Getting Ready For Lead Free Solders

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ABSTRACT

This paper reviews the status of lead-free solder developmental works. Some of the solder systems, Bi-Sn, Bi-Sn-Fe, In-Sn, Sn, Sn-Ag, Sn-Ag-Zn, Sn-Ag-Zn-Cu, Sn-Bi-Ag, Sn-Cu, Sn-Cu-Ag, Sn-In-Ag, Sn-Sb, Sn-Zn and Sn-Zn-In are discussed in more details, while the others are briefly commented on. In general, compared with eutectic Sn-Pb solder, all the lead-free solder alternatives investigated more or less exhibit some shortcomings, such as price, physical, metallurgical, or mechanical properties. Relatively, Sn-In-containing systems are more promising in terms of solder mechanical properties and soldering performance, although the price of In may be a concern. Eutectic Sn-Ag solder doped with Zn, Cu, or Sb exhibits good mechanical strength and creep resistance, due to refined microstructure. The Bi-Sn systems doped with other elements may have a niche in the low temperature soldering field. Eutectic Sn-Cu has a good potential due to its good fatigue resistance. Eutectic Sn-Zn system modified with In and/or Ag may be promising in mechanical properties. Finding a lead-free alternative for high temperature solders presents the biggest challenge to the industry.

Key Words: solder, soldering, lead-free, electronic, tin, lead, pb-free

INTRODUCTION

Lead-containing solders, particularly tin-lead solders, has been widely used in electronics industry for a long time. This is primarily due to a combined merit of low cost, good soldering properties, adequate melting temperature range, and proper physical, mechanical, metallurgical, and fatigue resistance properties. However, the concern about the toxicity of lead has led to an increase in controls and legislation on the use of lead. As a result, the use of lead in non-solder related materials such as gasoline, and paint have been banned for years. More recently, lead containing solders have been banned for use in potable water piping, food and beverage cans and automobile bodies where they were used in repair applications. As to the electronic industry, the concern on lead-containing solder mainly resides in the potential pollution from the landfill. Although the use of lead in solders for electronics assembly has not been banned yet, the strong trend of moving toward a green world is driving the industry to develop lead-free solder alternatives with an immense enthusiasm. In this article, the status of lead-free developmental works are reviewed and briefly discussed.

CRITERIA

To become a viable lead-free solder alternative for electronics assembly use, it is considered essential for this candidate solder to meet the following criteria:

1. melting temperature similar to Sn-Pb solders, particularly 63Sn-37Pb solder.
2. narrow plastic range.
3. adequate wetting properties to metallizations used in electronics industry.
4. physical properties no poorer than those of Sn-Pb solder.
5. good fatigue resistance.
6. compatible with existing liquid flux systems.
7. adequate shelf life and performance as a solder paste.
8. capable of fabrication into existing physical forms of solder, *i.e.* wire, preforms, ribbon, spheres, powder, paste etc.
9. relatively non-toxic.
10. low dross formation when used in a wave soldering operation.
11. low cost.

ALTERNATIVE ELEMENTS

Virtually all of the lead-free solder alternatives explored so far utilize tin as one of the primary constituent. The other elements which could be incorporated in the alloy systems in order to meet the melting temperature range requirement include, but not limited to, Bi, Cd, In, Zn, Au, Tl, Ga, Hg, Cu, Sb, and Ag. The pros and cons of the low melting point elements addition are briefly summarized in Table 1. On the other hand, the elements which often are used at a lower addition level are summarized in Table 2.

Table 1. Low melting point elements as alloy addition to tin.

Element	Possible wt addition (%)	Solidus range (°C)	Liquidus range (°C)	Toxicity	Cost	Availability
Bi	0-100	138	138-270	No	Acceptable	Moderate
Cd	0-100	188	177-320	High	Acceptable	Moderate
In	0-100	117-150	117-232	No	Medium	Low
Zn	0-90	198	198-400	No	Low	Good
Au	0-82	218-310	218-400	No	V. high	Low
Tl	0-100	165	165-300	V. high	?	Low
Ga	0-100	18	18-232	No	High	Low
Hg	0-100	140	-40-+232	V. high	High	Low

Table 2. Lower level alloying addition to tin.

