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White Paper

Alternative Pb-Free Alloys

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Introduction

While SnAgCu (SAC) alloys still dominate Pb-free selection in North America, especially Sn3.0Ag0.5Cu (SAC305), there are alternative material systems available. Any OEM that is concerned about the high reflow temperatures of SAC or relies on ODM, it is important to be aware of the most popular alternative Pb-free alloys and any potential concerns regarding quality and reliability.

The most popular alternative Pb-free alloys currently seem to be

- SnAgCuBi
- SnAgCuIn
- SnAgBiIn
- SnNiCu

This discussion on the reliability on these alloy systems will provide general trends in terms of performance, but all four systems share a lack of sufficient test data that would allow for the derivation of test-to-field correlation for thermal cycling and vibration.

Melting temperatures

The melt temperatures of all four alloy systems are shown below, with the major differentiator being the bismuth and indium composition [3-4% bismuth and 6-8% indium creates more of a drop in solution (185 – 195°C)].

Alloy	Solidus	Liquidus
Sn37Pb	183°C	183°C
Sn3.5Ag0.7Cu	216°C	220°C
Sn(3-4.5)Ag(0.5-2)Cu(0-5)Bi	208 - 217°C	
Sn3.0Ag2.5Bi6.0In	188°C	203°C
Sn3.0Ag2.5Bi2.5In	190°C	210°C
Sn3.0Ag2.0Cu8.0In	195°C	201°C
Sn3.0Ag0.5Cu8.0In	196°C	202°C
Sn3.0Ag2.5Bi3.0In	197°C	208°C
Sn3.5Ag0.5Bi8.0In	197°C	208°C
Sn3.5Ag0.5Bi6.0In	202°C	211°C

Material Properties

The best source by far for the basic material properties of the first three alloy systems (SnAgCuBi, SnAgCuIn, and SnAgBiIn) is Dr. Jeanne Hwang's Environment-Friendly Electronics: Lead-Free Technology. Information on SnNiCu alloy is primarily obtainable from the patent holder, Nihon Superior. In either case, repeatability and reproducibility is still an issue in characterizing Pb-free alloys and the expected range in alloy behavior has still not be completely defined. An example of variations in material properties from two sources is shown in

Figure 1.

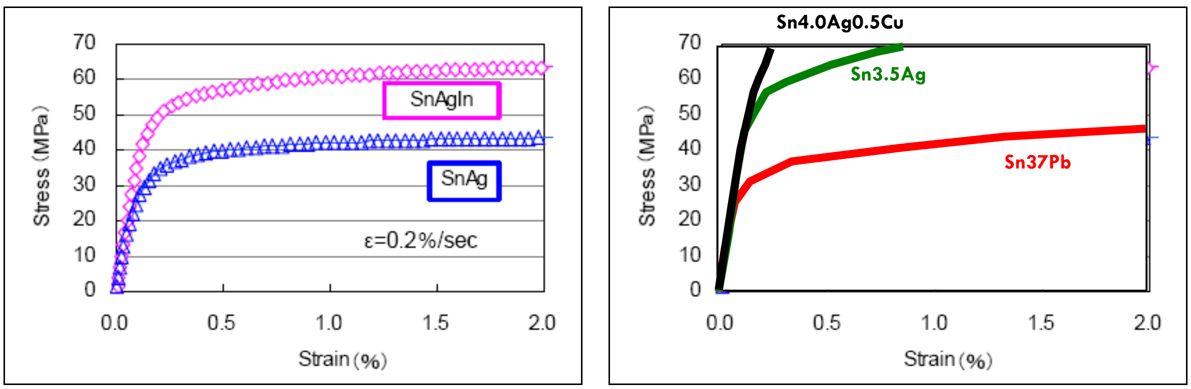

Figure 1: **Stress-strain behavior of Sn-based alloys[1].**

Pb-Contamination

There is the very real possibility that not all components placed on a Pb-free board will be Pb-free and some small population will have leads or terminations with Pb-containing plating. Current knowledge suggests that incompatibility with Bi-containing alloys could result in the creation of a low temperature alloy SnPbBi with a melt point of 97°C. An alloy with a melt point of 97°C would be significantly weaker and much more likely to fail within a short period of time.

