Low-Temperature Solders

The application of low-temperature solders in surface mount assembly processes for products that do not experience harsh temperature environments is technically feasible. One single alloy may not be appropriate as a universal solution.

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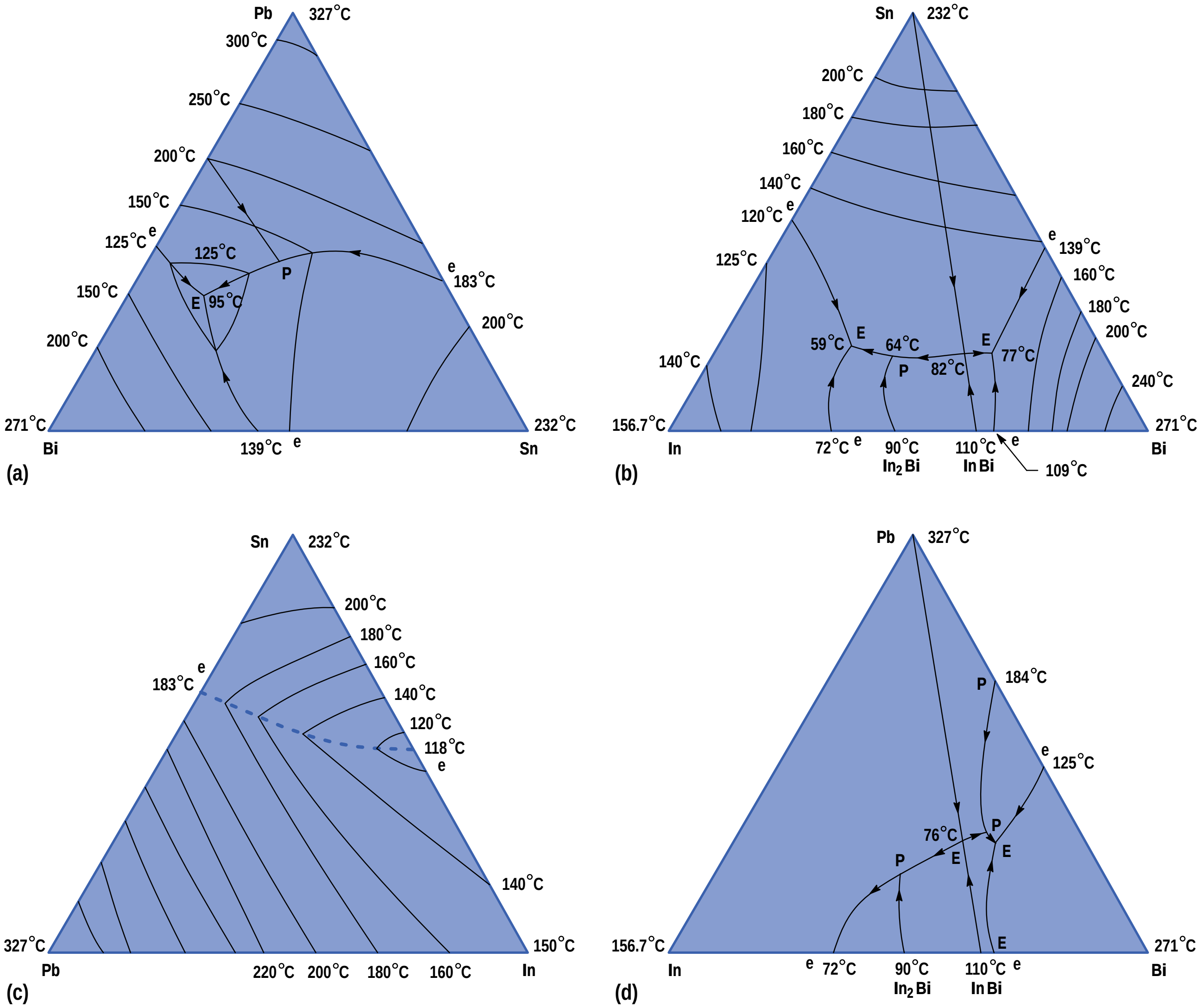
Low-temperature soldering has been a subject of research at HP's Electronic Assembly Development Center (EADC). Several benefits may come from developing this technology, including thermal shock reduction, step soldering capability, and possibly, lead (Pb) elimination.

Thermal Shock Reduction. The risk of thermally induced damages will be reduced if the peak exposure temperature is reduced. A significant decrease in the peak reflow temperature (the oven temperature at which the solder melts and makes the connections between the components and the board) will reduce damage to components. Currently, peak reflow temperatures are around 210°C to 230°C. These temperatures are sufficient to cause phenomena such as *popcorning*, a fairly well-known phenomenon in which air and moisture that have been trapped in the plastic package of an IC are heated to the point where they expand and cause the component case to crack open.

Fig. 1. *Melting points of ternary systems of all possible combinations of (a) BiPbSn, (b) BiInSn, (c) PbInSn, and (d) BiInPb.*



The damage from popcorning is immediate and usually detectable, but there are other thermally induced damages that can cause long-term problems, such as warping of printed circuit boards or damage to ICs, which would also be reduced with lower peak temperatures.

Step Soldering. The availability of solders with lower melting points will make multiple reflow processes on a single board possible. For example, all of the normal components that can tolerate higher reflow temperatures could be soldered to a board using the standard process, and then the lower-temperature components could be added in another reflow process. Since step soldering is a bulk reflow process, it takes less time and is more uniform than hand soldering, and doesn't take any different equipment or special training.

