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THE PROLIFERATION OF LEAD-FREE ALLOYS

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ABSTRACT

The advent of the EU's RoHS law has encouraged a significant amount of research to find an alloy, for electronic assembly, that will satisfy RoHS's lead-free requirement and have optimum process ability and field reliability. The resulting research, much of it lead by iNEMI, resulted in the near eutectic tin-silver-copper alloy SAC387 ($Sn_{95.5}Ag_{3.8}Cu_{0.7}$) as an initial favorite to fill this need in the early 2000s. By 2004 or so, many people were using SAC305, partially because of its greater resistance to tombstoning. It appeared that SAC305 would become the de-facto lead-free standard alloy for RoHS compliant electronic assembly. However, with the dramatic increase in silver prices in the last few years, SAC105, having 2% less silver was being evaluated and used for its obvious cost savings. Reliability testing of SAC105 also showed that although it did not perform as well as SAC305 in thermal fatigue cycle testing, it was better than SAC305 in drop shock tests. The explosive growth of mobile phone sales, over 1 billion per year, made SAC105's superior drop shock performance attractive for these and other portable devices.

In addition to research relating to SAC305 and SAC105, much work has been performed on the study of the effects of small quantities (<0.1%) of alloying metals on lead-free alloys' process ability and reliability performance. These "dopants" can dramatically affect an alloy's performance.

All of the above work has resulted in what many are calling lead-free alloy proliferation as more and more alloys are being considered for implementation. This proliferation drives up solder paste cost as manufacturers cannot achieve economies of scale. In addition, with so many alloys to consider, it is difficult for researchers to develop extensive data bases of process and reliability performance.

This paper is an overview of this lead-free alloy proliferation and an outlook on how alloy convergence might occur.

INITIAL WORK

By the late 1990s it was evident that the EU would initiate a ban of lead in solders for electronics. This ban was to be part of the Restriction of Hazardous Substances (RoHS) law. RoHS's main intent was to make recycling of electronics easier and safer. Hence, RoHS supported its sister recycling law the Waste of Electrical and Electronic Equipment (WEEE) law. In light of this lead-free solder need, the International Electronic Manufacturing Initiative (iNEMI), a consortium of electronics manufacturers, began a program to select an optimum lead-free alloy for electronic assembly. A detailed summary of their work is beyond the scope of this paper. However, by around 2000 iNEMI recommended the near eutectic lead-free solder $SnAg_{3.8}Cu_{0.7}$ (or SAC387). Early adopters, such as Motorola, used this alloy, for SMT assembly, with great success, starting as early as 2001. However, by 2004 or so, a significant number of companies were using the off eutectic alloy SAC305. It was subsequently shown, by Ning Cheng Lee, that this composition, because it has a "pasty range" is less prone to cause tombstoning. By the mid 2000s, the IPC's Solder Products Value Council (SPVC), another non-commercial industry organization, had coordinated round robin testing of SAC305, SAC405 and SAC357. This work's conclusion was "Based on the results of this study, it is the recommendation of the IPC SPVC that, due to the lower cost (compared to SAC405 and SAC357) and equivalent performance, the SAC305 alloy be the lead-free alloy of choice for the electronics industry." It would appear that lead-free alloy convergence was at hand. Unfortunately, this investigation did not look at lower silver SAC like SAC105, also it did not address wave soldering or rework, or drop shock testing.

THE SEEDS OF NON-CONVERGENCE

As the RoHS implementation date of 1 July 2006 approached, several things were clear. For wave soldering, SAC305 was not universally accepted. Whereas, the processing of lead-free solder pastes make the materials nearly a second order cost, the price of silver makes SAC305 wave solder bar too expensive. In investigating low silver containing solders, it was found that the addition of small amounts of nickel to these solders minimizes undercooling, resulting in more rapid solidification and hence shiner solder joints. These benefits were realized in Nihon Superior's SN100C ($SnCu_{0.7}Ni_{0.05}Ge_{0.006}$) which produced shiny, high reliability wave soldered joints at a much lower solder bar cost, making this alloy attractive. SN100C also attacked stainless steel solder pots less and was less prone to dissolve the copper on the PWBs. SN100C's main disadvantage being that it melted at about 227^{o}C vs SAC305's 217^{o}C. Unfortunately, SN100C has not been shown to provide as good hole fill as SAC305. This situation is a concern when one considers that even SAC305 has poor hole fill compared to SnPb eutectic solder.