Current literature suggests that the potential for the presence of Pb to influence Bi-containing Pb-free alloys exists at least down to 1.0 wt%Bi. Examples include

Strength degradation immediately after soldering SnPb-plated components with Sn3.0Ag5.0Bi (see

- Figure 2)
- Significant degradation in plasticity and fatigue life for a 93.3Sn/3.1Ag/3.1Bi/0.5Cu solder joint contaminated with 0.5% Pb[2].

[1] All lead free IGBT module with excellent reliability ,Y.Nishimura, K.Oonishi, A.Morozumi,E.Mochizuki, and Y.Takahashi, Proceedings of the 17 International Symposium on Power Semiconductor Devices & IC's, May 23-26, 2005 Santa Barbara, CA

Reduction in tensile strength after soldering Sn10Pb-plated components with Sn2.5Ag1.0Bi0.5Cu (see

- Figure 3).

In addition to the formation of a low temperature alloy, prior work by AIM Solder and Henkel has shown that SnPb-plated leadframes soldered with Pb-free solder can experience Pb segregation. Pb tends to migrate to the last area of the solder joint to cool. This can cause also early wearout failures (see

Figure 4). This behavior can be intermittent, so product qualification is not necessarily an appropriate method for detecting and controlling this issue.

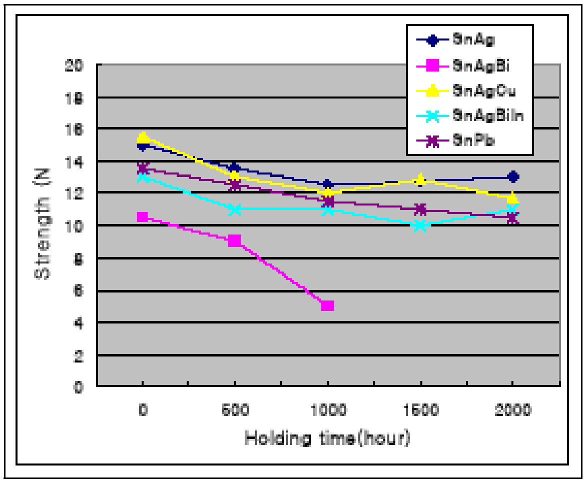

Figure 2: **Change in fracture strength after aging as a function of solder composition and SnPb plating**[3]

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[2] Chip Scale Review, May/June 2001, Jeanne Hwang, The Effects of Pb Contamination on the Material Properties of Sn/Ag/Cu/Bi Solder
[3] Chung-Ang University Young-Eui Shin