Possible Pb Elimination. Many low-temperature solders contain no lead.

Selection of Low Melting Alloys

We call a solder alloy *low melting* if it melts at temperatures below 183°C and above 50°C. Most of the alloys that meet this requirement are made of four elements: Sn (tin), Pb (lead), Bi (bismuth), and In (indium). The Cd (cadmium) bearing alloys are not considered because of their extreme toxicity. Various compositions of these elements produce alloys that melt at any given temperature between 50°C and 183°C. Commercially available low-melting alloys are listed in Table I. The numbers associated with each alloy in Table I are the percentages by weight of the components that make up the alloy.

To better understand the correlation between the alloy compositions and their melting temperatures, we can use the ternary diagram of melting temperature. A ternary diagram uses a triangle to represent chemical compositions of a three-element alloy system. A physical property, such as melting temperature, is plotted over the triangle. Figs. 1a to 1d show the melting points of ternary systems of all possible combinations of the elements BiPbSn, BiInSn, InPbSn, and BiInPb.

These diagrams show what are called the liquidus temperatures, as opposed to the solidus temperatures. A typical alloy melts not at a single temperature but over a temperature range. The solidus temperature is the highest temperature at which an alloy remains solid, while the liquidus temperature is the lowest temperature at which an alloy remains liquid. At the temperatures between the solidus and liquidus temperatures, an alloy is a mixture of solid and liquid. The solidus temperatures of these alloy systems are not shown in Fig. 1. However, for a few specific compositions labeled "e" or "E" in Fig. 1, the so-called eutectic alloys, the solidus and liquidus temperatures are equal. Alloys with eutectic compositions or small differences between their liquidus and solidus temperatures are often favored for soldering applications because they melt and solidify rapidly instead of over a range of temperatures.

Not all the compositions found on the ternary phase diagram are suitable for soldering applications. To determine which are most appropriate, see Table 1.

- Wettability. A metal is said to have *wetted with a surface* if it forms a sound metallurgical bonding with the surface. Wetting is essential in the soldering process because it ensures that the joint created won't come apart at the interface. Any new alloy must be able to wet to the common pad surface finishes: Cu, PbSn, and Ni coated with Pd or Au.
- Reliability. Lower-temperature alloys should still be reliable, so we measure the following properties to estimate how reliable solder joints made of an alloy will be: shear strength, creep resistance, isothermal fatigue resistance, and thermal fatigue resistance.
- Long-term stability. Microstructural evolution, grain growth, and recrystallization contribute to changes in the solder joint mechanical properties over time, so we want to make sure that the changes are slow and stable and won't reduce the mechanical properties of the solder joints to unacceptable levels over the life of the joint.
- Practicality. Alloys used for mass production should be cheap and widely available. It should be possible to make them into solder pastes so that they can be used in standard assembly processes, and suitable fluxes should be available. The alloys shouldn't be more toxic than what's currently used.

To begin our alloy selection and evaluation, we found references in the available literature to low-temperature alloys that might fit these requirements. Three alloys were selected for further evaluation:

- 43Sn43Pb14Bi. The solidus temperature of this alloy is 144°C and the liquidus temperature is 163°C, 20°C lower than 63Sn37Pb, but with similar mechanical properties.
- 58Bi42Sn. This composition is a eutectic alloy that melts at 139°C. It is lead-free and strong, but brittle. Also, its fatigue resistance is questionable.[1,2]
- 40Sn40In20Pb. The solidus temperature of this alloy is 121°C and the liquidus temperature is 130°C. It is soft and ductile. It doesn't have the problem of embrittlement when soldering to thick gold surfaces, like PbSn, because of the high In content. Unfortunately, the high In content drives the price of this alloy up because In is extremely expensive right now.

Table I
Low-Melting Alloys

Chemical Composition	Liquidus Temperature (°C)	Solidus Temperature (°C)
49Bi21In18Pb12Sn	58	58
51In32.5Bi16.5Sn	60	60
49Bi18Pb18In15Sn	69	58
66.3In33.7Bi	72	72
57Bi26In17Sn	79	79
54.02Bi29.68In16.3Sn	81	81
51.45Bi31.35Pb15.2Sn2In	93	87
52Bi31.7Pb15.3Sn1In	94	90
52.5Bi32Pb15.5Sn	95	95
52Bi32Pb16Sn	95.5	95
52Bi30Pb18Sn	96	96
50Bi31Pb19Sn	99	93
50Bi28Pb22Sn	100	100
46Bi34Sn20Pb	100	100
50Bi25Pb25Sn	115	95
56Bi22Pb22Sn	104	95
50Bi30Pb20Sn	104	95
52.2Bi37.8Pb10Sn	105	98
45Bi35Pb20Sn	107	96
46Bi34Pb20Sn	108	95
54.5Bi39.5Pb6Sn	108	108
67Bi33In	109	109
51.6Bi41.4Pb7Sn	112	98
52.98Bi42.49Pb4.53Sn	117	103
52In48Sn	118	118
53.75Bi43.1Pb3.15Sn	119	108
55Bi44Pb1Sn	120	117
55Bi44Pb1In	121	120
55.5Bi44.5Pb	124	124
50In50Sn	125	118
58Bi42Pb	126	124
38Pb37Bi25Sn	127	93
51.6Bi37.4Sn6In5Pb	129	95
40In40Sn20Pb	130	121
52Sn48In	131	118
34Pb34Sn32Bi	133	96
56.84Bi41.16Sn2Pb	133	128
38.41Bi30.77Pb30.77Sn0.05Ag	135	96
57.42Bi41.58Sn1Pb	135	135
36Bi32Pb31Sn1Ag	136	95
55.1Bi39.9Sn5Pb	136	121
36.5Bi31.75Pb31.75Sn	137	95
43Pb28.5Bi28.5Sn	137	96
58Bi42Sn	138	138
38.4Pb30.8Bi30.8Sn	139	96
33.33Bi33.34Pb33.33Sn	143	96
97In3Ag	143	143
58Sn42In	145	118
80In15Pb5Ag	149	142
99.3In0.7Ga	150	150
95In5Bi	150	125
42Pb37Sn21Bi	152	120
99.4In0.6Ga	152	152
99.6In0.4Ga	153	153
99.5In0.5Ga	154	154
100In	156.7	156.7
54.55Pb45.45Bi	160	122
70Sn18Pb12In	162	162
48Sn36Pb16Bi	162	140
43Pb43Sn14Bi	163	144
50Sn40Pb10Bi	167	120
51.5Pb27Sn21.5Bi	170	131
60Sn40Bi	170	138
50Pb27Sn20Bi	173	130
70In30Pb	175	165
47.47Pb39.93Sn12.6Bi	176	146
62.5Sn36.1Pb1.4Ag	179	179
60Sn25.5Bi14.5Pb	180	96
37.5Pb37.5Sn25In	181	134

