Future Lead-Free Solder Alloys and Fluxes – Meeting Challenges of Miniaturization

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Abstract

In general, new lead-free solder alloys with the following characteristics are desired in order to enable the continuation of miniaturization trend: (1) alloy with a reduced melting temperature, (2) alloy with a better solder spread, (3) alloy with a slower wetting speed at melting temperature, (4) a softer alloy, or alloy with a reduced voiding tendency or greater ductility, (5) alloy with a refined grain size, (6) alloy with low tendency to form large IMC plate, (7) alloy with a higher resistance toward corrosion and electrochemical migration, (8) alloy with a greater oxidation resistance. On the other hand, no-clean fluxes with the following features are needed: (1) reduced volatile, (2) halide-free, (3) greater fluxing capacity, (4) higher residue resistivity, (5) more resistant to oxidation and charring, (6) more efficient oxidation barrier, (7) lower activation temperature, (8) slower wetting speed when solder begins to melt, (9) less spattering, (10) higher probe penetratability, (11) capability of inducing nucleation of solder upon cooling, and (12) greater resistance against slump.

Introduction

The world is moving rapidly toward green manufacturing. Lead-free soldering, as originally driven by ROHS of Europe, are becoming the main stream for electronic industry, and the less toxic Sn-based alloys such as SnAg, SnCu, or SnAgCu are the prevailing choices. However, the selection of ideal lead-free alloys appears to be a moving target, since the miniaturization trend of the electronic industry is constantly imposing new criteria hence new challenges on the solder materials. With decreasing size of pad, through-hole, microvia, and pitch, the substrates and components structure becomes more delicate, and the solder joints become more vulnerable. Increase in portability of more devices further raises the bar for shock resistance of solder joints. Miniaturization also imposes a great challenge on the chemistry of fluxes, due to the increasing amount of oxides and requirements for no-clean applications. In this article, the desired features of future lead-free solder alloys and fluxes will be presented, and some of the promising approaches of achieving the targeted performance will be discussed.

Miniaturization Trend

Miniaturization is the most dominant trend in electronic industry for the past several decades. In order to pack more functions into a smaller device, everything within the device has to shrink in size. For example, Fig. 1 shows the High Density Interconnect Roadmap for Notebooks presented by Intel [1]. Both through-hole pitch and BGA pad pitch decrease with time. Furthermore, for BGA package, the inner diameter of microvia in pad (μVIP) will reduce from 125 microns for staggered pattern in 2008 to 88 microns for stacked pattern in 2012. A natural outcome of the miniaturization trend is emergence of a wide variety of portable devices, such as cell phones, PDA, camcorder, MP3, MP4, etc..

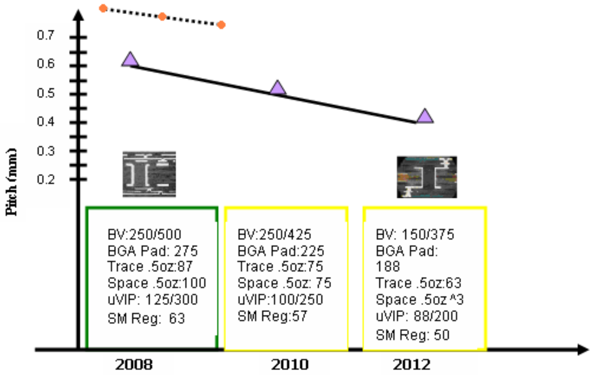


Fig. 1 HDI Roadmap for Notebooks [1]

While miniaturization is the dominant trend, also true is the drive toward cost reduction and environmentally sustainable manufacturing. The latter is best exemplified by the requirement of lead-free soldering dictated by the European RoHS legislation. The cost reduction trend is well illustrated by iNEMI roadmap, as shown in Fig. 2. Here the reduction in operating costs in 2015 is predicted to drop to 40% of 2003 level, through multiple practices such as the reduction in cycle time, setup time, and use of low temperature lead-free solder alloys.

Future Lead Free Solder Alloys

1. Process Temperature Challenge

Reduction in size of microvia in pad inevitably will result in a greater sensitivity toward mismatch in coefficients of thermal expansion (CTE). This is true whether this mismatch occurs between substrate materials and interconnect materials, or between components and printed circuit board. The higher the soldering temperature is, the greater the impact of mismatch in CTE will be.