Element	Possible wt addition (%)	Solidus range (°C)	Liquidus range (°C)	Toxicity	Cost	Availability
Ag	10	221	221-300	No	High	Moderate
Cu	3	227	227-320	No	Low	High
Sb	5	232-236	236-240	No	Moderate	Adequate

The lead content is 13 ppm in Earth's crust; and is 0.003 ppm in seawater. This ample supply results in a very low cost of lead. Therefore, chance is that any lower toxicity substitute metals for lead in solder will be more expensive than lead. It is estimated that 4500 metric tons of lead are consumed per year in the U.S. to manufacture electronic solder. The world wide consumption is about three times of this figure. This volume is quite significant. Consequently, in order to replace lead, the present and future availability of any substitute material should also be examined carefully.

The supply status of some potential candidate elements for lead-free solder alternatives is shown in Table 3. It appears that the current supply of Ga and In is less than the demand as a direct lead replacement option. This suggests that an increase in both capacity and production scale is required in order to allow those elements to become a direct overall lead replacement in solders. As to the rest elements, the world spare capacity is high enough to allow a reasonably short transition period for the lead to be phased out. In the case of Ag and Bi, some effort on the expansion of world production scale and world capacity may be needed if either one ends up as the primary substitute choice of industry.

ALTERNATIVE SOLDER ALLOYS INVESTIGATED RECENTLY

Table 3. Supply status of potential candidate elements for lead-free solder applications

Element	World production (tons)	World capacity (tons)	Spare capacity (tons)
Ag	13,500	15,000	1,500
Bi	4,000	8,000	4,000
Cu	8,000,000	10,200,000	2,200,000
Ga	30	80	50
In	120	> 240	120
Sb	78,200	122,300	44,100
Sn	160,000	241,000	81,000
Zn	6,900,000	7,600,000	700,000

Table 4. Lead-free solder alloys investigated recently.

Alloy category	Composition	Solidus (°C)	Liquidus (°C)	Note	Density	Manufacturer or investigator
Sn-Pb	63Sn-37Pb	183	183	Eutectic	8.40	(Control)
Au-Sn	80Au-20Sn	280	280	Eutectic	14.51	
Bi-Cd	60Bi-40Cd	144	144	Eutectic	9.31	Indium
Bi-In	67Bi-33In	109	109	Eutectic	8.81	Indium
Bi-In-Sn	57Bi-26In-17Sn	79	79	Eutectic		
Bi-Sn	58Bi-42Sn	138	138	Eutectic	8.56	
	95Bi-5Sn	134	251		9.64	Indium
Bi-Sn-Fe	54.5Bi-43Sn-2.5Fe		137			AT&T
Bi-Sn-In	56Bi-42Sn-2In		138			IBM
Bi-Sb	95Bi-5Sb	~275	~308			Ford
In-Ag	97In-3Ag	143	143	Eutectic	7.38	Indium
	90In-10Ag	141	237		7.54	Indium
In-Bi-Sn	48.8In-31.6Bi-19.6Sn	59	59	Eutectic?		
	51.0In-32.5Bi-16.5Sn	60	60	Eutectic	7.88	Indium
In-Sn	60In-40Sn	118	~127			
	52In-48Sn	118	118	Eutectic	7.30	Indium
	50In-50Sn	118	125		7.30	Indium
Sn	100Sn	232	232		7.28	Indium
Sn-Ag	96.5Sn-3.5Ag	221	221	Eutectic	7.36	Indium
	95Sn-5Ag	221	~250			
Sn-Ag-Cu	93.6Sn-4.7Ag-1.7Cu	216	216	Eutectic		Iowa State U
Sn-Ag-Cu-Sb	96.2Sn-2.5Ag-0.8Cu-0.5Sb	210	217			AIM (CASTIN)
Sn-Ag-Sb	65Sn-25Ag-10Sb		233			Motorola
Sn-Ag-Zn	95.5Sn-3.5Ag-1.0Zn		217			AT&T
Sn-Ag-Zn-Cu	95Sn-3.5Ag-1.0Zn-0.5Cu					AT&T
Sn-Bi-Ag	91.8Sn-4.8Bi-3.4Ag		211			Sandia
Sn-Bi-Ag-Cu	91.0Sn-4.5Bi-3.5Ag-1.0Cu		210			Senju
Sn-Bi-Cu-Ag	48Sn-46Bi-4Cu-2Ag					IBM
Sn-Bi-Cu-Ag-P	Bi 0.08-20%, Cu 0.02-1.5, Ag 0.01-1.5, P 0-0.20, rare earth mixture 0-0.20. balance Sn					Cookson
Sn-Cd	67.8Sn-32.2Cd	177	177	Eutectic	7.68	Indium
Sn-Cu	99.3Sn-0.7Cu	227	227			
	99Sn-1Cu	227	227	Eutectic		
	97Sn-3Cu	227	~330			Ford
Sn-Cu-Ag	95.5Sn-4Cu-0.5Ag	225	349 (260)			Engelhard (Silvabrite 100)
Sn-Cu-Sb-Ag	95.5Sn-3Cu-1Sb-0.5Ag		256			Motorola
Sn-In	70Sn-30In	120	~175			
	58Sn-42In	118	145		7.30	Indium
Sn-In-Ag	77.2Sn-20.0In-2.8Ag	175	187		7.25	Indium
Sn-In-Ag-Sb	88.5Sn-10.0In-1.0Ag-0.5Sb		211			Qualitek
Sn-In-Bi	90Sn-8In-2Bi					IBM
	80Sn-10In-10Bi	153	199			IBM
Sn-In-Bi-Ag	78.4Sn-9.8In-9.8Bi-2Ag					
	80Sn-10In-9.5Bi-0.5Ag	179	201			Ford
Sn-Sb	95Sn-5Sb	~234	240			Motorola
Sn-Sb-Bi-Ag	Sn approx 90-95%. Sb 3-5%, Bi 1-4.5, Ag 0.1-0.5					Willard Industries
Sn-Zn	91Sn-9Zn	199	199	Eutectic	7.27	Indium
Sn-Zn-In	87Sn-8Zn-5In	175	188			AT&T
Sn-Zn-In-Ag	87Sn-8Zn-5In-0.1Ag					AT&T
Sn-Zn-In-Cu	87Sn-8Zn-5In-0.1Cu					AT&T