These three were chosen mostly because there was more information available on them than on other low temperature alloys, not necessarily because we thought they would make the best solders. They provided a starting point.

Because the technical data on the low temperature alloys was limited and inconclusive,[3] we conducted a series of tests based on our selection criteria listed above.

Wetting and Solderability

Two types of tests were conducted to look at the wetting performance of these alloys: spreading tests and wetting balance tests.

In spread tests, a dollop of solder paste is deposited on a copper board or test coupon. The coupons are then heated to 30°C above the liquidus temperature of the alloy in an oven under a nitrogen atmosphere. The dollop of solder paste melts, and as long as the flux is active enough to remove the surface metal oxides, the solder forms a bead, or cap (see Fig. 2). The diameter and height of the solder cap can then be measured to determine the contact angle (α) of the solder to the board. This contact angle, or wetting angle, is a measure of how well the solder will wet in a surface mount process—smaller is better.

Fig. 2. *Solder bead formed by reflowing paste on a plain Cu surface. α is the wetting angle.*

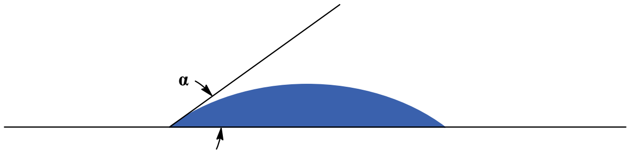
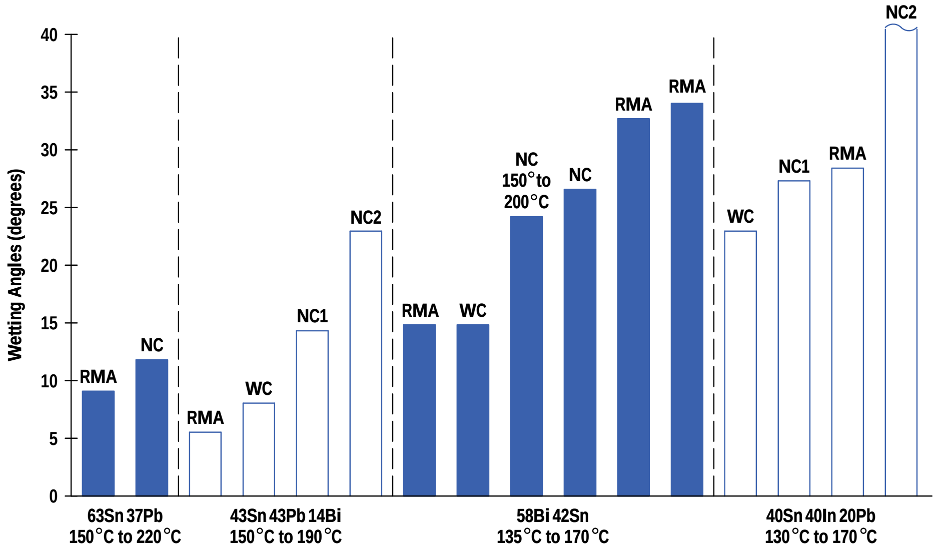


Fig. 3. *Wetting angles determined from spreading tests of solder pastes on copper, reflowed in a nitrogen oven. The x axis indicates the solder alloys and reflow temperatures. The fluxes are indicated at the tops of the bars (WC = water-clean, NC = no-clean, RMA = rosin mildly activated).*



Factors that affect the spread test include the activity of the flux, the surface tension of the molten alloy, and the alloy's ability to make a metallurgical bond with the surface metallization. All of these factors have to be taken into account when interpreting the results of spread tests.

The results of the wetting angle tests are shown in Fig. 3. The 63Sn37Pb and 43Sn43Pb14Bi alloys both wetted well and similarly with the same flux. The 58Bi42Sn and 40Sn40In20Pb alloys generally wetted the copper surface ($\alpha < 90°$), but not as well as the other two alloys, averaging two to three times the wetting angle with the same fluxes. In fact, the 40Sn40In20Pb alloy didn't wet at all with one no-clean flux (NC2). These differences may have to do with the fact that indium and bismuth oxides are more difficult to remove than tin and lead oxides. These alloys also have lower surface tensions than PbSn.