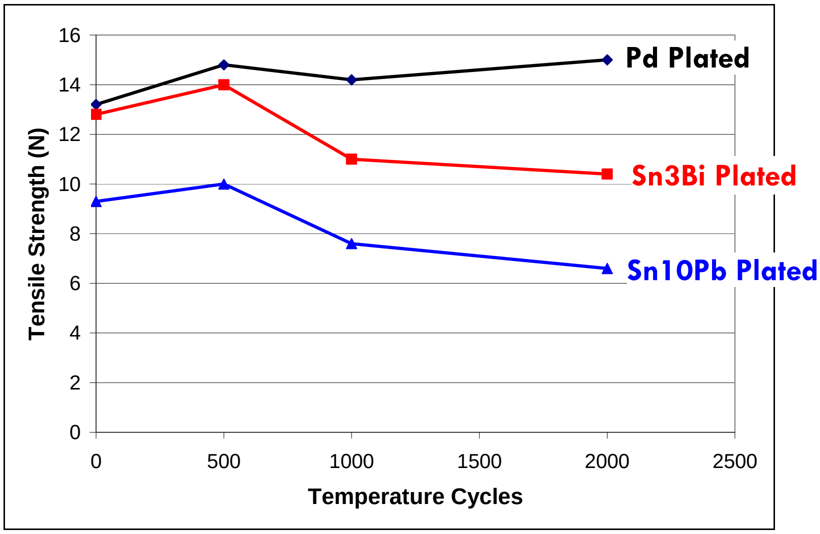

Figure 3: **Tensile strength of quad flat pack (QFP) leads attached with Sn2.5Ag1.0Bi0.5Cu solder**[4]

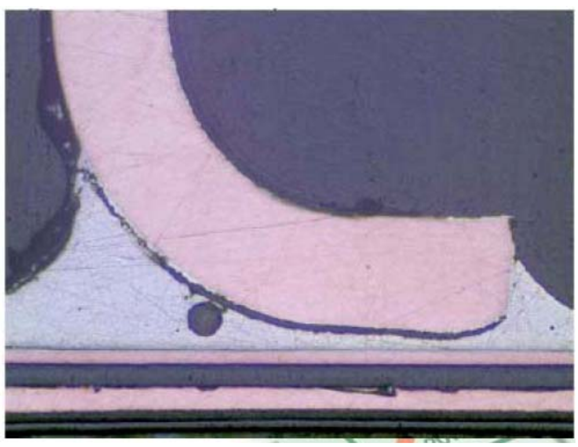

Figure 4: **Early wearout failure of SnPb plated component soldered with SAC alloy**

Control of Constituents

The currently alloys for reflow assembly is described as Sn3.5Ag0.5Bi3.0In. The reality is that the composition of each minor constituent will vary over some distribution. There are two concerns regarding constituent variation. The first is a change in the melt point, specifically an increase that may result in insufficient reflow. The second is reduced robustness. Therefore, it is very important to quantify this distribution in regards to absolute maximum and minimum content.

[4] http://www.smartgroup.org/nepcon2005/chrishunt.pdf, Sony LF Component Reliability Data

Actual quantifiable data on how key mechanical and fatigue properties vary by constituent are lacking. The majority of information available is in a qualitative format and is therefore of limited value. However, it does provide some guidance on ranges of concern. Specifically, the higher additive amounts are limited by

- Ag content greater than 4.0wt% could lead to degradation of mechanical properties
- Bi content greater than 1.0wt% could lead to embrittlement[5]

Lower concentrations are primarily limited by an increase in melt temperature, preventing adequate reflow. As a general rule of thumb, the alloy supplier should guarantee that the major constituents should not vary by more than 0.2wt% from nominal. Within this range, melt temperatures and material properties should be sufficiently steady to prevent the introduction of any unintended degradation in long-term reliability.

Thermo-Mechanical Reliability

A durability fatigue model or test-to-field correlation for any of the alternative alloys is non-existent in the public domain. While numerous published data shows all four Pb-free alloys outperforming SnPb, and in some cases SAC, the lack of an acceleration factor prevents anyone from extrapolating these results to actual field reliability.

To put it more directly, it is impossible for an OEM to know if a failure after 500 thermal shock cycles will mean potential failure in the field after 1 year, 5 years, or 20 years. Without this correlation, it can be particularly risky to use these alloys in high-reliability applications in relatively severe environments.

Mechanical Reliability (Vibration)

Just as with thermo-mechanical reliability, there is no durability fatigue model or test-to-field correlation for these four alternative alloys for vibration. Therefore, the same degree of uncertainty exists.

To some extent, vibration durability must be taken more seriously than thermomechanical reliability. The reason is that the primary Pb-free alloy, SAC, is known to have worse low-cycle fatigue performance then SnPb (see

Figure 5).

