Microstructure and Mechanical Properties of Pb-Free Solder Alloys for Low-Cost Electronic Assembly: A Review

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Lead-free solders, including Sn-58Bi, Sn-52In, and Sn-3.5Ag, are potential replacements for Sn-37Pb solder in low-cost electronic assembly. This paper reviews the literature on the microstructure and mechanical properties of these alloys. Because of the processing and testing conditions, many of the data are not predictive for electronic assembly applications. However, eutectic Sn-Bi seems to have properties approaching those of eutectic Sn-Pb under most conditions, while eutectic Sn-In seems far inferior in most respects. Eutectic Sn-Ag has many promising characteristics, but its relatively high melting temperature may preclude its use for this type of application.

Key words: Electronic assembly, lead-free, solder

INTRODUCTION

Recent interest in Pb-free solders was stimulated by the introduction of a bill in the U.S. Congress in 1990 that proposed to ban Pb from a wide variety of uses, including electronic solders. While an immediate ban on Pb in these solders now seems unlikely, Pb in the environment poses a risk to human health and further regulation in the United States of the purchase, use, and disposal of Pb and Pb-containing products is probable. Although some Pb-free solders have been in use for years, there is no obvious replacement for the eutectic and near-eutectic Sn-Pb alloys that are in common use for low-cost commercial microelectronics.[1,2] In response, most major electronics companies in the United States and solder and adhesive vendors worldwide are investigating Pb-free joining alternatives, including Pb-free solders and metal-filled conductive adhesives.

Low-cost commercial electronic assembly has distinct requirements that bound solder alloy selection. Typical products are used in an office environment and include computers and computer peripherals, instruments, and test and measurement equipment. Maximum interconnect temperatures in operation are less than 60 to 80°C. Cost dictates nearly exclusive use of FR-4 epoxy fiberglass printed circuit boards, which have a glass transition temperature of 110 to 125°C, and plastic packages for most semiconductor parts. Standard processing of mixed surface mount (SMT) and through hole assemblies uses conveyorized infrared or convection reflow or wave soldering and (with the elimination of CFCs) either aqueous cleaning or no cleaning whatsoever. These constraints differentiate this type of assembly from automotive under-hood and mainframe or supercomputer applications and impose a maximum alloy melting temperature of about 200°C.

In theory, many solder alloys could meet these requirements and replace eutectic or near-eutectic Sn-Pb solder in surface mount assembly. Sn-Bi, Sn-In, and Sn-Ag eutectic and near-eutectic alloys are already used in some applications because of specific advantages they offer over eutectic Sn-Pb, such as

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Table I. Physical Properties of Low Temperature Pb-Free Solder Alloys Including Liquidus (T_l) and Solidus (T_s) Melting Temperatures, Coefficient of Thermal Expansion (CTE), and Surface Tension

Alloy	T_s (C)	T_l (°C)	CTE (x 10^{-5}/°C) (at 20°C)	Surface Tension (mN/m) @ T_l + 50°C Air	Nitrogen
63Sn-37Pb	183		2.5	417	464
100Sn	232		2.6		
Sn-0.7Cu	227			491	461
Sn-3.5Ag	221			431	493
Sn-4Cu-0.5Ag	216	222			
Sn-9Zn	199			518	487
Sn-58Bi	138		1.5	319	349
Sn-52In	120		2.0		

Note: If only the solidus temperature is shown, the alloy is eutectic and the solidus and liquidus temperatures are the same.

lower process temperature, compatibility with particular substrates, or superior reliability under certain conditions. However, these alloys may not be suitable substitutes because of issues about processing, reliability, or the cost, availability, or toxicity of the raw materials. Consequently, many Sn-based ternary and quaternary systems are being investigated with the goal of developing new alloys with improved properties.

This review discusses some of the metallurgical issues affecting fit into the manufacturing environment and reliability of the finished assembly that must be considered to select a new solder alloy. The paper briefly summarizes the relevant data in the open literature (primarily on eutectic or near-eutectic Sn-based binary alloys containing Ag, Bi, In, and Cu). Compatibility with common metal finishes and the creep and fatigue resistance of these alloys are highlighted. Data on eutectic Sn-Pb solder are provided for comparison. Unfortunately, in many cases, the available data are incomplete, contradictory, or of questionable relevance to electronic assembly. In other cases, the relative desirability of these alloys depends strongly on the environment to which they would be subjected.

PHYSICAL METALLURGY

Physical Properties

Melting Temperature and Range

Melting temperature is a critical solder characteristic because it determines the maximum operating temperature of the system and the minimum processing temperature its components must survive. Table I gives the melting temperatures and thermal expansion coefficients of some solder alloys with melting points below 232°C (the melting temperature of Sn) that contain neither Pb nor Cd, which is even more toxic.[2–4] All compositions are given in weight percent.

