solder. The addition of small amounts of Ag to pure Sn brings several benefits, such as an increase of shear strength and ductility,[39] and an extension of thermal fatigue life of plated-through-hole solder joints.[15] The solderability of the Sn-Ag eutectic solder is more or less the same as that of pure Sn, while it is shown to be less favorable than Pb-Sn solder as shown in Table IV.

In one investigation of the Sn-3.5%Ag solder for flip chip application,[40] the effect of Au content on the mechanical properties is reported; i.e., the gold embrittlement effect. Tensile fracture elongation is found to be less sensitive for the Sn-Ag eutectic than for the Pb-Sn eutectic. It is also reported that the thermal fatigue life of Sn-Ag solder bumps is twice as long as that of the Pb-Sn solder bumps. In another flip chip application, Sn-rich solder alloy bumps were fabricated directly on Al pads by using conventional thermosonic wire bonding technique.[41] Small additions of Ag, Sb, and Zn were made to pure Sn to improve the shear strength of the joints and their reliability.[41] Due to improved creep properties, several quaternary compositions of the Sn-rich solders containing the alloy additions of Ag, Bi, Zn, Cd, and Sb have been reported for spring connector[42] and flip chip[43] applications. In a recent investigation, the beneficial effects of Zn additions on the mechanical properties of the Sn-Ag eutectic solder were found due to the uniform and refined microstructure of the Zn-alloyed eutectic solder.[44]

Sn-In Alloys

Because of its low melting point, extreme softness and ductility, and excellent wetting characteristics, indium has been widely used as an alloying element for many low temperature solders and fusible alloys.[33,36] However, because of its very high price (several times more expensive than silver), it is not economically feasible to use In-rich alloys for replacing the cost-effective Pb-Sn solders.[36] In addition, the world production of In metal is so small that it could meet only about one percent of the amount needed for substitution of Pb-based solders (assuming the alternative solder contains about 50% In).[45]

In electronic packaging applications, In-rich solders are selectively used where their unique properties are essential, for example flip chip interconnections of Josephson devices,[46,47] glass-sealing alloys of 52In-48Sn,[48] cryogenic solders for thin film joining,[36] thermally conductive die attachment in a multichip module,[49] and Pb-In alloys for controlled collapse chip connection (C4) applications.[50–52] In-rich solders are also used in place of Sn-rich solders to prevent gold scavenging, since gold dissolves in the In-rich solders at a slower rate than it does in the Sn-rich solders.[48]

In this section, two Sn-In solders, 51%In-49%Sn and 65%Sn-35%In, are considered as candidates for Pb-free solders. The first solder is the eutectic alloy with the melting point of 120°C, and the second one is hypoeutectic with the liquidus temperature of 162°C. Both solders have low tensile strength and large ductility, compared with the Pb-Sn eutectic solder (Table II). In-Sn eutectic solder joints also exhibit low shear strength and large elongation, (Table III). The solderability of the Sn-In solders is comparable to that of Pb-Sn eutectic solder with either Cu or Au/Ni metallization, but it is inferior to Pb-Sn on Ni metallization, Table IV.[15] Thermal fatigue life of In-Sn eutectic PTH joints is found to be much better than that of Pb-Sn joints tested under identical conditions, Table V. This is also true of In-Sn lap-shear joints tested at various conditions of strain amplitude, frequency, and temperature, in comparison with the Pb-Sn eutectic solder, Table VI.[53]

Table VII lists two sets of low cycle fatigue life data obtained from three eutectic solders including the In-Sn eutectic. Some discrepancy is noted with regard to the fatigue life of the In-Sn solder joint. In the early work of Wild,[53] a superior fatigue life of In-Sn joints was reported compared with Pb-Sn, while in the recent work of Mei and Morris,[18] the opposite was reported at apparently similar conditions. A detailed examination of these works has revealed that the results were obtained from solder joints formed differently and tested with different failure criterion. In Wild's work, the failure point of the solder joints was established by an electrical resistance increase, while Mei and Morris defined the failure point by the 50% reduction in the initial load amplitude. The solder joints used in Mei and Morris' work were formed by reflowing solder paste, while those in Wild's were formed by hand soldering, probably using solders in wire form. It is possible that the different solder materials/reflow methods would produce different microstructures and thereby a different fatigue life. However, in order to resolve the differences conclusively, experiments are needed where the solder joints would be formed by using the same type of material and reflow method.

The steady-state creep rate of In-Sn eutectic solder joints is reported in Table VIII, in comparison with Pb-Sn and Bi-Sn. Among the three solders, it is found that In-Sn joints display the weakest resistance against creep deformation at a given stress and temperature.[18, 21] In contrast, the total deformation to fracture of the In-Sn solder is the largest among them. Some superplastic behavior of this solder is also reported under shear loading at temperatures above 65°C.[21] This finding seems to explain why In-Sn solder joints have a superior fatigue life to other solders, as discussed earlier.

SUMMARY

Several Pb-free solders were reviewed in light of replacing the conventional Pb-Sn solders used for various electronic packaging applications. These candidates include solders such as Bi-Sn eutectic, Sn-5%Sb, Sn-3.5%Ag, and Sn-In alloys. Lead-free solders with a ternary and quarternary composition, which are being proposed or under development, have not been included in this review.

This brief review of the subject matter has brought up a few important points which are summarized as follows. First, none of the candidate solder alloys can replace directly the existing Pb-Sn solders without further research and development on the materials, processes, and product reliability. Fundamental studies on the solderability of a candidate solder in relation to different fluxes and surface finishes are required to fully assess its applicability. Process development for mass soldering as well as rework techniques should be demonstrated with a candidate solder in order to achieve the low defect as in the Pb-Sn solders. A very limited amount of product reliability data currently exists for any of the candidate solders.

Secondly, considering their melting point as well as other properties, the Sn-rich solders, such as Sn-5%Sb and Sn-3.5%Ag, can be candidates for high temperature soldering applied with ceramic substrates, while both Bi-Sn and In-Sn eutectic solders show potential for low temperature soldering involved with polymeric substrates. In particular, the Bi-Sn eutectic shows potential for replacing the mainstream Pb-Sn eutectic, at least in some applications.

Third, for Sn-rich solder applications, a good barrier layer should be developed in order to prevent an excessive dissolution of copper base metal during soldering or rework and thereby to improve solderability as well as solder joint reliability.

Lastly, we have also reached the same conclusion drawn earlier by other authors[45] that the problem of replacing Pb-Sn solders not only involves technical issues, but also broader issues of national economic competitiveness, public perception of the magnitude of an environmental hazard vs its proper scientific assessment, industrial ecology, and others.

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