[5] The improper dosage of Bi may result in Bi second phase precipitation, which can render the solder extremely brittle

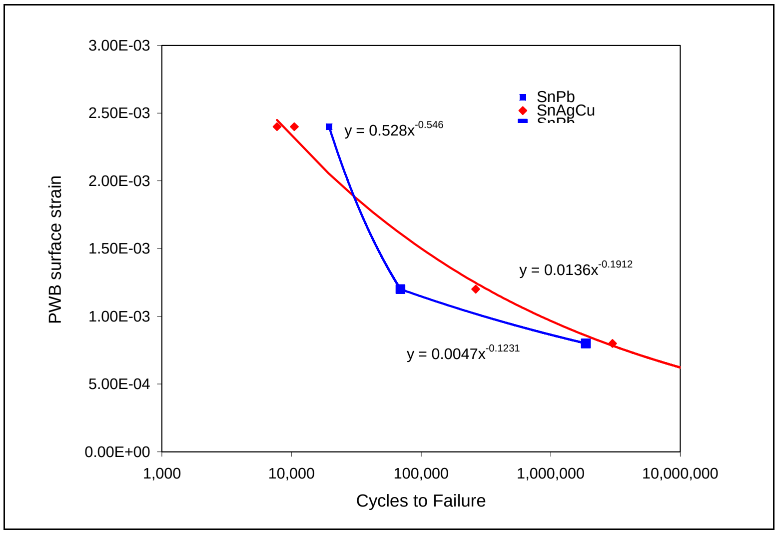

Figure 5: **Cycles to failure under mechanical cycling for SnPb and SAC solder**

Mechanical Reliability (Overstress)

Some studies show that SAC (SnAgCu) solder alloys can fail at loads up to 50% lower than SnPb when subjected to static board bending. This loss in performance seems to come from a combination of brittle intermetallics, board degradation due to higher reflow temperatures, and a greater transfer of stress because SAC is a stiffer material than SnPb. Other companies are focusing on maintaining better control over the manufacturing environment, specifically by reducing the maximum allowable strain values from 1,000 to 750 or 500 microstrain (1 µm of inplane movement for every millimeter of board length).

In this particular situation, the alternative Pb-free alloys show much promise. The Bi/In based alloys have a lower melt temperature and tend to be more compliant. Both these behaviors will make these alloys behave in manner more similar to SnPb. The SnCuNi alloy displays the best performance because of its compliance, with certain situations showing a higher degree of robustness than SnPb.

Mechanical Reliability (Mechanical Shock)

One of the benefits of mechanical shock testing is that no ‘acceleration’ is necessary. Most mechanical shock qualification requirements subject the unit to the same loads it would experience in the field.

While this is true, the primary influence on mechanical shock behavior is the intermetallics that form between the solder and the component and board bond pads. These intermetallics can grow over time and reduce the robustness of the component to mechanical shock conditions. This was often not a great concern for SnPb as the Pb-rich phases formed a natural barrier to intermetallic growth, greatly reducing the growth rate. No such barriers exist in Pb-free alloys that primarily consist of Sn-rich grains with secondary phases sparsely distributed.

Indium is especially known for its ability to form intermetallic compounds with copper, with reaction products reported at room temperature. Activation energies for tin-copper intermetallics formed in Pb-free solder have been reported to be approximately 50 kJ/mol (0.5 eV). Examples of some reported values are shown in

Table 1. By comparison, the activation energy for indium-copper intermetallics has been reported to be 20 KJ/mol (0.2 eV).

Aging experiments definitively show a thicker intermetallic layer for SnAgBiIn compared to SnPb or SnAgCu after 2000 hours of exposure to 80°C/90%RH (see
Figure 6). However, the board finish in
Figure 6 is electroless nickel/immersion gold (ENIG), resulting in tin-nickel intermetallics. The growth rate and strength of tin-nickel /indium-nickel intermetallics is likely to be completely different from tin-copper / indium-copper intermetallics. In fact, both AIM Solder and the Indium Corporation strongly recommend using a nickel barrier when soldering with indium-containing solder[6].