The lead-free solder alloys investigated recently are compiled in Table 4. Also shown are the melting temperature and density of those alloys, whenever they are available. Information shown here provides a profile about current effort of industry. Most of the systems investigated aim at electronic applications. A quick glance at this table confirms that Sn is indeed the primary choice as one of the alloy component.

PROPERTIES OF SOME ALLOY SYSTEMS

Some eutectic alloy systems, such as Bi-Sn, In-Sn, Sn-Ag, Sn-Cu, and Sn-Zn, have been studied very extensively in the past already. Some other systems such as Sn-Bi-Ag, Sn-In-Ag, Sn-Sb, or Sn-Zn-In systems or the eutectic alloys described above doped with other elements are investigated due to their promising mechanical strength and creep resistance. The results of those investigation are briefly summarized below.

58Bi-42Sn

58Bi-42Sn is relatively inexpensive and has a proven track record at IBM® where it has been used in wave soldering of printed circuit assemblies. However the melting point is lower than tin/lead eutectic. Compared with Sn63, the wetting of eutectic Sn-Bi is not as good, but acceptable. This is true for both bare copper and Ni-Au plated substrate. Au dissolves more slowly into molten eutectic 58Bi-42Sn solder than into eutectic Sn-Pb. This may contribute to a reduction in the wetting ability and the formation of intermetallics as well. In general, conventional solders, when Sn is replaced with Bi, are less prone to intermetallics formation. Although the wetting of 58Bi-42Sn seems to be acceptable, the allowed concentration of foreign elements is an order of magnitude lower for eutectic 58Bi-42Sn than for eutectic Sn-Pb solder. Therefore, presence of 0.0002% Phosphorus would cause wetting to degrade. This suggests a potential problem on electroless Ni which usually contains some Phosphorus.

At Sn-Bi soldering operation where Sn-Pb plated components got into the mixture, the 8Sn-52Pb-40Bi eutectic mixture (mp 95°C) formed and became molten during -40 to100°C thermal cycling. Very early failure and extensive porosity is observed, probably a result of local melting during cycling. The shear strength and life in creep rupture tests at 50-80°C decreased relative to joints made on plain Cu.