About the time of RoHS implementation date some manufacturers started using SAC105 solder paste for SMT assembly. With the high price of silver, this action was probably taken to reduce the cost of the solder paste. However, it soon became clear that SAC105 had another advantage, it performed better in drop shock tests. This result is not too surprising when one looks at the work of Clech [1], see Figure 1.

This graph suggests that lower silver SAC alloys (actually 0% silver in the $SnCu_{0.7}$ line) would likely perform better in drop shock tests (high strain range) than higher silver solders. This fact is now widely accepted, as higher silver solders suffer from silver embrittlement due to the formation of Ag_3Sn silver intermetallic. It is interesting to note that drop shock testing has only become a concern with the increased numbers of portable electronic devices, that are more at risk to dropping, such as mobile phones. In the past, the focus of reliability concern was thermal cycling. This topic is still the main issue for devices such as PCs, flat panel TVs and other electronics that are not designed to be dropped. However, the sheer number of portable devices, probably in the 2 billion per year range when one includes portable music devices with mobile phones, is making drop shock performance very important. Unfortunately, SAC105 does not perform as well as SAC305 in lower strain test such as thermal cycling, as seen in Figure 1. So, SAC105 may not be the best choice for devices such as PCs and others that are not designed to be dropped, but do experience thermal cycling.