Surface Tension

The surface tension at the liquid solder-flux interface plays an important role in determining the wetting behavior of a solder. The relatively high surface tension of Sn-Pb solder is also used for capillary flow self-alignment of SMT parts, to hold parts to the bottom of the board during second-side reflow, etc. The few surface tension data available for Pb-free solders are included in Table I.[5]

Resistivity

In most microelectronics applications, the resistivity of the solder interconnect is so low that its exact value does not affect the functionality of the circuit. The resistivities of all the alloys discussed here are similar (10–15 μΩ-cm vs about 1.7 for Cu) with the exception of that of 48Sn-52Bi, which is approximately twice as high (30–35 μΩ-cm).

Microstructure

Microstructure can be defined as the combination of the phases that are present in a material and their defects, morphology, and distribution. The composition and microstructure of a material determine its properties. The microstructure is in turn a function of the composition of the material and its thermal, mechanical, chemical, and, in some cases, electromagnetic history.

In electronic assembly, the primary processing variable that affects the initial solder microstructure is the cooling rate. The alloys described here are eutectic. The as-solidified microstructure is usually lamellar, but may be equiaxed if the solder is cooled very quickly. In both cases, faster cooling means a finer microstructure because there is less time for diffusion to occur. These microstructural differences may be significant; it has been shown for eutectic Sn-Pb solder that the fatigue life of the alloy is affected.[6] Unfortunately, most of the data for Pb-free solders have been obtained using microstructures generated at unspecified cooling rates. The time-temperature profile used to make the solder joint influences other aspects of the microstructure, including the intermetallic layer thickness and the quantity of intermetallic phases in the bulk solder.

This section reviews what is known about the microstructures of the most important Pb-free alloys. It focuses on the solder alloy itself, then on solder-substrate interactions, including wetting.

Bulk Solder Microstructures

Sn-Ag and Sn-Cu alloys

The alloys Sn-0.7Cu, Sn-3.5Ag (both eutectic) and Sn-4Cu-0.5Ag consist primarily of Sn with small concentrations of intermetallic phases. In the Sn-Cu eutectic, the Cu precipitates during solidification as the intermetallic Cu_6Sn_5, while in the Sn-Ag eutectic, the second phase is the intermetallic Ag_3Sn. Sn-4Cu-0.5Ag, a Cu-rich, near eutectic alloy that was developed as a Pb-free plumbing solder, contains both phases.

Because the continuous phase in these alloys is almost pure Sn, they may be prone to two phenomena observed in Sn that could cause reliability issues: whisker growth and tin pest (a low temperature phase transformation).

Sn-Bi

The eutectic composition in the Sn-Bi system is at 42Sn-58Bi. The equilibrium phases are Bi and Sn with about 4% Bi in solid solution. The Bi phase is not easily deformed. Bi has significant solubility in Sn at the eutectic temperature; consequently, as the alloy cools, Bi precipitates in the Sn phase. (Note that in eutectic Sn-Pb, the situation is opposite; the Sn phase is essentially pure Sn, while the Pb-phase contains Sn precipitates.) The volume ratio of the Sn-rich phase to the Bi-rich phase is 49:51 (cf. Sn-Pb 73:27).

For moderate cooling rates, the eutectic Sn-Bi microstructure is lamellar, with degenerate material at the boundaries of the eutectic grains (regions of lamellar alignment).[7,8] The as-solidified Sn-Bi microstructure is unusually resistant to coarsening.[7,9]

Sn-In

The eutectic composition in the In-Sn system is 50.9In-49.1Sn, but 52In-48Sn is a more commonly used alloy. The two phases that form are an In-rich pseudo-body-centered tetragonal phase, β, which is 44.8%Sn, and a hexagonal Sn-rich phase, γ, which is 77.6% Sn.

The In-rich β-phase contains Sn-rich γ-phase precipitates. The eutectic alloy is 87% β-phase by weight and very soft. The Sn-rich phase is relatively hard. Alloys containing between about 77 and 88% Sn are exclusively γ-phase.[10] The microstructure tends to be lamellar (except when dissolved substrate metallurgy alters the composition) and coarsens during prolonged room temperature aging.[7,11–13]

Solder-Substrate Interactions

A soldering process requires a solder, substrate, and flux system that is compatible with a specified soldering atmosphere and temperature profile. In addition to wetting, which is required for joint formation, other important characteristics of the system include intermetallic layer formation and dissolution of the substrate metallurgy into the solder. These interactions may affect the reliability of the final solder joint.