When the alloy has an equiaxed grain structure, it can be quite ductile and may exhibit superplastic behavior. When Sn63 solder has an equiaxed microstructure, its fatigue life is improved vs a lamellar microstructure. The advantage of Sn63 over 58Bi-42Sn is that an equiaxed microstructure is achievable for Sn63 at typical cooling rates, which seems not to be the case for 58Bi-42Sn . At 100°C, Sn63 is far superior to 58Bi-42Sn , presumably because 100°C is such a high homologous temperature (0.91) for 58Bi-42Sn.

The Utimate Tensile Strength (UTS) data for eutectic Sn-Bi (54-73 MNm^{-2}) are slightly higher than Sn63 (19-56 MNm^{-2}). Between 20 and 60°C, shear strength of eutectic Sn-Bi (25-50 MNm^{-2}) are comparable to eutectic Sn-Pb. At 100C, eutectic Sn-Bi is much weaker than eutectic Sn-Pb. Elongation of eutectic Sn-Bi is more sensitive than eutectic Sn-Pb (i.e. its elongation decreases more rapidly with increasing strain rate).

54.5Bi-43Sn-2.5Fe (Bi-Sn with Fe dispersoid particles)

Mechanical properties of solders can benefit from uniform dispersion of fine precipitates and small effective grain sizes. Therefore, magnetically distributed insoluble Fe particles retard both high-temperature deformation and microstructural coarsening, thus widening the useful service range of Bi-Sn eutectic alloys to much higher homologous temperature than are typical for Sn63. In addition, the presence of a magnetically dispersed three-dimensional network of finely dispersed iron particles in a Bi-43Sn eutectic solder under the same high temperature conditions resulted in a 5X increase in creep resistance at 100°C. Combination of high mechanical strength and high ductility is likely to yield improved fatigue resistance properties in the interconnection. Elements other than Fe can also be used to create fine precipitates. Hence, addition of 1% Cu dramatically slows coarsening of eutectic Sn-Bi, presumably via similar mechanism.

52In-48Sn

52In-48Sn is considered the lowest melting point practical solder. It is often used as the last step in a sequential soldering operation, and for soldering to metallizations on temperature sensitive components. Less than 1%Au is soluble in eutectic 52In-48Sn at 50°K above liquidus temperature. The intermetallic $AuIn_2$ resulted is an effective diffusion barrier to In, Sn, and Au, hence prevents further dissolution of Au plating. Eutectic 52In-48Sn displays fair to acceptable wetting behavior, but only with a relatively active flux. Wetting on Cu, Ni-Sn, and pretinned Kovar (53Fe-17Co-29Ni) can be acceptable at 215°C, but wetting on Au is sluggish and poor.

For a specified creep life, the load was approximately one quarter of the load for eutectic Sn-Pb. Creep behavior of 52In-48Sn is characterized by rapid and extensive deformation leading to early failure. There is no microstructural change like coarsening & recrystallisation that occur in Sn63. This stability is due to rapid recovery of deformation. The isothermal fatigue behavior and fatigue life in temperature cycling test of 52In-48Sn are poorer than that of eutectic Sn-Pb. Compared with high Sn alloys, In alloys is slow in crack propagation. This behavior may contribute to the better fatigue performance of In alloys at low cyclic strain rates versus that of high Sn alloys.

Between 20 and 60°C, shear strength of eutectic 52In-48Sn is much weaker than eutectic Sn-Pb. Rapid drop in shear strength for 52In-48Sn reflect the fact that the homologous temperature at which the testing was done is much higher for eutectic Sn-In (mp 121°C) than for Sn63 (mp 183°C). For 52In-48Sn, the shear strength on Ni is almost 50% lower than for samples on Cu. This may be due to the dissolved Cu into In-Sn, which takes the alloy away from eutectic composition and may harden it as well.

52In-48Sn is relatively ductile. Elongation is reported to be 83% (vs 32% for Sn63) and 36% (vs 22.5% for Sn63). This higher elongation is a result of superplastic behavior in creep under shear loading at temperature above 0.8 of their mp. The superplastic microstructure generally has a longer isothermal fatigue life than non-superplastic. Pb-Sn formed a recrystallized band of material along a region of concentrated shear deformation. This microstructural changes did not occur in the 52In-48Sn samples.