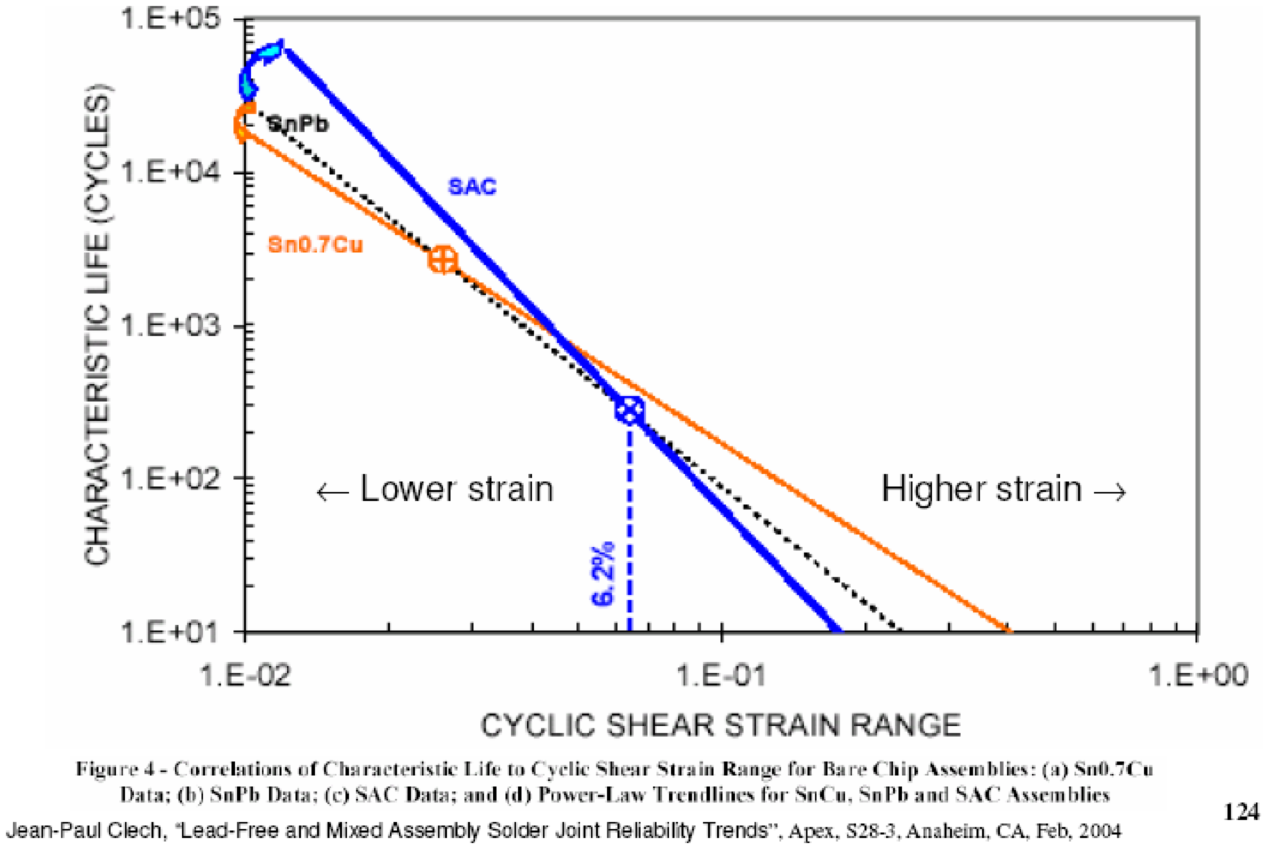

Figure 1. Characteristic Life versus Cyclic Strain Range

Another troubling aspect of low silver containing solders is that it is likely the first time in electronics history that price is driving solder selection versus performance and reliability. This trend is somewhat surprising when one considers that solder is <<0.5% of the cost of a typical electronic product.

The proliferation of lead-free alloys nearly assures that most electronic products will have some mixed alloy solder joints, as an example a BGA with SAC305 solder balls that was assembled with SAC105 solder paste. The many possible combinations of alloy mixes will hinder development of reliability data bases.

With the increased interest in drop shock performance, researchers began investigating the effects of the inclusion of small amounts of metals in lower silver SAC alloys. Our Indium Corporation colleague, Dr. Ning-Cheng Lee, developed the data in Figure 2. Note that a small amount of manganese (Mn) increases the drop shock performance by about a factor of 10. The alloy demonstrating the greatest drop shock resistance, in this graph, is $SnAg_{1.1}Cu_{0.64}$, $Mn_{0.12}$. This work and the success of small amounts of Ni dramatically improving flow, joint shininess and other properties of $SnCu_{0.7}$ has led to an explosive growth in the amount of investigations of the effects of small amounts of other alloying metals. Adding these small amounts of metals to soldering alloys has been called "doping," although some have criticized this moniker.

It should be evident at this point in the paper, that in addition to the move to lead-free solder, concurrently the explosive growth of small, portable electronic devices has created new challenges to electronic assembly. Addressing this miniaturization in electronics and the resulting smaller solder joints, may exacerbate alloy proliferation. These challenges will now be discussed in some detail.

VOIDING

Voiding is predominantly caused by entrapped flux and can usually be minimized by using a thermal "soak" profile in the reflow oven, however lower silver SAC alloys have a greater tendency to void, so if voiding is an issue after tweaking the profile and optimizing the flux, SAC305 will likely produce less voids than SAC105. In addition, lowering the surface tension of the alloy reduces voiding, some dopants that may help in this regard are bismuth, phosphorus and antimony.