Parameter	Definition	2003	2005	2007	2009	2015
Solder Pastes	Lead-free % US	<1%	10%	20%	25%	95%
	Lead-free % WW	<5%	50%	75%	90%	95%
	Alloy	SnPb	SAC	SAC	SAC	Low Temp.
	Halogen-free	80%	80%	85%	90%	95%
	Recycle Ratio	<1%	<1%	5%	10%	25%
Parameter	**Metric**	**2003**	**2005**	**2007**	**2009**	**2015**
Stencil Capability	Extreme for solder paste volume	0402-pin in paste	.4mm CSP's-pin in paste	0201- pin in paste	01005-pin in paste	01005- pin in paste
Total Cycle Time	Transport in, board alignment, transport out	10 seconds	6 seconds	5 seconds	4 seconds	3 seconds
Total Setup Time	Total change time of existing products	20 mins	15 mins	10 mins	8 mins	3-5 mins
Parameter	**Metric**	**2003**	**2005**	**2007**	**2009**	**2015**
Cost of Operation, Energy and Consumption	Reduction in operating costs	100%	70%	60%	50%	40%
Flux Management	Collection of flux and solvent volatiles in reflow	Single Pass Collection	Filters	Full System Filter	Self Clean	Advanced materials and flux chemistries to reduce contaminates
Lead-Free Processing	The ability to produce lead-free and financial impact	Concerns about ability, initial investigation . Investment in new equipment	Qualifying products Qualifying processes, new equipment and upgrades, nitrogen processing	Required proven capability	Required , proven	New possible alloys

Fig. 2 SMT industries latest trends - board assembly [2]

Conductive anodic filament (CAF) is another issue. CAF is formation of conductive copper salt filament, starting from anode and growing toward cathode, along the delaminated interface between resin binder and glass fiber [3], as demonstrated in Fig. 3. Often it is initiated by the cracks formed between resin and fiber during mechanical through-hole drilling process, and is aggravated by delamination caused by a high soldering temperature [4]. Even in the absence of mechanical drilling, such as substrates with microvia in pad, the CAF symptom can still be observed, and CAF is a concern within industry at via-via spacing less than 15 to 20mils [1]. With reduction in pitch dimension, chance of circuit short caused by CAF will increase significantly.

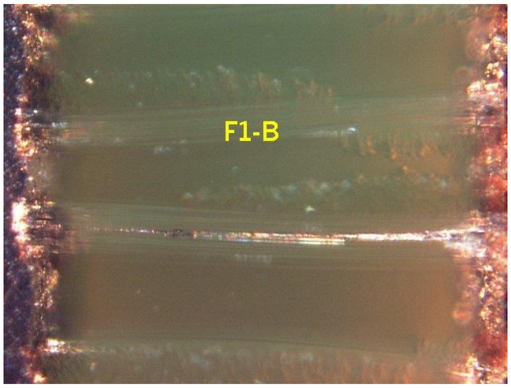


Fig. 3 Formation of conductive anodic filament [1].

Apparently, to avoid the problems described above, a lower soldering temperature is highly desirable. In other words, a solder with a lower melting temperature will be desired. Alloys of this type can be achieved with the use of Bi or In, such as 58Bi42Sn or 52In48Sn. The reflow process of the former can be conducted using a profile with a peak temperature of 170ºC [5].

Those low melting temperature alloys can be further improved by adding a small amount of additives, such as 57Bi42Sn1Ag (138-140°C) [6]. In this case, addition of Ag greatly increases the ductility of eutectic BiSn alloy.

2. Wetting Spread Challenge

Miniaturization often results in a reduced wetting. Upon soldering, even if the flux quantity and dimension of parts/pads are reduced in proportion, the oxide thickness does not decrease in proportion, thus consequently results in a poorer wetting.

At wave soldering, reduction in hole size and increase in aspect ratio of through-hole constantly result in an increase in difficulty in hole filling at wave soldering [7-9], as demonstrated in Fig. 4. This reduction in hole filling may be attributed to a more constrained laminar fluid flow within a tube. This viscosity constraint can be addressed by process, including (1) allowing a longer flow time, such as a longer contact time [9], (2) reducing the viscosity, such as use of a higher solder pot temperature [9]. Use of a longer contact time actually also causes an increase in board temperature, thus indirectly results in a reduced liquid solder viscosity within the barrel.