Phase Formation

Because Sn is the reactive species, Sn and eutectic Sn-Ag, Sn-Cu, and Sn-Bi all form the same intermetallic compounds at the solder/substrate interface as eutectic Sn-Pb on both Cu (Cu_3Sn and Cu_6Sn_5) and Ni (primarily Ni_3Sn_4, but also Ni_3Sn_2, and $NiSn_3$).[14,15] In all cases, both the liquid and solid-state reactions proceed much more slowly on Ni than on Cu.[4] In comparison to the other alloys, Sn-Bi intermetallics form much more slowly in the liquid state (perhaps because the proportion of Sn atoms is lower) and somewhat more rapidly in the solid state (at a given temperature and, therefore, a higher homologous temperature). For Sn-Bi, as Sn is depleted, a Bi-rich layer is formed adjacent to the interface.[16]

Sn-In solder behaves differently, in that both In and Sn are involved in the reactions. Both In and Sn are incorporated in the intermetallics that form at the solder/copper interface.[12,17] The intermetallic layer at a Ni interface is extremely thin and slow growing; its composition has not been determined.[12]

Substrate Dissolution

Gold dissolves rapidly into all of these alloys except Sn-In, potentially embrittling the solder joint as it does eutectic Sn-Pb. Sn-Ag is more tolerant of Au than Sn-Pb;[18,19] there are no data for Sn-Bi. In In-Sn, the intermetallic $AuIn_2$ forms instead of $AuSn_4$.[17,18]

Caution should be exercised when using Sn-Bi solders with Sn-Pb substrate metallization (on printed circuit boards or component lead terminations). The Sn-Bi-Pb system contains a ternary eutectic (8Sn-52Pb-40Bi) which melts at 95°C.[18] The average composition of a joint made using 42Sn-58Bi solder will be considerably more Sn-rich; however, the local concentration at the solder/copper interface could approach this composition since Sn forms intermetallic compounds with copper, while Pb and Bi do not. There is some evidence that the ternary eutectic is approached in real joints. In one test, extensive porosity, probably a result of local melting, developed during thermal cycling;[20] in another test, the shear strength and life in creep rupture tests at 50–80°C decreased vs joints made on plain Cu.[21]

Wetting Behavior

The literature to date gives only general indications of what can ultimately be expected from these alloys in production, because wetting behavior is a strong function of the flux and soldering temperature. (In one case, 42Sn-58Bi wet Cu five times faster at 210°C than at 170°C using the same fluxes.)[22] Much further work is needed in this area. Almost none of the fluxes that have been tested are no-clean fluxes and little work has been done using solder paste or an inert atmosphere. Furthermore, fluxes suitable for low temperature soldering have yet to be developed.

Wetting behavior of these alloys on Cu has been characterized for a variety of fluxes. Compared to eutectic Sn-Pb, wetting of Sn is superior, Sn-4Cu-

0.5Ag and Sn-Bi acceptable, and Sn-3.5Ag quite poor.[3,8,23–26] The wetting behavior of Sn-3.5Ag did not improve significantly in an inert atmosphere.[3,26] Sn-In displayed fair to acceptable wetting, but only with a relatively active flux. It is unlikely that a no-clean flux can be developed for this alloy.[10,25]

On a NiAu-plated substrate, eutectic Sn-Pb wets better than any of the other alloys tested. Wetting of eutectic Sn-Ag was sufficiently improved over wetting on Cu to be better than Sn-Bi, which was still acceptable,[3,26] but no different than on Cu. Wetting of Sn-In on Au was sluggish and poor, even with an active flux.[10]

Wetting of Sn-Bi on Ni-Pd and Ni-Sn surfaces is comparable to eutectic Sn-Pb.[22,27] Sn-In has fair to good wetting behavior on Ni-Sn with a halide-activated or organic acid flux.[10,27]

MECHANICAL PROPERTIES

The mechanical properties of a material describe its response to externally imposed stresses and strains. The conditions under which the stresses or strains are imposed may be divided up into three broad categories: time-independent monotonic deformation, for example in tension or shear, time-dependent monotonic deformation, or creep, and cyclic deformation, or fatigue.

Creep occurs by a variety of processes, all thermally activated. For the solders of interest here, room temperature is well above half the melting temperature; consequently, creep is the most important deformation mechanism of solder. Understanding creep is also valuable because the failure modes in creep and in thermal fatigue (important in service) are similar, at least in eutectic Sn-Pb alloys.[28]

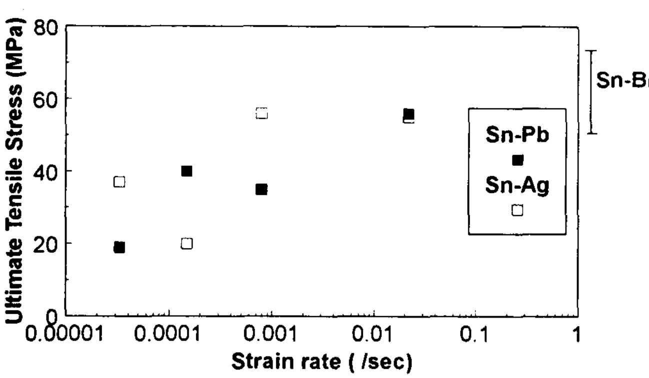

Fig. 1. Ultimate tensile strength at room temperature as a function of strain rate for eutectic Sn-Ag and Sn-Pb. Data for eutectic Sn-Bi are shown at right since most of the strain rates are unknown.