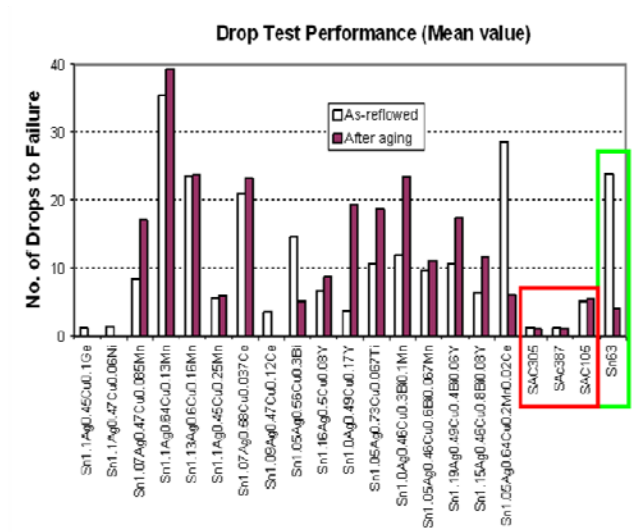

Figure 2. Drop Shock versus Alloy Type. Note that SAC305 is poor and SAC105 better, however additions of small quantities of Manganese, added to SAC105, dramatically improve performance.

TOMBSTONING

In the reflow soldering process, unequal solder surface tension forces on the ends of passive discrete components can result in a failure mechanism called tombstoning. The unequal surface tension flips one end of the passive up so that it looks like a "tombstone." This failure mechanism occurs when using tin-lead solder, but increased noticeably when SAC387 (near eutectic) was first used. Subsequently, it was shown that SAC305 dramatically reduced tombstoning. See Figure 3.

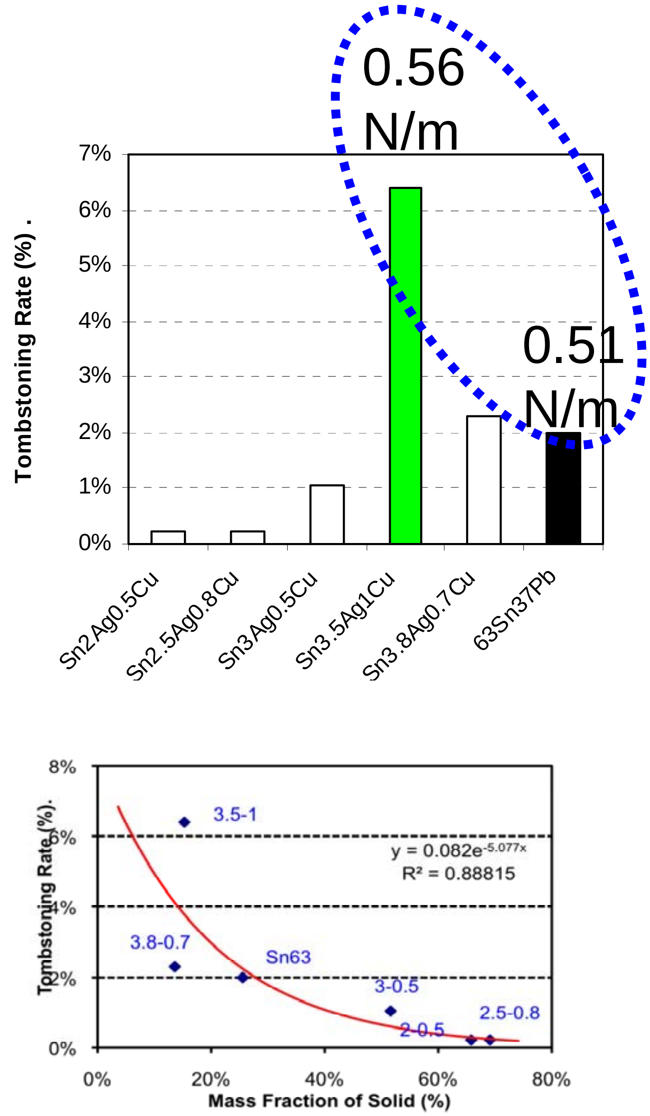

Figure 3. The top graph shows the increase in tombstoning with SAC3510 (near eutectic) as compared to tin-lead solder. Note that with SAC305 tombstoning is much reduced. The bottom graph shows the mass fraction of solid at the melting point versus the tombstoning rate.