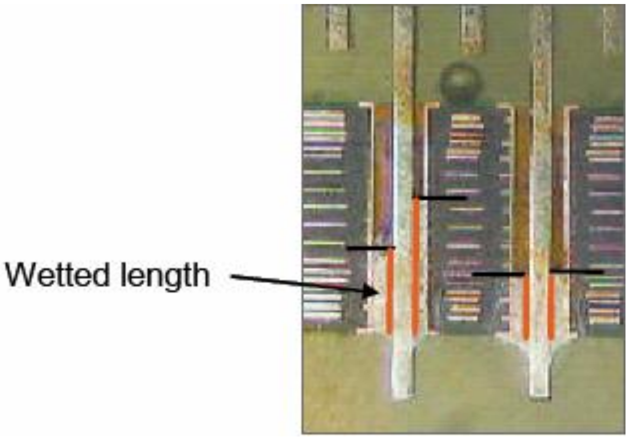


Fig. 4 Partial hole-fill at wave soldering [7].

Alloy-wise, use of solder alloy with a lower viscosity should help both solder spread and hole-filling directly. On the other hand, alloy with a lower surface tension helps spreading or wicking [10]. Use of elements with low surface tension, such as Bi, P, or Sb, in the alloy often improves wetting considerably. Table 1 shows the surface tension of several elements used in solders [11]. Fig. 5 shows that wetting time reduces with decreasing surface tension [12].

Table 1 Surface tension of some elements used in solders [11].

Elements	Surface Tension (N/m) at mp	Atm.
Ag	0.926	Vac.
Al	0.865	Vac.
Au	1.130	He
Bi	0.376	Vac.
Ce	0.740	Vac.
Co	1.880	Vac.
Cu	1.300	Vac.
Fe	1.880	Vac.
Ga	0.708	Vac.
Ge	0.589	Vac.
In	0.558	Vac.
La	0.720	Vac.
Mn	1.100	Ar
Ni	1.725	Vac.
P	0.071	--
Pb	0.462	Vac.
Pd	1.500	Vac.
Pt	1.865	Vac.
Si	0.727	He
Sb	0.350	Ar
Sn	0.537	Vac.
Ti	1.650	Vac.
Zn	0.768	Vac.

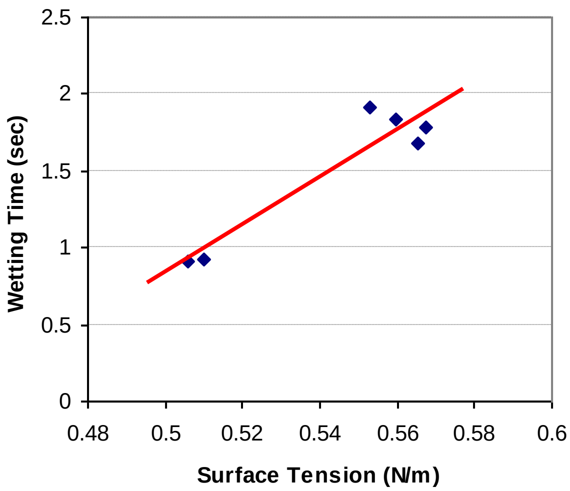


Fig. 5 Relation between solder surface tension and wetting time [12]

3. Voiding Challenge

A reduced joint size is also more prone to have void formation, mainly due to a greater difficulty in wetting, as discussed in previous section. At soldering, the void formation is caused by joint interior outgassing when the solder is at molten state [10], and can be reduced by either reducing the flux outgassing or by increasing the liquid solder wetting. Hence, approaches for improving the solder wetting will also reduce voiding. For instance, decrease in solder surface tension will reduce the voiding [12], as shown in Fig. 6.

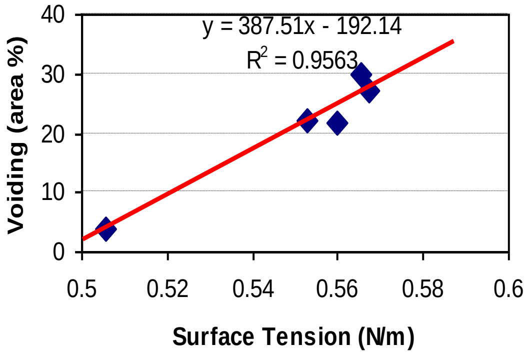


Fig. 6 Relation between solder surface tension and voiding [12].

4. Wetting Speed Challenge

Decrease in discrete component size inevitably will result in an increase in vulnerability toward tombstoning, skewing, or billboarding. This is attributed to a greater difficulty in an accurate registration at component placement [10]. Although many approaches can be used to reduce these types of defect rate, such as decrease in flux wetting speed or increase in reflow soaking time, the most effective approach will be a decrease in solder wetting speed at onset of solder melting [10,12].