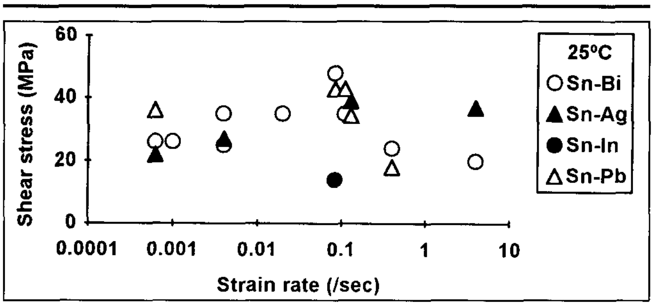

Fig. 2. Shear strength of eutectic solder alloys at room temperature as a function of strain rate.

Fatigue may be isothermal (imposed cyclic displacement at a constant temperature) or thermal (cyclic displacement imposed by a change in temperature when two materials with dissimilar thermal expansion coefficients are joined). Fatigue in solder alloys is complex because creep occurs in parallel.

Thermal fatigue is an important failure mechanism in eutectic Sn-Pb solder alloys and their potential replacements. Modeling the thermal fatigue life of real joint geometries presents many difficulties. Often the time-independent monotonic properties of the alloy (its constitutive equation) are used in a finite element model (FEM) to determine the stresses and strains that develop during a single thermal cycle. Isothermal creep or fatigue data are used to predict the life of the alloy. There are a number of subtleties involved in making this connection; consequently, it is important to understand the behavior of a new solder alloy under monotonic loading in shear and in tension, and under various creep and fatigue conditions.

Monotonic Tensile and Shear Behavior

Ultimate Tensile Strength

The ultimate tensile strength (UTS) is the maximum engineering stress (stress computed with respect to the original specimen cross section) a material can withstand in tension. For solders, the scatter in values is quite large because of the strong dependence of the UTS on both microstructure (including aging time after solidification) and strain rate. Ultimate tensile strengh data for eutectic Sn-Bi at room temperature range from 50 to 75 MPa and tend to be slightly higher than for eutectic Sn-Pb.[19,29,30] Ultimate tensile strength data for Sn-3.5Ag are comparable to or slightly higher than eutectic Sn-Pb (and slightly lower than Sn-Bi), ranging from 35 to 55 MPa.[4,10,22,24] The data in Fig. 1 for eutectic Sn-Ag, Sn-Bi, and Sn-Pb illustrate two other trends found in the monotonic deformation data: the strong dependence of the results on strain rate and the high strain rates used in some tests of thin solder joints. The tensile strength values of Sn-In alloys are low and decrease with increasing proportion of the indium-rich β phase. Values of 20 and 12 MPa for 50In-Sn and 52In-Sn, respectively (both at unspecified strain rates) have been reported.[4,10]

Shear Strength

The shear strength is analogous to the ultimate tensile strength, except that because the test is conducted in shear, plastic instability does not intervene. It is similarly sensitive to composition, microstructure, and testing conditions. Literature data as a function of strain rate are shown in Fig. 2.[4,24,31–35] Between 20 and 60°C, the shear strengths of Sn-Bi and Sn-Ag are comparable to Sn-Pb (25 to 50 MPa). Only Sn-In is much weaker. At 100°C, eutectic Sn-Bi is significantly weaker than eutectic Sn-Ag or Sn-Pb, presumably because its melting temperature (138°C) is approached.

Elongation

Elongation is geometry-dependent because in tension, it is largely determined by the onset of necking. The tensile elongations here are total elongations, which include localized deformation in the neck. In shear, elongation is macroscopically uniform. For solders, it is common for most of the shear elongation to occur after the maximum shear stress.

Elongation is an important property because high ductility enhances the low cycle fatigue resistance of a material. It is also essential to prevent failures if the assembly is inadvertently strained during handling. Although there are many mentions of the low ducitility of eutectic Sn-Bi in the literature, the available data suggest that eutectic Sn-Pb is more ductile than eutectic Sn-Bi only under certain processing and test conditions. Eutectic Sn-Bi seems to be more strain rate sensitive that eutectic Sn-Pb (i.e., its elongation decreases more rapidly with increasing strain rate), but even that is not entirely clear. The values in the literature for the ductility of eutectic Sn-Bi solder scatter widely (see Fig. 3).[4,19,24,30–33,36–38] Sn-Ag has comparable elongation to Sn-Pb at moderate strain rates at room temperature, but is considerably less strain rate sensitive (i.e., the elongations will be higher at high strain rates and lower at very low strain rates).[19,30,31] There are few data for eutectic Sn-In, but it appears to be very ductile.[33]