Although it is true that eutectic lead-free solder will tombstone more than eutectic leaded solders, the favored lead-free solders are "off eutectic" and exhibit less tombstoning than eutectic tin-lead solder. However, this lead-free advantage can be eliminated if the thermal gradients in the reflow process are not minimized, a considerable challenge given lead-free assemblies higher reflow temperatures.

Experiments depicted in Figure 3 showed that the reason SAC305 can reduce tombstoning was that it contains a higher mass fraction of solids at the melting point. This situation creates a slower wetting speed, hence reducing tombstoning. Any dopants that reduce the wetting speed would further minimize tombstoning.

FRAGILITY

As the size of the electronics is reduced and the functionality increased, the size of components and their accompanying solder joints is becoming smaller and smaller. Examples are 01005 passives and 0.3 mm CSPs. The solder joints for such components are so small that they can form a single solder grain after reflow. Such a single grain solder joint would likely have poor mechanical properties and be vulnerable to drop shock. This situation is of greatest concern if the C axis of the grain is parallel to the pad surface. Dopants such as titanium, which suppresses undercooling and nickel and cobalt which refine the grain size may help to minimize such single grain solder joints.

COPPER-TIN INTERMETALLIC THICKNESS

The formation of copper-tin intermetallic (Cu_6Sn_5) is vital to the soldering process. Without this intermetallic the solder joints could not form. However, if the intermetallic is too thick, its brittle nature can cause cracking in solder joints. Smaller solder joints may more susceptible to this failure mechanism. Some dopants, such as manganese, titanium and others may help to minimize intermetallic thickness.

GRAPING

Graping is a phenomenon which appears as un-reflowed solder particles atop the solder mass. See Figure 4. Graping occurrence has increased due to the higher lead-free reflow temperatures, the decrease in volume of the printed paste deposit, and finer powder particle sized solder pastes required in miniaturized electronics. The combination of these factors, puts a lot of "pressure" on the solder paste flux to remove the surface oxides. In addition, during the reflow process, the flux can "run-away" from the solder powder particles, spreading and pooling about the deposit. The exposed powder particles become oxidized. With no flux to protect or remove the oxide, these particles do not coalesce into the solder joint.

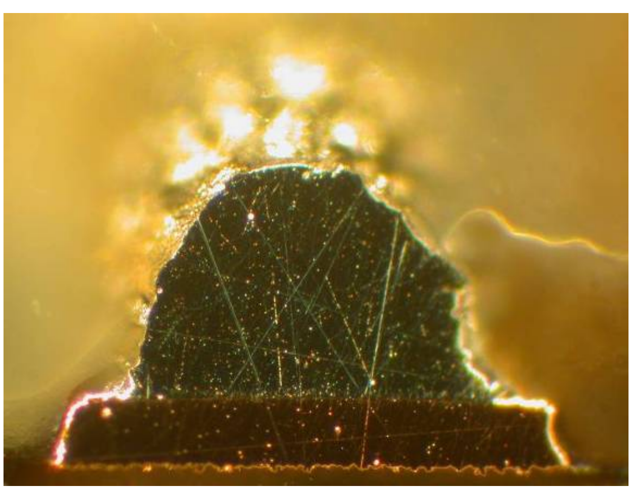

Figure 4. A Cross-section of a solder joint exhibiting graping

With smaller print deposits, the surface area exposed to the reflow oven environment increases in relation to the total amount of solder paste deposited. This ratio of flux to powder decreasing means there is less flux available to remove oxide from the joining surfaces and the solder powder particles within the solder paste itself. This situation can lead to graping.

Lower silver content (e.g. SAC105) solder balls used in BGAs and CSPs can exacerbate graping in the solder paste as they require higher temperatures (227 ^{o}C vs 217 ^{o}C) for ball collapse than SAC3xx alloys. These higher process temperatures may also increase tombstoning.