There has been some indication that the more recent low indium content alloys, 4 to 8 wt%, are relatively resistant to this weakening phenomenon, but publicly available quantitative data is difficult to obtain. To assess a potential issues, OEMs that wish to qualify indium containing solders for environments with mechanical shock should perform a preconditioning step consisting of high temperature exposure for some period of time. For example, if one assumes primarily a diurnal cycle as the primary driver for high temperatures in the field, then an initial aging step designed to induce intermetallic growth equivalent to 10 years in the field would be

- 3 months a year, 8 hours a day, of 50°C for 10 years = 7200 hours of 50C
- 2 months a year, 8 hours a day, of 45°C for 10 years = 4800 hours of 45C
- 2 months a year, 8 hours a day of 40°C for 10 years = 4800 hours of 40C
- Assume intermetallic growth rate at lower temperatures is minimal

Using the intermetallic growth rate defined in

Figure 7 (0.5 eV), the equivalent time at 85°C is approximately 2000 hours. This is a relatively long preconditioning period. As an alternative, an OEM could precondition at 100°C for approximately 1000 hours or 125°C for approximately 330 hours (two weeks). Since the unit does not need to be operational during preconditioning, this exposure should not influence the operational performance.

Table 1: **Reported activation energies for intermetallic formation**

[6] Statement from Indium Corporation: “The copper-indium intermetallic can result in a weakening of joint strength and may result in joint failure under certain circumstances. Because this phenomenon is a function of temperature and time, the weakening effect of the diffusion may not be immediately evident. One effective method to prevent this diffusion is to have a barrier layer of a minimum of 50 microinches of nickel plated between the copper and indium.”

Surface Mount Solder Paste	BGA Solder Ball Metallurgies	Activation Energy (kJ/mol)
63Sn-37Pb	63Sn-37Pb	45
Sn-4.0Ag-0.5Cu	63Sn-37Pb	48
	Sn-4.0Ag-0.5Cu	33
	Sn-2.5Ag-1.0Bi-0.5 Cu	68
	Sn-0.75 Cu	50
	Sn-3.5Ag	31