Although increase in solder surface tension will reduce the wetting speed, as shown in Fig. 5, it will also cause an increase in horizontal pulling force of components, thus aggravating the problem. The net effect is found to be an increase in defect rate. Fig. 7 shows that eutectic 95.5Sn3.5Ag1Cu exhibits a higher tombstoning rate than eutectic 63Sn37Pb at vapor phase reflow [12]. The surface tension of 95.5Sn3.5Ag1Cu and 63Sn37Pb is 0.56 and 0.51 N/m, respectively.

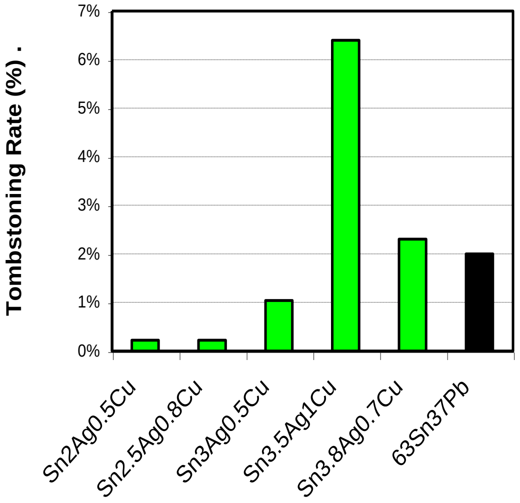


Fig. 7 Tombstoning rate of solder pastes with vapor phase reflow process. Here SnAgCu and SnPb pastes were reflowed at 260°C and 215°C, respectively [12].

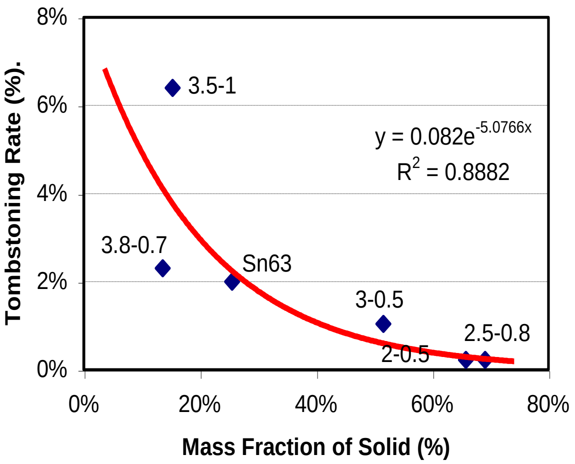


Fig. 8 Relation between mass fraction of solid at onset of melting and tombstoning rate of SnAgCu system. The X and Y in data label refer to Ag and Cu content respectively of given SAC alloys [12].

However, an increase in liquid solder pasty behavior will definitely slow down the wetting speed, thus reduce the defect rate. Fig. 8 shows the tombstoning rate decreases with increase solid content of solder at onset of melting temperature. This phenomenon is also illustrated in Fig. 7, where SnAgCu family is listed in the order of increasing Ag content, with 95.5Sn3.5Ag1Cu as ternary eutectic composition. The solid content of solder increases with increasing deviation in Ag content from 3.5Ag, as shown in Fig. 9.

5. Fragility Challenge

This reduction in the size of solder joints increases vulnerability toward shock cracking. This vulnerability is further aggravated by the shift of solder alloy from SnPb to lead-free solders, due to a higher hardness of the lead-free alloys such as SnAgCu. Although reduction in Ag or Cu content will reduce the hardness and consequently the fragility [13], the joints are still more prone to drop failure than eutectic SnPb joints [14].

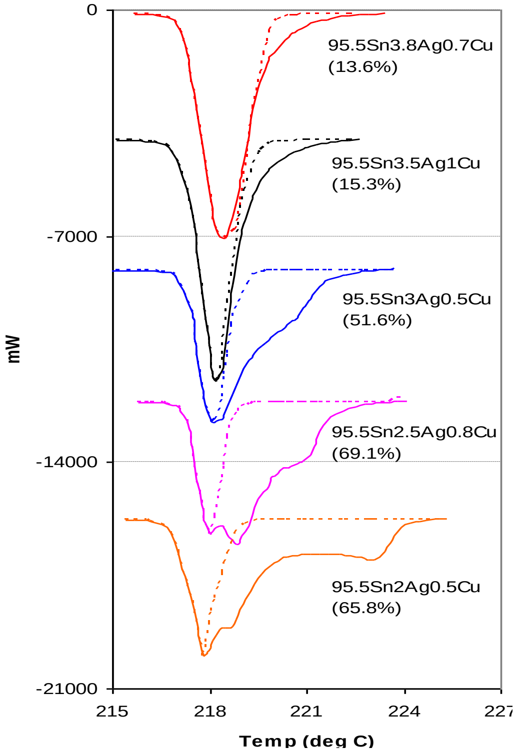


Fig. 9 Determination of fraction of solid (expressed in percentage) of SnAgCu alloys at onset of melting based on symmetry approximation [12].