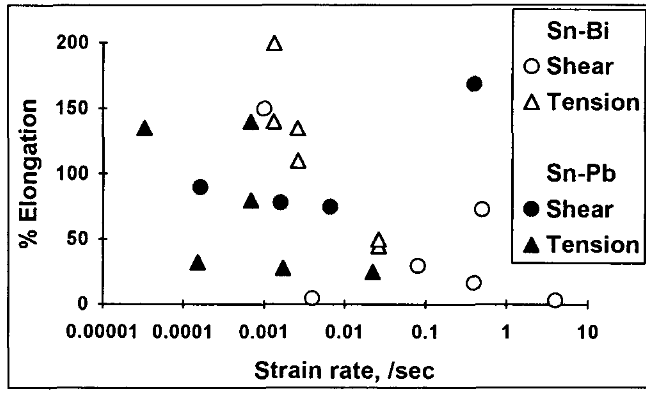

Fig. 3. Percent elongation to failure for eutectic 42Sn-58Bi and 63Sn-37Pb solder joints tested at various strain rates at room temperature. Data measured in shear can be compared to data measured in tension by using the von Mises' equivalent strain $\varepsilon = \gamma/\sqrt{3}$ if the true strains in tension and shear are known.

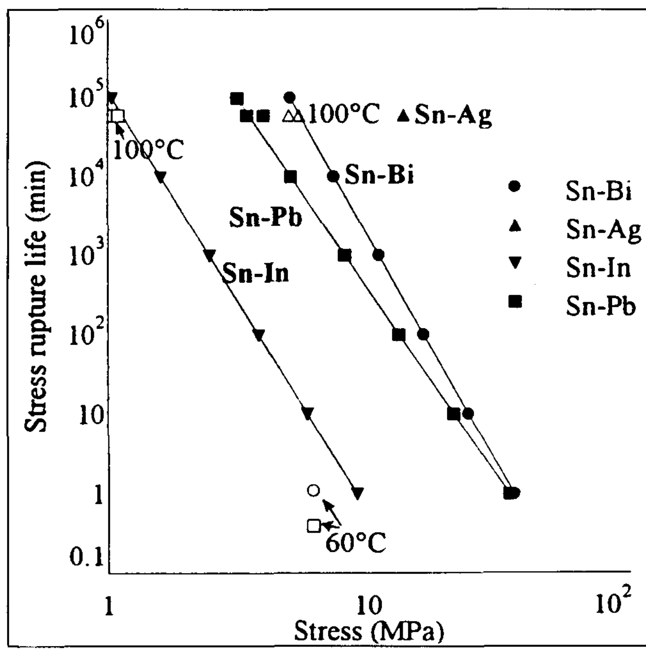

Fig. 4. Stress rupture life of eutectic Sn-Ag, Sn-Bi, Sn-In, and Sn-Pb solders as a function of applied stress. Solid symbols are for room temperature data. Open symbols represent data collected at the indicated higher temperatures.

Creep Resistance

Creep is the most important deformation mechanism of solder because room temperature is such a high homologous temperature for these metals. Unfortunately, the creep resistance of the various Pb-free solders relative to each other and to eutectic Sn-Pb solder remains in question. While the uncertainty is due to a lack of data in part, the complexity of the creep phenomenon and its strong dependence on microstructure also play a significant role. There are two common types of creep tests, stress rupture in which the test load is fixed, and stress relaxation, in which the specimen is loaded to a specified initial stress and the displacement is fixed during the test. Stress rupture tests are more common because the variation of the steady state creep rate with temperature and stress provides insight into the creep mechanism. However, the stress rupture life is influenced by the total creep strain the material can withstand before failure, as well as the creep rate. Although the results of stress rupture and stress relaxation tests are closely related, the relative rankings of different materials can change depending on the relative sensitivity of the creep rate to stress and the microstructural evolution that occurs during the test. Both stress rupture and stress relaxation tests are analogous to loading conditions experienced by solder interconnects during thermal cycling. Leadless joints experience a large initial displacement and corresponding stress, similar to the conditions of a stress relaxation test. In leaded geometries, the compliant lead acts like a spring that initially maintains the stress at nearly constant levels as the joint creeps, analogous to the stress rupture test.

Figure 4 compares data for the stress rupture life of solder joints made from Pb-free eutectic alloys with the behavior of eutectic Sn-Pb controls.[33,34,39,40] In the temperature range 25 to 100°C, eutectic Sn-Ag is clearly superior to the other alloys, including eutectic Sn-Pb. Sn-Bi also outperforms eutectic Sn-Pb in the tested range, 25 to 60°C. Eutectic Sn-In has the shortest life, characterized by rapid, extensive deformation leading to early failure.[11,12]

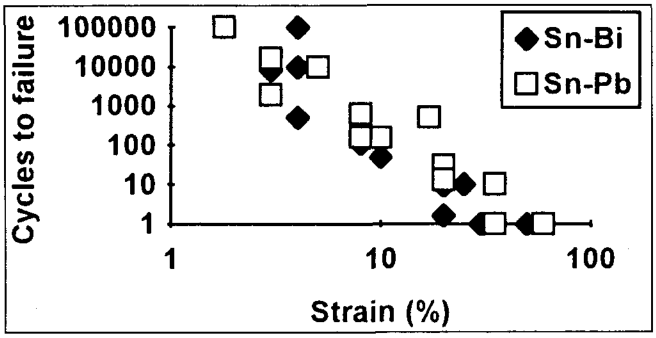

Fig. 5. Cycles to failure in displacement-controlled isothermal fatigue tests conducted at room temperature at various cycling frequencies (and, therefore, strain rates) for eutectic Sn-Pb and Sn-Bi.