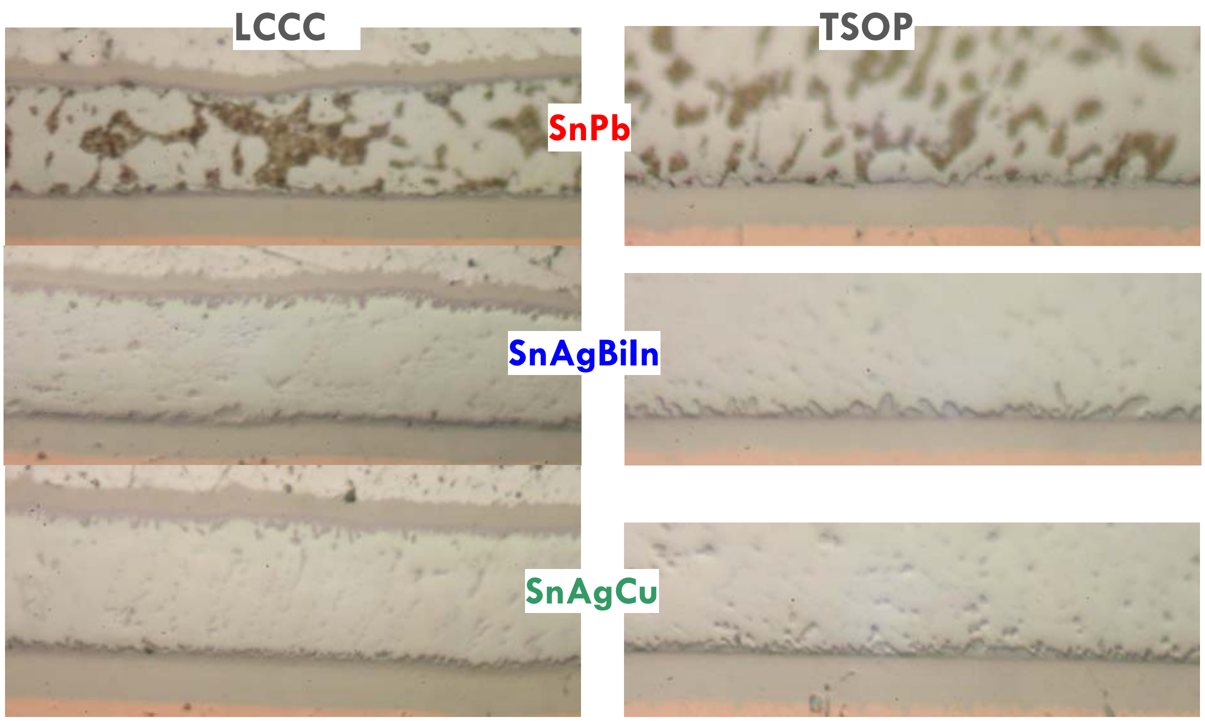

Figure 6: **Intermetallic thickness as a function of solder material after 2000 hours at 80C/90%RH**

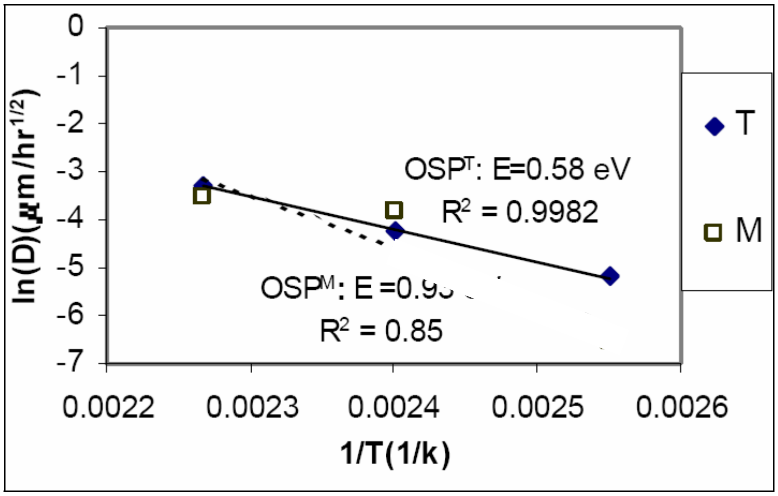

Figure 7: **Intermetallic growth rates of SAC alloy on board coated with OSP**

Electrochemical Reliability (Corrosion and Dendritic Growth)

Previous studies on tin alloys with high indium content (>20wt%) has shown significant corrosion when halides are present with moisture. Indium oxide reacts with chlorine to form indium chloride, which then reacts with carbon dioxide to form indium hydroxide.

$$4\ In + 3\ O_2 = 2\ In_2O_3$$
$$2\ In_2O_3 + 12\ HCl = 4\ InCl_3 + 6\ H_2O$$
$$4\ InCl_3 + 6\ H_2O + 6\ CO_2 = 2\ In_2(CO_3)_3 + 12\ HCl$$
$$2\ In_2(CO_3)_3 + 6H_2O = 6\ CO_2 + 4\ In(OH)_3$$

The concern is so great that the Indium Corporation recommends a hermetic seal or conformal coating to prevent corrosion. The corrosion resistance of tin alloys with lower indium content less well known, but as with the concern regarding intermetallic formation, there is some indication that lower indium contents are less susceptible. However, since most corrosion testing is performed in clean environments (test chambers), the probability of standard temperature/humidity/bias testing inducing these reactions is low.

Ductile to Brittle Transition

One final concern regarding Pb-free alloys is their tendency to transition from ductile behavior to brittle behavior at cold temperatures. It is already known that SAC can experience this transition within a temperature range close to the -40C minimum temperature of outdoor usage. Different compositions may increase this temperature and need to be explored.