This fragility can be reduced by adding small amount of elements such as Mn, Ti, Ce, Bi, Y as reported by Liu et al [14], or Ni, Co, Pt as reported by Amagi [15]. Fig. 10 demonstrates the effect of adding Mn, Ti, etc. to SAC105 on drop test performance before and after

150ºC aging for 4 weeks [14]. The performance of some doped SAC105 alloys is better than that of SnPb joints, particularly after harsh thermal aging treatment.

The fragility could also be reduced by dopants which reduce Kirkendall void formation, such as Ni, In [16], high Cu [17], or by employing high Cu content which reduces intermetallic compound spalling phenomenon [18] and converts the solder to ductile material at 2w/w% Cu concentration [19].

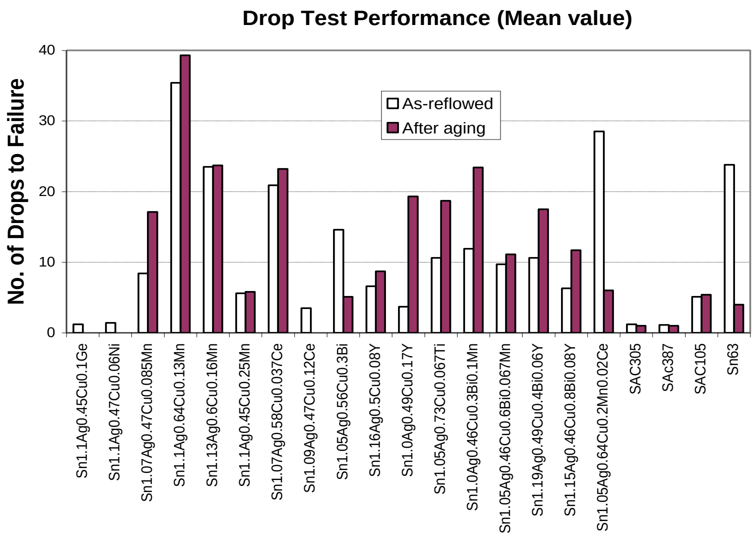


Fig. 10 Mean values of drop test results for as-reflowed and after aging (150°C/4 weeks) for solder joints formed between NiAu and NiAu finishes [14].

The fragility of lead-free solder joints can also be aggravated by formation of single grain for the solder joint. This probability is expected to increase with decreasing joint size. Since Sn is the dominant constituent of lead-free alloys, the crystal formed is primarily anisotropic Sn crystal, with elastic modulus and CTE of Sn crystal shown in Fig. 11 [20]. When the c-axis is parallel to the Cu pad, the CTE of solder will be about 2 times of Cu, which is 16 ppm/°C, and the rigidity of solder is the highest in this orientation, therefore being the least compliant. As a result, the joint will be most prone to cracking upon drop.

Since it is difficult to control the orientation of Sn crystal, refining the grain size appears to be a more feasible approach in nullifying the unfavorable orientation effect of Sn crystal, and can be achieved by adding small amount of dopants. Elements such as Ti, which suppress the undercooling hence suppress instantaneous formation of large crystals, or Ni, Co are possible candidates in refining the grain size.

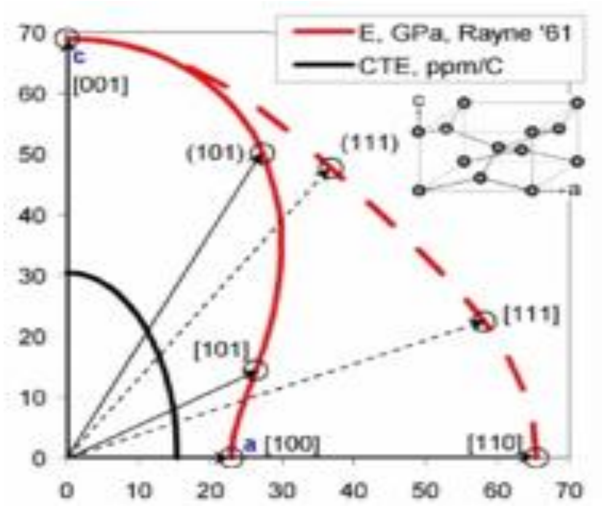


Fig. 11 Anisotropic elastic (red) and thermal expansion (black) properties of the tin unit cell vary by a factor of 3 or 2, respectively (the length of the vector from the origin to the indicated line gives property value). The CTE is isotropic only on the (001) plane [Courtesy of Bieler et al.].