Another factor in how the lower-temperature alloys performed is that the current water clean and no-clean fluxes were developed for 63Sn37Pb and activate at about 150°C. They may not be suitable for the low-temperature solders since most of the low-temperature solders melt at temperatures below 150°C. Wetting balance tests were conducted to find fluxes that would be appropriate for use at lower temperatures, and the results of those tests are presented in reference 4 and in ***Article 11***.

Reliability and Long-Term Stability

Before we could suggest that anyone change from PbSn solder to an alternative alloy, we needed to understand the mechanical properties of the alloy well enough to know what the trade-offs would be. Therefore, the bulk of the tests we did to evaluate the alloys focused on the areas of shear, creep, isothermal fatigue, and thermal fatigue.

Shear. Solder joints experience shear because of coefficient of thermal expansion mismatches. To look at the behavior of solder joints of different alloys in shear, we used specimens as shown in Fig. 4. These specimens have nine solder joints of dimensions 0.050 by 0.080 by 0.010 inch sandwiched between two copper plates. When the ends are pulled in a testing machine at different temperatures and strain rates, the stress in the solder joints can be measured. Plotting the measured maximum stress against the strain rates gives us the relative shear strength of the different alloys and allows us to compare them to PbSn.

Our shear tests were conducted at three temperatures (25°C, 65°C, and 110°C) and at three strain rates (10^{-2}, 10^{-3}, and 10^{-4} per second). The results of the shear strength tests for the low-temperature solders and several high-temperature solders are plotted in Fig. 5.

From these plots we can see that at 25°C, under the same strain rates, 58Bi42Sn is the second strongest, inferior only to a high-temperature Pb-free alloy. 43Sn43Pb14Bi had about the same strength as 63Sn37Pb, while 40Sn40In20Pb is the softest. As the temperature increased to 110°C, the low-temperature solders became much softer while the high-temperature solders were still relatively strong.

Creep. If a constant load is applied to a material while it is held at an elevated temperature, it will deform, or flow, over time. This time dependent deformation is called creep, and is most significant at absolute temperatures greater than about half the melting point of the material. Since creep is the main deformation mechanism in solders, it's important to know how creep resistant a new solder alloy will be.

Fig. 4. *Specimen for shear and creep tests.*

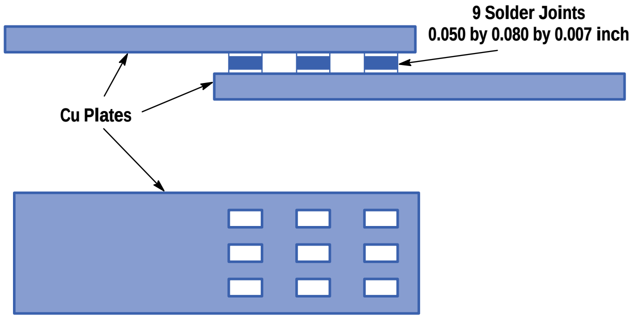


Fig. 5. *Results of shear strength tests for the low-temperature solders and several high-temperature solders at (a) room temperature, (b) 65°C, and (c) 110°C.*