Sn

Tin is mostly consumed by the electronics industry, which uses 60,000 tonnes/yr. Replacing toxic Pb in solders with nontoxic Sn could increase consumption in electronics solders by one third. Compared with Sn63, the wetting of Sn on Cu is superior. Feasibility for eliminating tin lead plating of electronic components by tin plating could be acceptable in many applications where device would not be subjected to sub-zero temperature or where whisker growth would not present problems. Sandia National Lab considers that 100Sn is a viable candidate as a substitute for 60Sn-40Pb.

96.5Sn-3.5Ag

Au dissolves more rapidly into Sn than into eutectic Sn-Pb solder for the same amount of superheating. The same is true for eutectic 96.5Sn-3.5Ag, but it is more tolerant of Au than eutectic Sn-Pb. 96.5Sn-3.5Ag containing 5% Au is ductile and the elongation deteriorated only very little, due to much smaller $AuSn_4$ IMC grain size. On the other hand, Sn63 containing 5% Au is brittle and the elongation decreased dramatically.

Compared with Sn63, the wetting of 96.5Sn-3.5Ag is quite poor. Wetting of 96.5Sn-3.5Ag did not improve significantly in inert atmosphere, perhaps because Ag is not readily oxidized. The poor wettability of 96.5Sn-3.5Ag is caused by high interfacial tension between solder and flux that is probably related to the high surface tension of Ag.

The UTS data for 96.5Sn-3.5Ag (20-56 MNm^{-2}) are comparable with or slightly higher than Sn63 (19-56 MNm^{-2}) (and slightly lower than eutectic Sn-Bi (54-73 MNm^{-2})). Between 20 and 60°C, shear strength of eutectic Sn-Ag (25-50 MNm^{-2}) are comparable to eutectic Sn-Pb. Eutectic 96.5Sn-3.5Ag has comparable elongation to Sn-Pb at moderate strain rates at R.T., but is probably less strain rate sensitive (i.e. its elongation does not rise as rapidly at slow strain rates). At strain rate of $6.2\ x10^{-4}s^{-1}$, strain hardening and softening rates of Sn63 is much faster than 96.5Sn-3.5Ag.

Creep resistance in descending order was: Sn62 > 96.5Sn-3.5Ag > Sn63 > 58Bi-42Sn > 60Sn-40Pb > 70Sn-30In > 60In-40Sn. 96.5Sn-3.5Ag absorbed considerably more strain before failure than Sn63. The acceleration factor in a thermal cycling test vs field service will be greater for 96.5Sn-3.5Ag than for Sn63. 96.5Sn-3.5Ag has far superior R.T. isothermal fatigue behavior to Sn63 at high shear strain amplitudes (due to the resistance of 96.5Sn-3.5Ag to fatigue crack initiation), but is far inferior to Sn63 at low strain amplitudes. For 95Sn-5Ag, no microstructure coarsening occurred. Only the IMC layer thickness increased. Cracks propagated at the solder/intermetallic interface and through the solder. However, no complete failures were observed after 70 cycles.

96.5Sn-3.5Ag eutectic solder has superior overall property and is suitable for solder interconnects in thick film automotive electronics packages when used with a mixed bonded Ag conductor.

95.5Sn-3.5Ag-1Zn

95.5Sn-3.5Ag-1Zn (mp 217C) can significantly improve mechanical strength of 96.5Sn-3.5Ag by as much as 48% while maintaining the same level of ductility. The high temperature creep resistance of Zn-containing alloy improved more than an order of magnitude. Strengthening is attributed to a substantial refinement of precipitates in the solidification microstructure. It also significantly improved creep resistance. Zn is incorporated in the more corrosion resistant Ag_3Sn precipitates, leaving Sn-rich matrix primarily free of Zn in solid solution. It refines the microstructure and suppresses formation of Sn dendrites while making Ag_3Sn precipitates finer & more spherical. Zn also suppresses mp slightly. The continuous Sn phase may be prone to whisker and tin pest.

95Sn-3.5Ag-1Zn-0.5Cu

Addition of small amount (<1%) of Cu refines the effective grain size while retaining uniform distribution of Ag_3Sn precipitates in the solidification microstructure, thus dramatically improves ductility in the 95.5Sn-3.5Ag-1Zn alloy. The quaternary 95Sn-3.5Ag-1Zn-0.5Cu has better mechanical property than 96.5Sn-3.5Ag because it has a uniform fine dispersion of precipitates and small effective grain size. Addition of Cu or Zn >1% is not desirable as it causes precipitates of additional IMC phases that deplete the finely dispersed precipitates in the surrounding matrix and induces non-uniformities in microstructure that consequently deteriorates the mechanical properties.