Stress relaxation data are available only for eutectic Sn-Bi and Sn-Pb. At both room temperature and 60°C, stress relaxation occurs much more rapidly in Sn-Bi joints than in eutectic Sn-Pb control specimens, resulting in times to failure of less than one half.[33]

The creep mechanism for the various Pb-free solders has not been extensively studied, as it has for eutectic Sn-Pb solder. However, Freer Goldstein and Morris have shown recently that eutectic Sn-Bi undergoes similar microstructural changes to eutectic Sn-Pb, while eutectic Sn-In does not.[41] The behavior of eutectic Sn-Ag does not seem to have been studied.

Thermomechanical Fatigue Resistance

Both the relative and absolute resistance of the various low-melting point, Pb-free solders to isothermal and thermal fatigue are unclear. For most of the alloys, there are very few data and most are not accompanied by characterization of the stress and strain conditions during the test, the starting alloy microstructure, or the eventual failure mechanism, making it impossible to sort out contradictions in the results. Lea's summary of the literature is that eutectic Sn-Pb has the *lowest* fatigue resistance (under unspecified conditions) of any of the alloys he considers.[42] In increasing order of fatigue resistance were: 64Sn-36In, 42Sn-58Bi, 50Sn-50In, 99.25Sn-0.75Cu, 100Sn, and 96Sn-4Ag. Other investigators believe that eutectic Sn-Pb solder is at the least superior to eutectic Sn-Bi and Sn-In. A unique ranking under all conditions probably does not exist.

Isothermal Fatigue Data

Sn-58Bi

Room temperature fatigue data for 42Sn-58Bi solder joints on Cu substrates are plotted in Fig. 5.[3,8,24,33,35] There is a small frequency effect that has been neglected. The data collected by these investigators for eutectic Sn-Pb solder are included. Based on these data, eutectic Sn-Bi solder is inferior to eutectic Sn-Pb solder in low cycle fatigue at large shear strains (e.g., 10–20%), but has comparable fatigue resistance at smaller strains. Under vibration conditions, eutectic Sn-Bi performed better than eutectic Sn-Pb.[43]

A possible explanation for the poorer fatigue resistance of eutectic Sn-Bi solder at large shear strains is that the fatigue life is dominated by inhomogeneous deformation and early recrystallization of the lamellar microstructure.[8,44] When eutectic Sn-Pb solder has an equiaxed microstructure, its fatigue life is improved vs a lamellar microstructure. The advantage of eutectic Sn-Pb over eutectic Sn-Bi is that an equiaxed microstructure is achievable at typical cooling rates, which seems not to be the case for eutectic Sn-Bi. Wild attributes the improvement in fatigue resistance at lower strain levels to the increased ductility of the alloy at lower strain rates (because frequency was constant in his tests, the strain rate decreased along with the cyclic strain).[33]

The fatigue behavior at 100°C has also been tested. Eutectic Sn-Pb solder seems to be far superior to eutectic Sn-Bi at this temperature,[3,33] presumably because 100°C is such a high homologous temperature for eutectic Sn-Bi solder.

Sn-3.5Ag

Sn-3.5Ag is far superior to eutectic Sn-Pb at high shear strain amplitudes, but far inferior to Sn-Pb at low strain amplitudes.[35] The superior behavior of Sn-3.5Ag at large strain amplitudes must be due to the resistance of this alloy to fatigue crack initiation rather than to crack propagation, since Sn-3.5Ag actually had the lowest crack growth resistance of the alloys studied. Tests carried out by other investigators under somewhat different conditions have shown that Sn-3.5Ag was comparable to or better than Sn-Pb at 20°C and better at 100°C particularly at higher stresses.[3,30,34]

Sn-52In

Recent work indicates that the Sn-In eutectic has lower isothermal fatigue resistance than eutectic Sn-Bi and 40Sn-10In-20Pb alloys.[44]

Thermal Fatigue

Thermal fatigue data for low melting point solders are scarce and appear contradictory.[7,21,39,45,46] Some of the apparent contradictions are probably real in the sense that they reflect differences in relative performance under different test conditions (e.g., high or low strain, cycling frequency, thermal cycle). No author has compared all of the solders of interest. Furthermore, only one author described the starting microstructures and their evolution during the test, essential to interpreting the results.[46] (It is also worth noting that if the results are to be used to predict behavior under different conditions, the acceleration factors will be different for each alloy as well.)