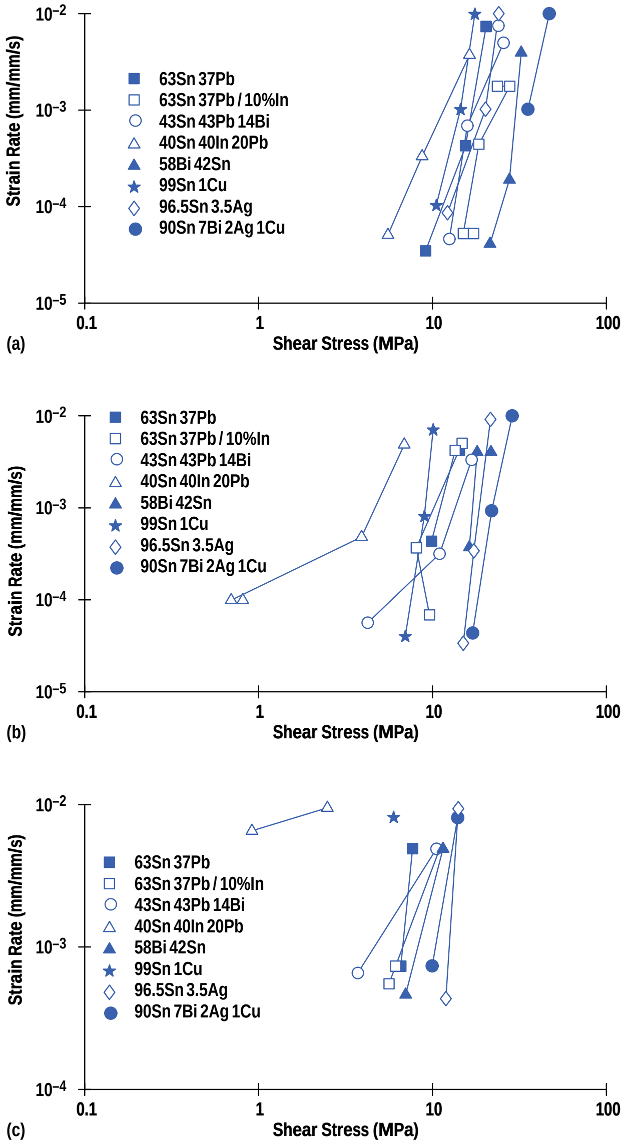
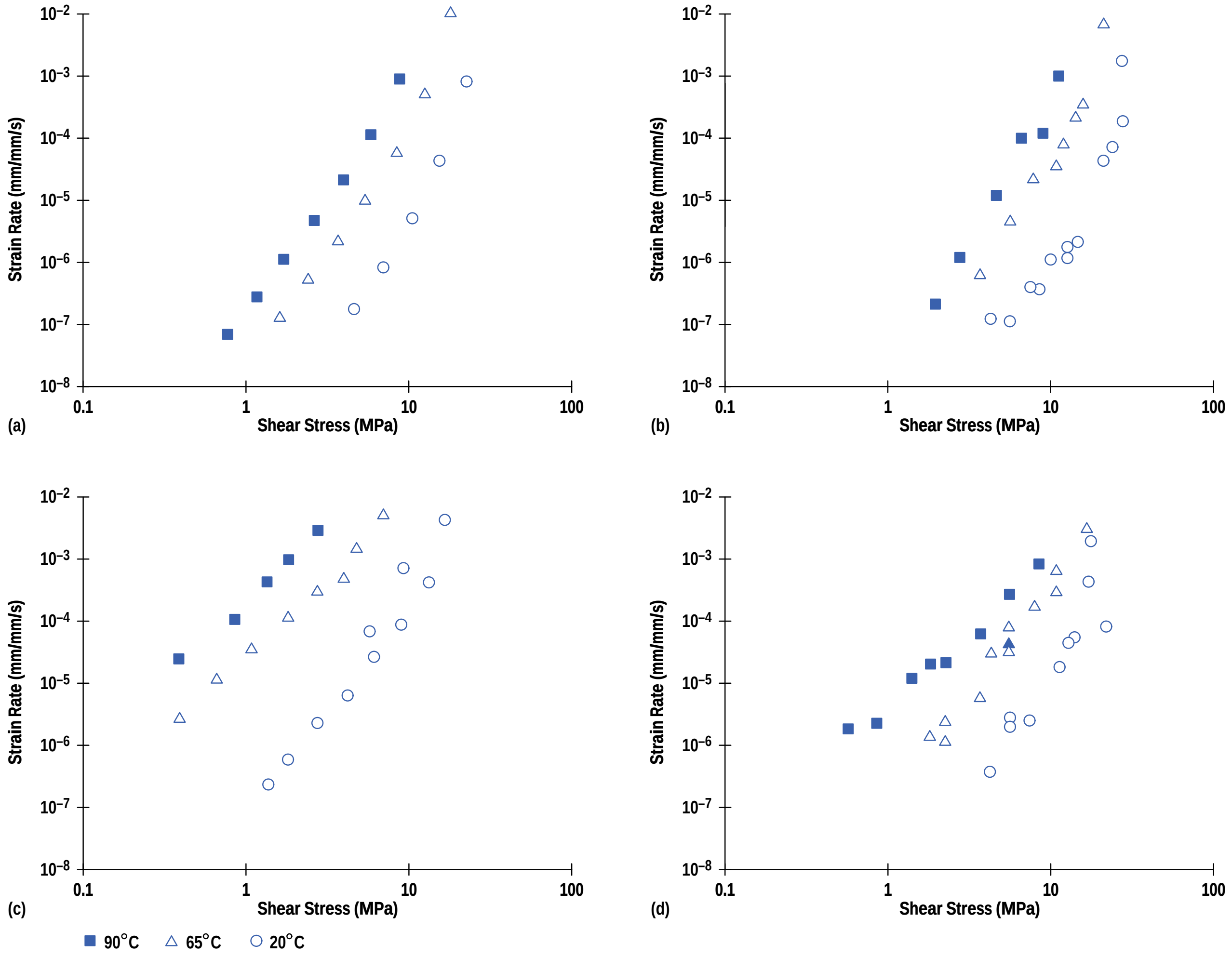


***Fig. 6.** Steady-state creep (strain) rates at 20°C, 65°C, and 90°C as a function of shear stress for 63Sn37Pb (a) and the low temperature solders: (b) 58Bi42Sn, (c) 40Sn40In20Pb, and (d) 43Sn43Pb14Bi.*



The same kind of specimens used in shear tests were used in the creep tests. The steady-state strain rates as a function of shear stress at 25°C, 65°C, and 90°C are plotted in Fig. 6. The data has been fitted with standard creep (Dorn) equations:

$$\frac{d\gamma}{dt} = A\tau^{n}e^{-\Delta H/RT},$$

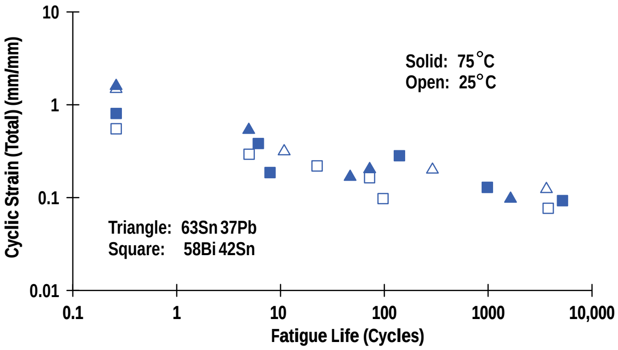
where γ is the shear strain or creep, A is a materials constant, τ is the shear stress, n is an empirical constant typically between 3 and 7, H is the activation energy, R is the gas constant, and T is the absolute temperature in K. The resulting Dorn equation parameters are listed in Table II.