91.8Sn-4.8Bi-3.4Ag

Sandia Lab has developed 91.8Sn-4.8Bi-3.4Ag with liquidus temperature 211°C. In the study of AT&T, this alloy and four other alloys: eutectic Sn-Bi and Sn-Ag, 77.2Sn-20In-2.8Ag (Indium), 96.2Sn-2.5Ag-0.8Cu-0.5Sb (AIM) are investigated. All are concluded to be feasible for 0.4 mm pitch SMT assembly but with narrower processing windows. A similar alloy with composition 91.0Sn-4.5Bi-3.5Ag-1.0Cu was developed by Senju with a reported liquidus temperature 210°C.

99.3Sn-0.7Cu

Alloys based on the binary 99.3Sn-0.7Cu eutectic compositions showed the good potential as replacements for Sn-Pb in Pb-free wave and reflow soldering processes. In increasing order of fatigue resistance were: 63Sn-37Pb; 64Sn-36In; 42Sn-58Bi; 50Sn-50In; 99.25Sn-0.75Cu; 100Sn; 96Sn-4Ag.

95.5Sn-4Cu-0.5Ag

Engelhard developed a Pb-free plumbing solder, 95.5Sn-4Cu-0.5Ag (Silvabrite 100) with liquidus temperature 260°C, to meet new safe drinking water regulations. This is a Cu-rich near eutectic alloy, consisting of Sn with small concentration of intermetallic phases. The solidified solder film is very grainy and exhibits a lumpy appearance. Sandia Lab concluded that 96.5Sn-3.5Ag, 95.5Sn-4Cu-0.5Ag, 95Sn-5Sb, and 100 Sn are all viable candidates as substitutes for Sn60. Contact angle of 96.5Sn-3.5Ag is between 60 and 75 degree, due to the inability of flux to significantly lower solder/flux interfacial tension. It also wets slower than other solders. 95Sn-5Sb and 95.5Sn-4Cu-0.5Ag exhibit a contact angle between 35 and 55 degree. The wetting rate is comparable to Sn60. 60Sn-40Pb shows the smallest contact angle, between 20 and 35 degree.

HP studied the wetting of several alloy systems. Compared with Sn63, the wetting of Sn on Cu is superior, 95.5Sn-4Cu-0.5Ag and eutectic Sn-Bi acceptable, and 96.5Sn-3.5Ag is quite poor.

Motorola developed a similar alloy system, 95.5Sn-3Cu-1Sb-0.5Ag, with a reported liquidus temperature 256°C.

77.2Sn-20.0In-2.8Ag

In general, the physical properties of 77.2Sn-20.0In-2.8Ag are fairly comparable to those of 63Sn-37Pb. In addition, this alloy has both a higher tensile strength and shear strength than 63Sn-37Pb. Besides, although having a higher modulus, the tensile elongation of 77.2Sn-20.0In-2.8Ag is still greater than that of 63Sn-37Pb. This behavior suggests that this Pb-free alloy has adequate ductility to be fabricated into various physical forms, such as wires, ribbons, preforms, etc. The identical value in Poisson's ratio for both solders eliminates concern on the possible impact due to variation in the solder volume under stress of this Pb-free alloy. Overall, the data indicate that in bulk form, 77.2Sn-20.0In-2.8Ag exhibits superior mechanical properties than 63Sn/37Pb.

The steady creep rate of 77.2Sn-20.0In-2.8Ag is about two and half orders of magnitude lower than that of 63Sn-37Pb. This superior creep resistance behavior suggests an improved solder joint reliability of 77.2Sn-20.0In-2.8Ag alloy.

Melting of this alloy occurs between 174.7°C and 186.5°C. Regardless of the small temperature difference at the onset of melting process, the softening point of 77.2Sn-20.0In-2.8Ag is found to be almost identical to that of 63Sn-37Pb. This result strongly suggests that the upper limit of the service temperature of both solders should be very comparable.