6. Intermetallic Compound Plate Challenge

SnAgCu tends to form Ag_3Sn intermetallic compound (IMC) plate upon extended heating or slow cooling [21, 22]. In the case of solder bump, the plate may pre-exist in the solder sphere, and protruding out upon ball mounting, as shown in Fig. 12. The interface between IMC plate and solder is more prone to cracking due to mismatch in CTE, thus compromises the reliability of solder joints [22]. In a study of IBM, 97Sn2.3Ag0.5Cu0.2Bi is concluded as a relatively optimal composition.

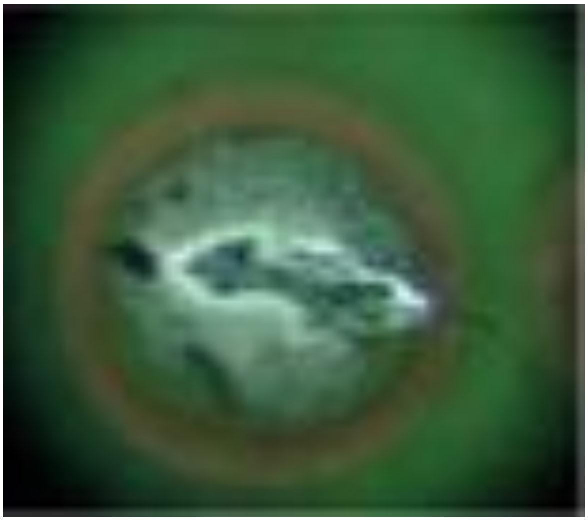


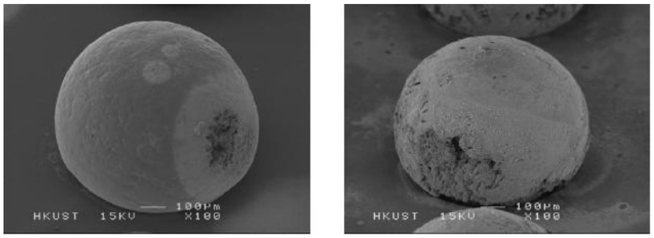
Fig. 12 Ag_3Sn IMC plate formed at 95.5Sn3.8Ag0.7Cu ball mounting.

This IMC plate threat increases with further miniaturization. Reducing Ag content will decrease the probability of IMC plate formation [22], but likely at the expense of creep resistance. Adding additives such as Zn has been observed to effectively suppress this IMC plate formation [17], possibly due to reduction in undercooling of joints.

7. Corrosion Challenge

The threat on reliability caused by corrosion is aggravated by miniaturization. Corrosion rate is normally expressed as μm metal etched/year. For a given set of solder material and corrosive reactants, the corrosion rate is typically constant, regardless of the extent of miniaturization. In other words, when everything else being equal, a smaller solder joint will be depleted by corrosion sooner than a bigger joint. Changing from SnPb solders to lead-free solders further worsens the problem, since lead-free solders are more prone to corrode than SnPb solders, as demonstrated by Fig. 13 [23]. The greater vulnerability of lead-free solders toward corrosion is attributed to galvanic corrosion induced by the presence of Ag (see Table 2).

Corrosion can also aggravate electrochemical migration (ECM). With reducing pitch and spacing, the tolerance of electronic products toward dendrite formation diminishes rapidly. For instance, J-STD-004A pass criterion for ECM test is "no filament growth that reduces the conductor spacing by more than 20%". Accordingly, formation of a 4 mil dendrite will be acceptable for a 25 mil spacing application, but not acceptable for a 10 mil spacing application.



96 hours (Sn-Pb) 96 hours (SAC)

Fig. 13 Surface morphology changes of solder ball after the salt spray test [23].