Table II
Creep Equation Parameters for Three Solder Alloys

Alloy	A	n	ΔH (kcal/mole)
40Sn40In20Pb	4.0488×10^{4}	2.98	22.00
58Bi42Sn	5.5403×10^{-7}	4.05	16.85
43Sn43Pb14Bi	0.11552	2.94	17.05

The rupture strains of the low-temperature solders were also determined from the creep tests. 58Bi42Sn showed the slowest creep rate but the least rupture strain for the same stress compared with the other low-temperature solders and the 63Sn37Pb, while 40In40Sn20Pb exhibited the fastest creep rate but the largest rupture strain.

Fig. 7. *Isothermal shear fatigue test results.*



Isothermal Fatigue. When materials are subjected to small repeated loading, they can eventually fracture. This process of gradual fracture is called fatigue. Solder joints experience loading because of coefficient of thermal expansion mismatches. These loads are cyclic, caused by temperature excursions during operation. Isothermal strain cycles can be used to rapidly simulate joint exposure to show relative fatigue lives of different solder alloys. There is a relationship called the Coffin-Manson Law, which is one way of estimating the fatigue life of the material. Fatigue life is defined as the number of cycles at a given strain that will cause failure in the material.

Coffin-Manson relations for the low-temperature solders have been determined at both 25°C and 75°C. The data for 58Bi42Sn and 63Sn37Pb is shown in Fig. 7. The isothermal fatigue life of 58Bi42Sn is shorter than 63Sn37Pb under the same cyclic strains.

Thermal Fatigue. Although isothermal fatigue can be used to estimate fatigue life, we also do actual thermal cycling to show how the joints will perform as the temperature cycles. For our thermal fatigue tests, a new type of test vehicle was designed (see Fig. 8). Five ceramic plates, all 1/16 inch thick, and 4, 2, 1, 1/2, and 1/4 inch square respectively, were soldered onto a 1/8-inch-thick FR-4 board. Eight solder joints 0.010 inch thick and 0.050 inch in diameter, located in a ring, were sandwiched between each ceramic plate and the FR-4 board. Each solder joint was individually tested for electrical continuity while being temperature cycled in a thermal chamber. Two temperature profiles were used, 25°C to 75°C and −20°C to 110°C.

The results of the −20°C-to-110°C test are plotted in Fig. 9. Since the test is still in progress, only the fatigue data for the failed solder joints is plotted. 63Sn37Pb lasted longer than 58Bi42Sn, and approximately the same number of cycles as 43Sn43Pb14Bi. The 40Sn40In20Pb solder joints have the longest fatigue lives.

Practicality

To examine the practical side of using these alloys, we did a prototype build. Since the 40Sn40In20Pb alloy is so expensive, it's an unlikely candidate for large-scale production, so we excluded it from the prototype builds. The 58Bi42Sn alloy is harder to solder than 43Sn43Pb14Bi (it has a lower melting temperature and its oxide is harder to remove), so we chose to test the worse case of the two remaining alloys and build with 58Bi42Sn.

The 58Bi42Sn alloy was made into a solder paste with a water-soluble RMA flux.[5] This kind of flux was used because, unlike most standard no-clean fluxes, it is active at the lower oven temperatures used with BiSn. The assembly we chose for this build had a variety of components, including 0.025-inch-pitch components.

Fig. 8. *Test vehicle for thermal fatigue tests.*

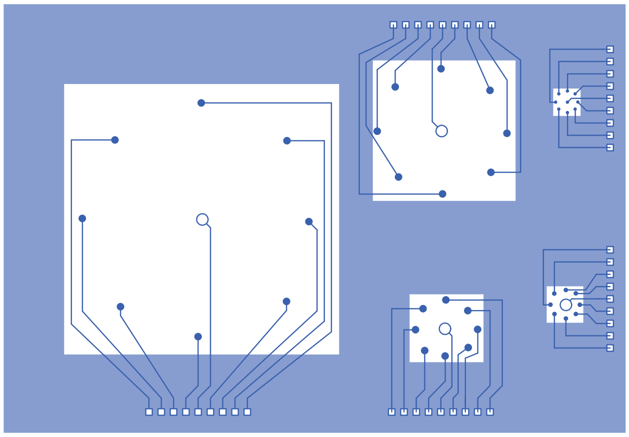
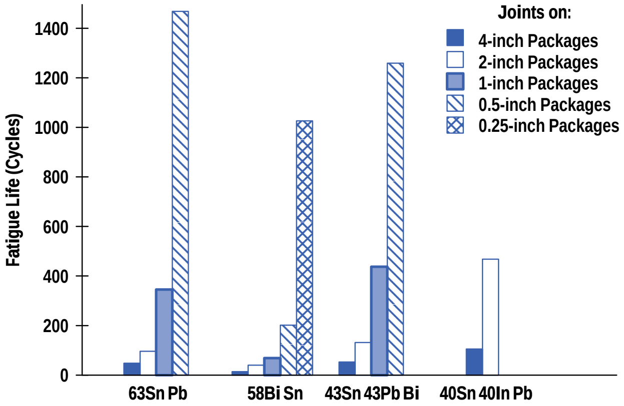


Fig. 9. *Results of the −20° C-to-110° C thermal fatigue test. Fatigue lives are shown only for joints that had failed at the time of writing.*



Two types of board platings were used: organic coated copper (OCC) and hot air solder leveling (HASL). These coatings protect the copper pads from oxidation before the reflow process. For OCC, the copper pads are coated with a thin layer of a polymer that preserves the solderability of the surface by preventing the oxidation of the copper underneath, but burns off during the reflow process to allow for metallurgical bonding between the surface and the solder. HASL or HAL (hot air leveling) accomplishes the same protection but uses a thin layer of PbSn solder that has been blown level with air knives.