Although graping is most successfully addressed by flux and reflow profile modifications, anti-oxidation dopants such as phosphorous and germanium may help minimized this phenomenon.

HEAD-IN-PILLOW

The head-in pillow (HIP) defect is the failure of BGA or CSP solder balls to "collapse" and form a continuous, robust solder joint with the mating pad. Figure 5 shows a HIP defect.

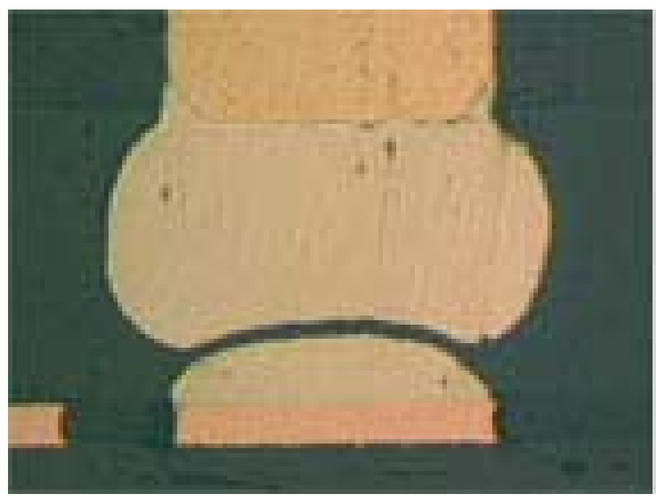

Figure 5. A Head-in-Pillow Defect.

HIP defects can be caused by PWB or BGA warpage, solder sphere oxidation, poor stencil printing, off center component placement, improper reflow oven temperature profiles and solder paste flux exhaustion. Related to lead-free alloy proliferation, high silver containing solder balls can experience silver segregation at the surface of the solder ball, resulting in HIP during reflow. This silver segregation can be so extreme that as much at 36% by weight silver has been observed at a BGA solder ball surface. Such silver segregation can make soldering difficult and can lead to HIP.

Although warping is the primary cause of HIP, it is possible that certain alloy properties can accentuate/mitigate the issue. One unique example is undercooling. Undercooling of a solder joint is typically thought of as a negative attribute. However, more undercooling could help reduce HIP. As a PCB begins to cool down from its peak temperature, warped components tend to "unwrap." The longer the solder stays molten the better the chance that the molten solder ball and molten paste can coalesce together. Greater undercooling means the solder stays molten longer. Pure Sn has the greatest amount of undercooling. As the alloy approaches pure Sn, it has more undercooling. Therefore, SAC105 exhibits more undercooling than SAC305. Therefore, an alloy like SAC105 could actually help to reduce HIP. Because there are so many factors affecting HIP, it is unlikely that any single change (other than eliminating component warp) will guarantee no HIP.

CONCLUSIONS

The combination of the move to lead free solders, the miniaturization of solder joints, the explosive growth of portable electronics, and the high price of silver has resulted in a proliferation of lead-free solders to meet these varying needs. Undoubtedly, individual companies seeking competitive advantages in the marketplace have further driven alloy proliferation. Additionally, the discovery that dopant levels of certain metals in lead-free alloys can dramatically improve certain properties further exacerbates the proliferation problem.

Groups such as iNEMI and IPC are working to help minimize the proliferation problem as alloy proliferation makes costs high and minimizes the amount of reliability data on any specific alloy. Although these efforts are encouraging, the vested interests of some companies may somewhat thwart this effort.

However, we still see a certain type of convergence on the horizon. It could be said that even today, three lead-free solder "platforms" exist: SAC305, SAC105 and $SnCu_{0.7}$. Each of the platforms may have certain dopants added, which are still being investigated, to optimize performance. We believe that these three platforms will continue to exist, as they each have benefits that support their use. The matter of dopants in each of the platforms is harder to predict. We expect that research will determine optimum dopants and eventually the marketplace will recognize the better dopant combinations and winnow out the poor ones. Unfortunately, this winnowing process may take some time.

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