77.2Sn-20.0In-2.8Ag wets somewhat slower than the conventional 63Sn-37Pb. However, the difference in the wetting time is fairly insignificant when compared with the soldering time typically employed by the assembly process. The wetting force of 77.2Sn-20.0In-2.8Ag also appears to be slightly lower than that of 63Sn-37Pb. The small difference observed suggests that any effect should be negligible. Therefore, it can be concluded that, in a practical sense, the wetting behavior of 77.2Sn-20.0In-2.8Ag is comparable to that of 63Sn-37Pb solder. Evaluation results based on surface mount assembly and temperature cycling tests indicate that this Sn-In-Ag solder is a very viable candidate as substitute for Sn63.

Two quaternary alloy systems invloving Sn-In-Ag are also developed. 88.5Sn-10.0In-1.0Ag-0.5Sb (Qualitek) is reported to exhibit liquidus 197°C (and 211°C), solidus 188°C, and a dull gray appearance. 80Sn-10In-9.5Bi-0.5Ag (Ford) exhibits liquidus 179°C and solidus 201°C, and is reported to be creep and fatigue resistant. The latter has a composition similar to the system 80Sn-10In-10Bi (liquidus 153°C, solidus 199°C) investigated by IBM.

95Sn-5Sb

95Sn-5Sb is a viable candidates as substitutes for Sn60. The contact angle of wetting for 95Sn-5Sb is between 35 and 55 deg. This is larger than that of 60Sn-40Pb (contact angle between 20 and 35 deg). However, the wetting rate is comparable to that of Sn60. 95Sn-5Sb has excellent shear strength at 100°C.

91Sn-9Zn

91Sn-9Zn has been used to solder aluminum using specialized fluxes. Because of its corrosion potential, zinc poses a concern. Solder paste incorporating this alloy would have a poor shelf life due to attack on the metal spheres by the organic acids or bases present in the flux vehicle. Additionally, the alloy drosses excessively when used in a wave soldering operation. The contact angle of some binary eutectic alloys studied, using rosin-isopropanol flux is shown below: 58Bi-42Sn 40 deg (166°C) < 96.5Sn-3.5Ag 45 deg (250°C) < 91Sn-9Zn 60deg (225°C). These angles were little affected by a number of 1% ternary additions to the solders.

86Sn-9Zn-5In

AT&T investigated 86Sn-9Zn-5In (mp 175-188°C), and found that active flux was needed under air atmosphere. In addition, presence of small amount of 108°C ternary eutectic 52In-46Sn-2Zn may be detrimental to mechanical property. However, small alloying additions of Ag dramatically improve mechanical property of 87Sn-8Zn-5In alloy, due to elimination of the coarse and nonuniform distribution of plate-like dendrites and refining effective grain size in solidified microstructure.

PROS AND CONS OF PB-FREE ALTERNATIVES

Table 5 lists a brief description about the pros and cons for some lead-free solders. Apparently, none of the alloys investigated can meet all the criteria listed above. Relatively, Sn-In-containing binary, ternary, or quaternary alloy systems are more promising in terms of solder and soldering performance, although the price of In may be a concern. Eutectic Sn-Ag solder doped with Zn, Cu, or Sb exhibits good mechanical strength and creep resistance, due to refined microstructure. However, the melting range is about 30 to 40°C than eutectic Sn-Pb, therefore may have only limited potential. Bi-containing alloys also show very good potential. The Bi-Sn systems doped with other elements are particularly interesting, and may have a niche in the low temperature soldering field. Eutectic Sn-Cu has a good potential due to its good fatigue resistance, although the melting point may be slightly too high. Eutectic Sn-Zn system modified with In and/or Ag may be promising in mechanical properties. However, excessive drossing and high reactivity toward flux may be a concern. Finding a lead-free alternative for high temperature solders, such as 95Pb-5Sn, with melting temperature around or higher than 300°C presents the biggest challenge to the industry. So far, only Au-Sn, Bi-Sb, and Sn-Cu systems may be somewhat close in terms of melting temperature range.