To minimize corrosion issue, future alloys should avoid composition with propensity toward galvanic corrosion, such as combination of Sn with noble metals, as exemplified in Table 2. For Sn-based alloys, promising alloying additions for low galvanic corrosion propensity may include elements such as Ni or Co. The possible IMC formation with Sn may include Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4 for Ni, and Co_3Sn_2, CoSn, $CoSn_2$ for Co.

Table 2 Electrochemical potential of some reactions [11].

Reaction	E°, V
$Au^{+} + e \Rightarrow Au$	1.692
$Pt^{2+} + 2e \Rightarrow Pt$	1.118
$Pd^{2+} + 2e \Rightarrow Pd$	0.951
$Ag^{+} + e \Rightarrow Ag$	0.7996
$Cu^{+} + e \Rightarrow Cu$	0.521
$Cu^{2+} + 2e \Rightarrow Cu$	0.3419
$Ge^{2+} + 2e \Rightarrow Ge$	0.24
$Ge^{4+} + 4e \Rightarrow Ge$	0.124
$Pb^{2+} + 2e \Rightarrow Pb$	-0.1262
$Sn^{2+} + 2e \Rightarrow Sn$	-0.1375
$Ni^{2+} + 2e \Rightarrow Ni$	-0.257
$Co^{2+} + 2e \Rightarrow Co$	-0.28
$In^{3+} + 3e \Rightarrow In$	-0.3382
$Ga^{2+} + 2e \Rightarrow Ga$	-0.560
$Zn^{2+} + 2e \Rightarrow Zn$	-0.7618
$V^{2+} + 2e \Rightarrow V$	-1.175
$Mn^{2+} + 2e \Rightarrow Mn$	-1.185
$Ti^{2+} + 2e \Rightarrow Ti$	-1.630
$Al^{3+} + 3e \Rightarrow Al$	-1.662
$Y^{3+} + 3e \Rightarrow Y$	-2.372
$La^{3+} + 3e \Rightarrow La$	-2.522

8. Oxidation Challenge

The combined trend of miniaturization and low cost greatly challenges the tolerance of solder toward oxidation. For reflow soldering under air, oxidation of the fine solder powder will increase with reducing particle size due to the increasing exposure surface area of powder. Furthermore, the oxidation accelerates when the powder is getting very small, as reflected by the higher oxide thickness observed for very fine powder (see Fig. 14).

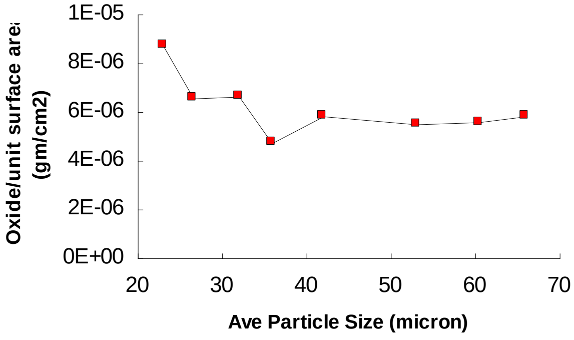


Fig. 14 Relation between Sn63 powder size and oxide thickness [24]

Shifting from SnPb to Pb-free soldering enhances the challenge of oxidation due to a higher reactivity of Sn than Pb, as indicated by the higher Gibb's free energy of formation of tin oxide than lead oxide (see Table 3) [25]. Furthermore, Pb-free alloys containing rare earth metals or transition metals often are prone to oxidize. For instance, 96.5Sn3.0Ag0.5Cu0.019Ce oxidizes easily under harsh reflow condition, mainly due to the high free energy of formation of Ce oxide [26]. In order to minimize the tendency of oxidation, addition of elements such as Ge or P may be beneficial.

Table 3 Gibbs free energy of metal oxide formation

Metal Oxides	ΔGº (J/mol)
Ce_2O_3	-1,599,101
Al_2O_3	-1,508,241
Ga_2O_3	-907,243
In_2O_3	-729,731
SnO_2	-430,398
NiO	-173,741
PbO	-153,024
Cu_2O	-124,461
CuO	-64,793
PdO	-49,041

Note: ΔGº value was calculated for oxides formed at 223ºC (500ºK) based on the coefficient value published in CRC Handbook of Chemistry and Physics, 75th edition [25].

Future Fluxes

In the course of advancing toward miniaturization, the flux technology has to advance as well in order to cope with the increasing demand on performance. With no-clean being the primary industry trend, the discussion here will focus on the desired traits of no-clean flux technologies.

1. Reduced Emission of Volatiles

The major driver for this feature is (1) environmental consideration, (2) low cost driver for oven flux management consideration, and (3) reduced tendency toward voiding [27].