Nonetheless a few generalizations can be made. It seems clear that Sn-Ag alloys (Sn-3.5Ag and Sn-5Ag) have improved thermal fatigue resistance over eutectic Sn-Pb solder. Failure is postponed because the localized microstructural coarsening that leads to failure in Sn-Pb alloys does not occur in the Sn-Ag alloys.[46] Eutectic Sn-In appears to have extremely poor thermal fatigue resistance except under conditions where the imposed strain is so large that the rapid creep of this alloy is advantageous. Results for eutectic Sn-Bi are contradictory. Some authors find a considerable improvement over Sn-Pb, while others find somewhat decreased life.

CONCLUSION

There are three binary low-temperature Pb-free solder systems that have been investigated in some depth—42Sn-58Bi, 52In-48Sn, Sn-3.5Ag—and several other systems such as Sn-0.7Cu and ternaries and quaternaries comprised of these elements that have not been studied, but may be of interest in the future. Even for the binary systems that have been studied, there are many holes in the data and, where it does exist, much of it is contradictory or of uncertain relevance to electronic assembly. It is clear that there are important dependencies on microstructure (and, therefore, processing conditions and aging time and temperature), stress and strain rate regime, and so on that are not understood. However, it is possible to draw a few tentative conclusions regarding the suitability of the Sn-Bi, Sn-In, and Sn-Ag eutectic alloys for microelectronic assembly. Further work is required to confirm these results, especially for microstructures typically achieved under typical surface mount conditions.

Eutectic Sn-Bi has properties approaching eutectic Sn-Pb under most conditions. The alloy appears to have reasonable wettability on substrates of engineering interest. Substrates plated with Sn-Pb alloys should be avoided because of the low melting point ternary eutectic in the Sn-Pb-Bi system. The alloy also has reasonable strength, even up to 100°C, in spite of its low melting point. While eutectic Sn-Bi does have a high strain rate sensitivity that results in low elongations at high strain rates, it has good ductility at low strain rates. Eutectic Sn-Bi equals or exceeds the creep resistance of eutectic Sn-Pb in the range 20-65°C. The isothermal fatigue resistance of eutectic Sn-Bi is generally within a factor of two of eutectic Sn-Pb and there are hints that it may be extremely good at low strain. In thermomechanical fatigue testing, the results are contradictory. Parallel to the isothermal fatigue case, eutectic Sn-Bi seems to perform better when the thermal cycle is small.

Eutectic Sn-In is far inferior to eutectic Sn-Pb in most respects. This alloy has displayed satisfactory wettability only with active fluxes containing organic acids or brominated activators. It has very low strength compared to the other alloys. The creep behavior of this alloy is characterized by rapid and extensive deformation, leading to early failure in stress rupture tests, isothermal fatigue tests, and most thermal fatigue tests.

Eutectic Sn-Ag is worthy of serious consideration, particularly for applications in which large stresses or strains will be applied to the solder joints, although its relatively high melting point may be a serious obstacle. The wetting ability of eutectic Sn-Ag on common substrates appears to be marginally acceptable on copper substrates and acceptable on NiAu. An advantage of this alloy is that it is extremely tolerant of dissolved Au. Like eutectic Sn-Pb, Sn-3.5Ag is quite strong, even at 100°C. It has acceptable ductility at high strain rates. It is not particularly strain rate sensitive; at low strain rates, its ductility is inferior to the other alloys. At large stresses or strains, Sn-3.5Ag is extremely creep resistant compared to other alloys. It has similarly excellent isothermal fatigue resistance at large strain amplitudes, although at small strain amplitudes, eutectic Sn-Pb is superior. In two studies of its thermomechanical fatigue resistance, it also performed extremely well.