SUMMARY

This paper reviews the status of lead-free solder developmental works. Some of the solder systems, including Bi-Sn, Bi-Sn-Fe, In-Sn, Sn, Sn-Ag, Sn-Ag-Zn, Sn-Ag-Zn-Cu, Sn-Bi-Ag, Sn-Cu, Sn-Cu-Ag, Sn-In-Ag, Sn-Sb, Sn-Zn and Sn-Zn-In are discussed in more details, while the others are briefly commented on. In general, compared with eutectic Sn-Pb solder, all the lead-free solder alternatives investigated more or less exhibit some shortcomings, such as price, physical, metallurgical, or mechanical properties. Relatively, Sn-In-containing systems are more promising in terms of solder mechanical properties and soldering performance, although the price of In may be a concern. Eutectic Sn-Ag solder doped with Zn, Cu, or Sb exhibits good mechanical strength and creep resistance, due to refined microstructure. The Bi-Sn systems doped with other elements may have a niche in the low temperature soldering field. Eutectic Sn-Cu has a good potential due to its good fatigue resistance. Eutectic Sn-Zn system modified with In and/or Ag may be promising in mechanical properties. Finding a lead-free alternative for high temperature solders presents the biggest challenge to the industry.

Table 5. Pros and cons of lead-free solders investigated recently.

Composition	Advantages	Disadvantages
63Sn-37Pb	Overall good properties, low cost	Structural coarsening; prone to creep
80Au-20Sn	Creep & corrosion resistant	Hard & brittle; melting point too high; expensive
60Bi-40Cd		Toxic
67Bi-33In		Poor wetting on Cu
57Bi-26In-17Sn		Melting point too low
58Bi-42Sn	Good fluidity	Strain rate sensitivity; poor wetting
95Bi-5Sn		
54.5Bi-43Sn-2.5Fe	Creep & fatigue resistance	Developmental stage
56Bi-42Sn-2In		
95Bi-5Sb		
97In-3Ag		Poor wetting; expensive
90In-10Ag		
48.8In-31.6Bi-19.6Sn		
51.0In-32.5Bi-16.5Sn		
60In-40Sn		
52In-48Sn	Au soldering	Mp too low; poor fatigue & mechanical properties; expensive
50In-50Sn		
100Sn	Wetting	Whisker & tin pest growth
96.5Sn-3.5Ag	Good strength; creep resistance	Poor isothermal fatigue at low strain; mp slightly too high
95Sn-5Ag	No coarsening	
93.6Sn-4.7Ag-1.7Cu		
96.2Sn-2.5Ag-0.8Cu-0.5Sb		Slightly high melting point
65Sn-25Ag-10Sb	High strength	Expensive; melting point too high
95.5Sn-3.5Ag-1.0Zn	Good mechanical strength	Slightly high melting point
95Sn-3.5Ag-1.0Zn-0.5Cu	Good ductility	Slightly high melting point
91.8Sn-4.8Bi-3.4Ag		
48Sn-46Bi-4Cu-2Ag		
Bi 0.08-20%, Cu 0.02-1.5, Ag 0.01-1.5, P 0-0.20, rare earth mixture 0-0.20. balance Sn		
91.0Sn-4.5Bi-3.5Ag-1.0Cu		
67.8Sn-32.2Cd		Toxic
99.3Sn-0.7Cu	Fatigue resistance	
99Sn-1Cu		
97Sn-3Cu		
95.5Sn-4Cu-0.5Ag		Melting range too wide and too high
95.5Sn-3Cu-1Sb-0.5Ag		Melting point too high
70Sn-30In		Poor creep
58Sn-42In		
77.2Sn-20.0In-2.8Ag	Creep resistant; virtually drop-in replacement	Slightly expensive
88.5Sn-10.0In-1.0Ag-0.5Sb		
90Sn-8In-2Bi	High strength	Melting point too high
80Sn-10In-10Bi		
78.4Sn-9.8In-9.8Bi-2Ag		
80Sn-10In-9.5Bi-0.5Ag	Creep and fatigue resistant	Slightly expensive
95Sn-5Sb	Creep resistant; good high temp shear; mechanically strong	Melting point too high
Sn approx 90-95%. Sb 3-5%, Bi 1-4.5, Ag 0.1-0.5		
91Sn-9Zn	Good strength; abundant	Poor corrosion resistance & wetting; high drossing
87Sn-8Zn-5In		Poor wetting; eutectic 52In-46Sn-2Zn (106C) a concern
87Sn-8Zn-5In-0.1Ag		