The entire assembly process was the same as for 63Sn37Pb, except that a different reflow profile was used. The low-temperature profile had a preheat period of 4 minutes at 130°C and a peak period of 1.5 minutes at temperatures between 138°C and 175°C (0 to 39°C above the melting point of the alloy).

Twenty boards were built with no defects. The boards passed functional tests as well as out-of-plane random frequency vibration (45 minutes at 6g) and board environmental stress testing (BEST—thermal cycling from −45°C to 100°C, 1 hr/cycle, functionality monitored throughout).

Failure of 58Bi42Sn on Pb-Containing Surface

During the thermal cycling of the prototype boards, we observed a thermal fatigue failure mechanism of the BiSn solder on Pb-containing surfaces.[6] Some components on the prototype boards fell off after about 500 cycles of BEST. Boards soldered with 63Sn37Pb failed after about 900 cycles.

Fig. 10 shows top views of the 58Bi42Sn solder joints before and after BEST. Before BEST, the solder joint surfaces were smooth. After BEST, the solder joints between OCC boards and the components with Ni-Pd coating remained smooth, but the solder joints between either the HAL boards or the components with PbSn coating developed very rough surfaces. This roughness corresponded to the extraordinary grain growth as shown in the cross-sectional views of solder joints in Fig. 11.

The reason for the accelerated grain growth and phase agglomeration was that the Pb from component leads and HAL coatings on the pads had dissolved into the BiSn joints during the reflow process and formed 52Bi32Pb16Sn, the ternary eutectic phase of the BiPbSn system (point E in Fig. 1a), which melts at 95°C. Since each cycle of the test took the temperature to 100°C, that phase became liquid at the grain boundaries and provided channels for fast atom transportation.

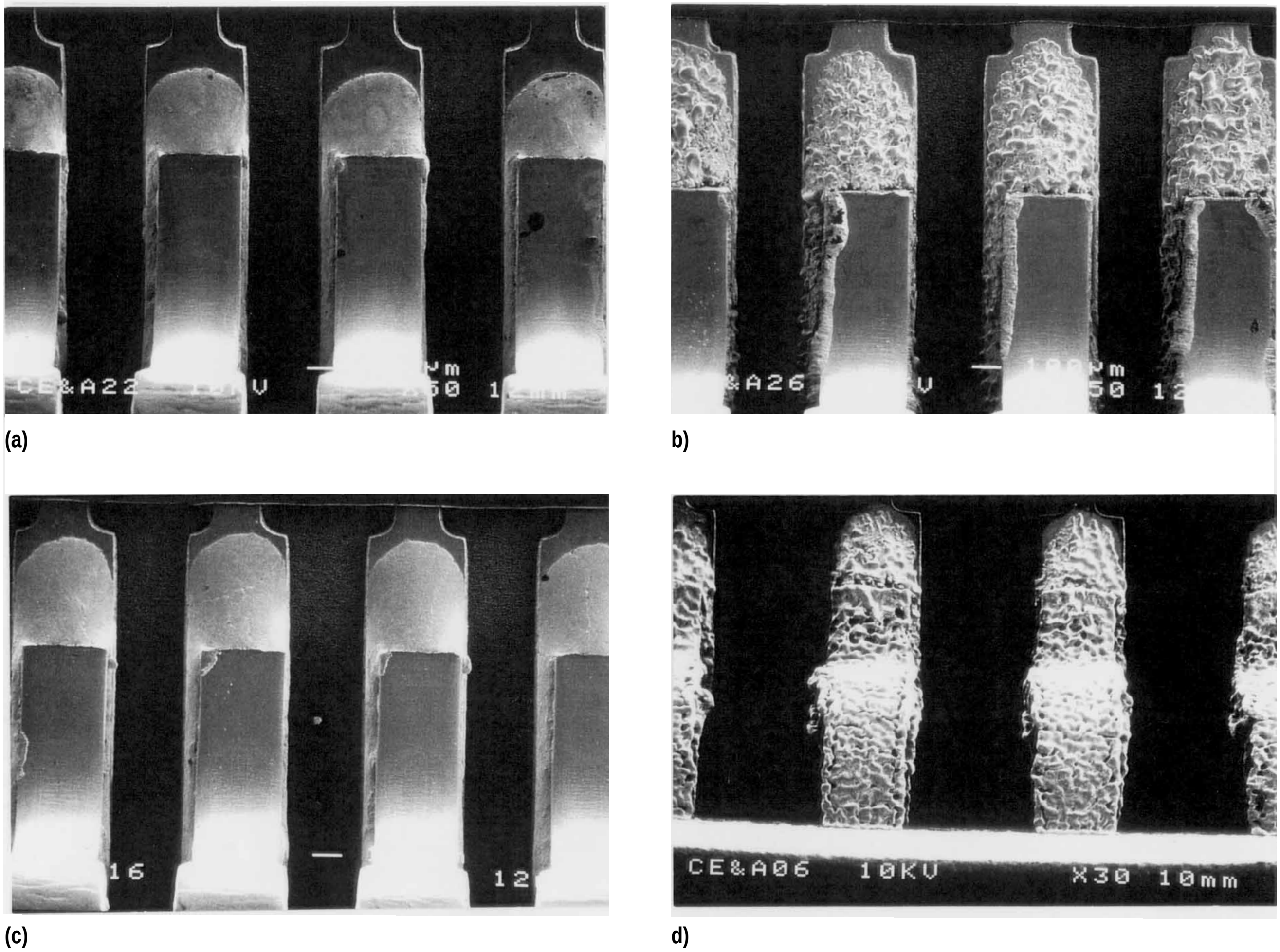
Although only a tiny percentage of Pb on the boards or on the component leads dissolved into the BiSn joints, the small amount of the ternary eutectic ruins the mechanical properties over the course of thermal cycling to 100°C. The joint goes from having a fine microstructure (as formed) to essentially having large chunks of Sn and Bi held together by some weak BiPbSn, which indicates that BiSn is only compatible with Pb-free surfaces.