2. Halide-Free

Although the presence of halide in flux is not necessarily related to the corrosion and SIR behavior of flux residue, the questionable perception of halide being corrosive is still driving industry slowly toward a halide-free flux system.

3. Greater Fluxing Capacity

The demand for a greater fluxing capacity is due to unbalanced scale-down at miniaturization. While the flux volume deposited may reduce in proportional with decreasing pitch and pad dimension, the oxide thickness of parts, pads, and powder does not reduce in parallel. Consequently, a greater fluxing capacity will have to be imparted in order to achieve acceptable soldering performance. Since a polar functional group is typically required to react with oxide at fluxing, a greater amount of hygroscopic ingredients in the flux residue is expected. This will challenge the ECM and SIR performance of the no-clean system.

4. Higher Residue Resistivity

The electrical resistance of material decreases with decreasing path length. As a result, with reducing pitch, the resistivity of flux residue has to be elevated in order to prevent a decreasing resistance between electrodes.

5. More Resistant to Oxidation and Charring

When the flux dot size decreases with decreasing pitch, the rate of flux oxidation and charring under air will increase due to an increase in surface area per unit volume of flux. An oxidized and charred flux is expected to be less effective in fluxing reaction.

6. More Efficient Oxidation Barrier

For a smaller flux/solder paste dot, oxidation of powder, pads, and parts will be more significant due to a shorter oxygen diffusion path. This can be particularly detrimental for alloys sensitive to oxidation, such as SnAgCuCe. Therefore, fluxes with a more efficient oxidation barrier capability will be needed. This can be achieved by employing flux chemicals with low free volume across the material, such as a high concentration of covalent bonds or hydrogen bonding. The former may cause too high a viscosity, and the latter may cause a hygroscopic flux residue thus a problematic SIR performance.

7. Lower Activation Temperature

Fluxes with a low activation temperature are required if a low melting alloy is to be used, as discussed earlier. However, a flux which is active at low reflow temperature often is also active enough at ambient temperature to cause paste stability issue or corrosion.

8. Slower Wetting Speed When Solder Begin To Melt

This is critical for suppressing tombstoning, wicking, walking parts caused by reduced component size. Yet, a flux with a slower wetting speed often requires a higher soldering temperature, hence prevents the possibility of being a low activation temperature flux.

9. Less Spattering

For some applications, miniaturization means a reduced distance between solder paste dots and gold fingers, thus a more stringent requirement for non-spattering. This can be achieved by employing a non-hygroscopic flux plus a slow fluxing speed [10].

10. Higher Probe Penetratability

A soft residue is critical for a high probe testability [28]. With solder dots getting smaller and smaller, the flux residue is more prone to harden due to more oxidation. To assure the residue remain soft, the free volume of the residue needs to be kept high. This high free volume requirement conflicts with the low free volume requirement needed for good oxidation barrier capability.

11. Capability of Inducing Nucleation of Solder Upon Cooling

As discussed earlier, solder with a refined grain size is vital in order to avoid unfavorable grain orientation on pads. This refined grain structure can also be accomplished by using fluxes which could induce nucleation of solder upon cooling [29].

12. Greater Resistance Against Slump

Solder paste with a finer powder at the same viscosity often is more prone to slump. This is mainly caused by a reduced tendency to cold weld [10] due to a greater amount of powder oxide. This slump resistance requires the use of fluxes with a higher molten viscosity, or molecules with a higher molecular weight.

Summary

In general, new lead-free solder alloys with the following characteristics are desired in order to enable the continuation of miniaturization trend: (1) alloy with a reduced melting temperature, (2) alloy with a better solder spread, (3) alloy with a slower wetting speed at melting temperature, (4) a softer alloy, or alloy with a reduced voiding tendency or greater ductility, (5) alloy with a refined grain size, (6) alloy with low tendency to form large IMC plate, (7) alloy with a higher resistance toward corrosion and electrochemical migration, (8) alloy with a greater oxidation resistance. On the other hand, no-clean fluxes with the following features are needed: (1) reduced volatile, (2) halide-free, (3) greater fluxing capacity, (4) higher residue resistivity, (5) more resistant to oxidation and charring, (6) more efficient oxidation barrier, (7) lower activation temperature, (8) slower wetting speed when solder begins to melt, (9) less spattering, (10) higher probe penetratability, (11) capability of inducing nucleation of solder upon cooling, and (12) greater resistance against slump.

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