REFERENCES

1. B.R. Allenby, et al. *Proc. Surface Mount Intl.* 1992, p. 1.
2. P.G. Harris and M.A. Whitmore, *Circuit World* 19 (2), 25 (1993).
3. C. Melton, A. Skipor and J. Thome, *Nepcon West. '93,* p. 1489.
4. R.W. Wild. *Tech. Rpt. 171200408*, IBM Federal Systems Division Laboratory, Owego NY 1971.
5. J.H. Vincent et al., *Circuit World* 19 (3), 32 (1993).
6. Z. Mei and J.W. Morris, Jr., *ASME Winter Annual Meeting,* Dec. 1–6, 1991, Atlanta, GA, 91-WA-EEP-20.
7. J. Seyyedi, *Soldering and Surface Mount Tech.* 13 (2), 26 (1993).
8. Z. Mei and J.W. Morris, Jr., *J. Electron. Mater.* 21, 599 (1992).
9. E.W. Hare, R. Corwin and E.K. Riemer, *Proc. ASM Intl. Elec. Packaging Matls. and Processes Conf.*, Oct. 1985, (Materials Park, OH: ASM Intl., 1986), p. 109.
10. K. Seelig, D. Sklarski. L. Johnson and J. Sartell, *Nepcon East.* 1987.
11. Z. Mei and J.W. Morris, Jr., *J. Electron. Mater.* 21, 401 (1992).
12. J.L. Freer and J.W. Morris, Jr., *J. Electron. Mater.* 21, 647 (1992).
13. J.L. Freer Goldstein and J.W. Morris. Jr., submitted to *Met. Trans. A.*
14. M.E. Warwick and S.J. Muckett, *Circuit World* 9 (4), 5 (1983).
15. J. Haimovich, *Weld. Res. Supp.* March, 102s (1989).
16. L.E. Felton, C.H. Raeder and D.B. Knorr. *JOM* 45 (7), 28 (1993).
17. A.D. Romig, F.G. Yost and P.F. Hlava, *Microbeam Analysis—1984,* eds. A.D. Romig, Jr. and J.I. Goldstein, (San Francisco Press, 1984), p. 87.
18. G. Humpston and D.M. Jacobson, *Principles of Soldering and Brazing*, (Materials Park, OH: ASM Intl., 1993).
19. R. Satoh, *Thermal Stress and Strain in Microelectronics Packaging,* ed. J.H. Lau, (New York: Van Nostrand Reinhold, 1993), p. 500.
20. K.G. Schmitt-Thomas and S. Wege, *Brazing and Soldering* 11, Autumn, 27 (1986).
21. R. Strauss and S. Smernos, *The Bulletin of the Bismuth Institute* 49, 1 (1986).
22. C.A. MacKay and W.D. von Voss, *Mater. Sci. Technol.* 1, 240 (1985).
23. P.T. Vianco, F.M. Hosking and J.A. Rejent, *Nepcon West 1992*, p. 1730.
24. W.J. Tomlinson and I. Collier, *Mater. Sci. Eng.* 1835 (1987).
25. F.M. Hosking, P.T. Vianco, C.L. Hernandez and J.A. Rejent, *Proc. Surf. Mount Intl.,* San Jose, CA, Aug. 29–Sept. 2, 1993, p. 476.
26. C. Melton, *Proc. 43rd ECTC,* June 1–4, 1993 Orlando, FL (New York: IEEE), p. 1008.
27. F.M. Hosking, P.T. Vianco and D.R. Frear, *Sandia National Laboratories Rpt.* No. SAND90-3248C.
28. J.W. Morris, Jr. and Z. Mei, *Solder Mechanics–A State of the Art Assessment,* eds., D.R. Frear et al., (Warrendale, PA: The Minerals, Metals and Materials Society, 1991).
29. J.S. Hwang and R.M. Vargas, *Soldering and Surf. Mount Tech.* 4 (2) 27 (1990).
30. C.J. Thwaites and W.B. Hampshire, *Weld. Res. Supp.* (1976),

p. 323s.
31. W.J. Tomlinson and A. Fullylove, *J Mater. Sci.* 27, 5777 (1992).
32. L.E. Felton. C.H. Raeder. C.K. Havasy and D.B. Knorr, *1992 IEEE / CHMT Int'l. Elec. Mfg. Tech. Symp.*, Sept. 28–30, 1992, Baltimore, MD, p. 300.
33. R.W. Wild, *NEPCON 1974,* p. 105.
34. M. Warwick, *Brazing and Soldering* 8, Spring, 20 (1985).
35. Z. Guo, A.F. Sprecher, Jr., H. Conrad and M. Kim, *Materials Developments in Microelectronic Packaging,* (Materials Park, OH: ASM, 1991).
36. L. Quan, D.R. Frear, D. Grivas and J.W. Morris, Jr., *J. Electron. Mater.* 16, 203 (1987).
37. D.R. Frear, Ph.D. Thesis, University of California–Berkeley, June 1987.
38. S. Pattanaik and V. Raman, *Materials Developments in Microelectronic Packaging: Performance and Reliability,* (Materials Park: OH: ASM Intl., 1991), p. 251.
39. J.R. Getten and R.C. Senger. *IBM J. Res. Dev.* 26, 379 (1982).
40. J. London and D.W. Ashall, *Brazing and Soldering* 10, Spring 17 (1986).
41. J.L. Freer Goldstein and J.W. Morris, Jr., *J. Elect. Mater.* 23, 477 (1994).
42. C. Lea, *A Scientific Guide to Surface Mount Technology,* (Ayr, Scotland: Electrochemical Publications, 1988).
43. S. Wege, *Proc. Conf. Weichloeten in Forschung und Praxis* Munich. Feb. 1986, DVS Berichte nr. 104, p. 134.
44. J.W. Morris, Jr., J.L. Freer Goldstein and Z. Mei, *The Mechanics of Solder Alloy Interconnects,* eds., D.R. Frear, H. Morgan, S. Burchett and J.H. Lau, (New York: Van Nostrand Reinhold, 1994), p. 7.
45. D.M. Jarboe, *Bendix Kansas City Div. internal report,* 1980, DBX-613-2341. Referenced in D.R. Frear, *Solder Mechanics—A State of the Art Assessment,* eds., D.R. Frear. et al. (Warrendale, PA: The Minerals, Metals and Materials Society, 1991).
46. J.L. Marshall and S.R. Walter, *Intl. J. Hybrid Microelectron.* 10, 11 (1987).