Discussion

With all the data we've collected, it's still difficult to conclude which low-temperature alloy is the best in general. Each has different advantages and disadvantages. They offer a spectrum of melting ranges: 43Sn43Pb14Bi melts at 144°C to 163°C, 58Bi42Sn melts at 138°C, and 40Sn40In20Pb melts at 121°C to 130°C. Each has certain benefits we might want, such as 40In40Sn20Pb soldering on Au-coated surface without embrittlement, but also has trade-offs, such as BiSn's intolerance for Pb on the printed circuit board and component leads or In's extremely high cost.

Most of the test data obtained so far is positive, with a couple of exceptions. These results seem to indicate that low-temperature soldering with one or more of the alloys we investigated (or some closely related alloys) is feasible as a manufacturing technology. The exceptions include (1) the nonwetting of 40In40Sn20Pb with the no-clean flux, and (2) microstructural coarsening and early failure during the thermal cycling of 58Bi42Sn joints on Pb-containing surfaces. The first problem is being addressed in a flux development program, working with paste vendors to create fluxes intended for use in low-temperature applications with the harder-to-solder alloys such as 58Bi42Sn and 40In40Sn20Pb. The solution for the second problem has not been obtained, although several options are being pursued.

Fig. 10. *BiSn joints (a) between a Ni-Pd component lead and an organic coated copper board before thermal cycling from −45° C to 100° C, (b) between a Ni-Pd component lead and an organic coated copper board after thermal cycling, (c) between a Ni-Pd component lead and a hot air leveled board after thermal cycling, and (d) between a PbSn-coated component lead and an organic coated copper board after thermal cycling. (Reprinted from ASME Technical Paper 95-WA/EEP-4. © Copyright 1995 ASME. Reproduced with permission.)*



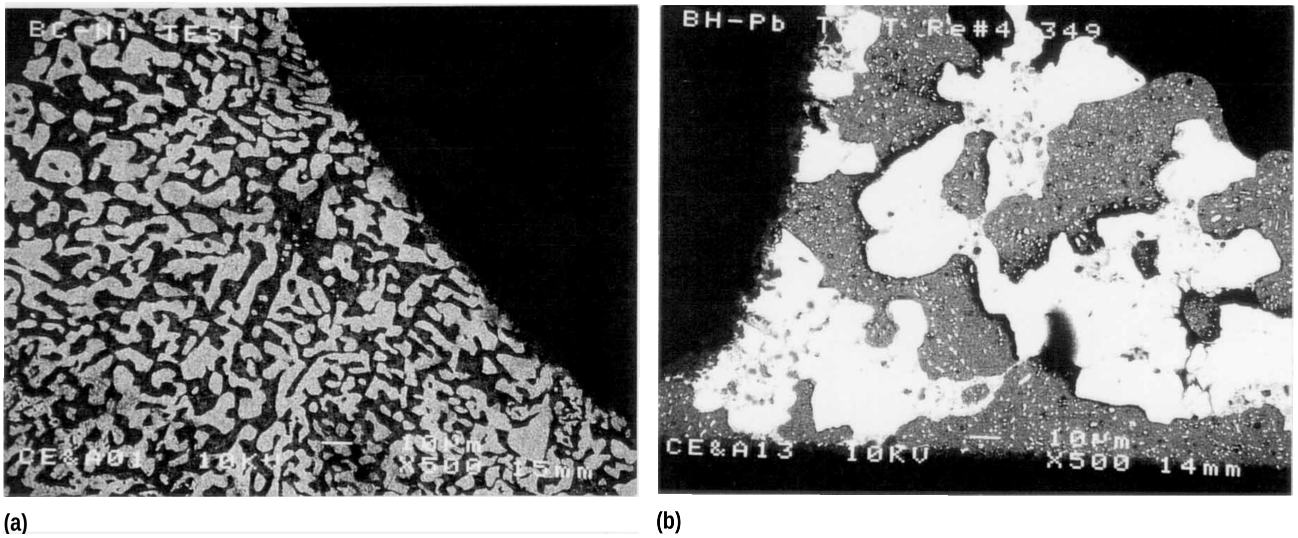
(a)

b)

(c)

d)

Fig. 11. *SEM cross section views of two solder joints at the same magnification after thermal cycling. (a) BiSn joint between a Ni-Pd component and an organic coated copper board. (b) BiSn joint between between a PbSn-coated component and a hot air leveled board. (Reprinted from ASME Technical Paper 95-WA/EEP-4. © Copyright 1995 ASME. Reproduced with permission.)*



(a)

(b)

Conclusion

The application of low-temperature solders in surface mount assembly processes for products that do not experience harsh temperature environments is technically feasible. Low-temperature assembly appears promising as an addition to the surface mount landscape as a way of increasing process flexibility and component reliability. However, one single alloy won't be a universal solution. Specific component and assembly requirements will have to be considered in choosing or tailoring the best solder alloy for each application.

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