

SECOND GENERATION Pb-FREE ALLOYS

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ABSTRACT

This paper will discuss the shortcomings of current LF alloys (namely SAC305) and present recent data for various new alloys which show promise as replacement materials. These newer alloys offer important reliability improvements but do have some issue that need resolution before mass implementation. Shock and vibration data will be provided, as well as thermal cycle data. The primary focus will be on SnCuNi and SAC105X alloys and how they can be used effectively in the Pb-free electronics industry going forward.

Keywords: Pb-free, solder, reliability, SnCuNi, SAC105.

INTRODUCTION

It has been a full 3 years since RoHS went into effect and Pb-free products hit the market in high volume. Many companies had only 1-2 years to prepare ahead of the deadline. Though there was a wide assortment of Pb-free alloys available to choose from at the time, Sn-Ag-Cu (SAC) alloys eventually won out. SAC305 (3%Ag and 0.5%Cu) became the primary alloy adopted for surface mount solder paste and solder balls on ball grid array (BGA) packages. Since 2005, hundreds of millions of products have been built with SAC305 solder and these products covered a wide range of applications from hand held devices and notebook computers up to work stations and servers. From this wide spread use and a few years of field reliability to draw on, there is now a much better understanding of the strengths and weaknesses of SAC alloys, both which will be discussed in greater detail in this paper. There has been a great deal of alternative Pb-free solder development work performed in the industry to improve on the properties of SAC305.¹ Industries that have thus far been exempt from Pb-free requirements are in a good position to benefit from the lessons learned and adopt Pb-free alloys that will better suit the requirements of their products. Such industries would include medical, defense, aerospace, measurement equipment, and makers of high end routers, storage, and server systems.

BACKGROUND

Much of the initial investigation of SAC alloys is credited to Consortia efforts by NCMS and iNEMI. SAC alloys

(particularly those with 3-4%Ag) were advantageous because their liquidus temperature was near 217°C. This melting temperature was significantly greater than eutectic SnPb (183°C) but less than many of the other Pb-free options. There was an early debate over whether SAC305 or SAC405 was better. Reliability data was similar between the two, but eventually SAC305 won out. The lower cost from reduced silver was only a small factor considering that the cost of a solder paste is primarily driven by fabrication costs and not cost of the metal in it. The more significant reason was a reduced volume fraction of Ag₃Sn precipitates which decreased the flow stress and made the alloy more compliant, as shown in Figure 1.

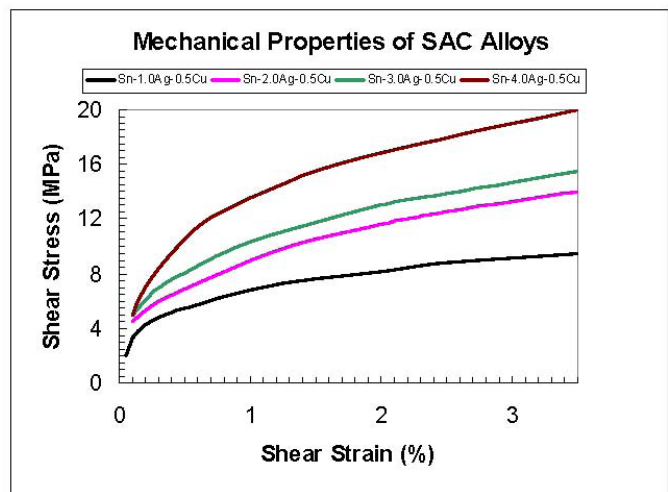


Figure 1. Shear stress-strain curves for SAC alloys with varying amounts of Ag (1-4%).²

A handful of other alloys were being seriously considered as the primary Pb-free alloy back in the 2003 timeframe. The following is a list of some of them along with a brief explanation of why they were not selected for surface mount applications.

SnCu

SnCu(0.5-0.9%Cu) had the benefit of low cost when compared to other alternatives and royalties were not an issue. However, its liquidus temperature of 227°C was a full 10°C higher than SAC and its wetting properties were not as

favorable. With the concern for heat damage to boards and components, the extra 10°C was undesirable. However, SnCu did gain use as a wave solder alloy for more simple PCBs with easy to fill vias. The poor wetting properties (bridging and inadequate hole fill) make it insufficient for more challenging applications. For this reason SAC was initially adopted for many wave solder operations which was quite costly (over 2 times the cost of Sn-Cu) and resulted in high copper dissolution.

SnAg

Tin silver alloys (3-4%Ag) had a liquidus of 221°C, only 5 degrees higher than SAC305. It apparently did not get selected as a surface mount alloy because it did not offer any meaningful cost or performance advantages to overcome this small disadvantage. This alloy was costly for wave solder and the rate of copper dissolution was quite high, thus it is rare to see this alloy in use outside of early adopters that used the elevated melt temperature for improved performance in under-hood and down-hole applications.

SnBiZn

Sn-3Bi-8Zn was an alloy that showed promise in Japan because its liquidus was only 198°C and thus could be assembled with near eutectic SnPb oven conditions (220°C peak). This alloy lost favor due its sensitivity of the solder paste to oxidation (thus low shelf life) and its tendency to suffer stress corrosion cracking in high humidity environments.³

SnAgBi

Tin-silver-bismuth alloys such as Sn-3.4Ag-4.8Bi showed great promise due to their favorable mechanical properties and good performance in thermal cycling and shock testing (more similar to SnPb). Its liquidus was 215°C and the cost was similar to SAC. Its Achilles heel was a significant drop in strength in the event that it was accidentally mixed with a SnPb alloy (due to formation of a 95°C melting temperature ternary $\text{Sn}_{16}\text{Pb}_{32}\text{Bi}_{53}$ phase that grows at the grain boundaries). Woodrow demonstrated the issue with thermal cycle testing.⁴ The potential for Pb contamination in the assembly line or during rework was too high to allow use of this alloy during the early stages of Pb-free adoption. It is possible it could resurface as an alternative after Pb has been largely purged from the industry.

SnBi

Tin bismuth alloys are attractive due to their lower melting temperature capabilities (depending on the ratio). At lower percentages of Bi the ductility of the alloy is low due to solid solution hardening; this results in poor fracture toughness.⁵

However, in the range of 30-40% Bi, the elongation is actually better than SnPb and favorable thermal cycle results are achieved.⁶ But the ductility drops quickly with high strain rate so resistance to drop testing is sacrificed. The melting temperature of Sn-40Bi-0.1Cu is 138-170°C. For some applications this might be favorable, but for many others it would actually be too low. Finally, as was stated above, a major obstacle is still the concern with accidental mixing with Pb. Some SnBi alloys may be favorable for special applications but would have difficulty becoming main-stream.

Disadvantages of SAC305/405

The most widely recognized shortcoming of the high silver SAC alloys is the poor performance under high strain rate and/or shock conditions. The high elastic modulus (25% higher than SnPb) combined with high yield strength results in a stiff solder joint, unlike the compliant nature of eutectic SnPb. Mechanical tensile testing was performed of SAC305 and SnPb to create stress strain curves at various temperatures. The results are shown in Figure 2. At -40°C the curves are similar for the two solders (though the elastic slope or modulus is higher for SAC), however as the temp increases, the SnPb becomes much more compliant and deforms with less stress. For example, at room temperature it requires considerably more stress to deform the SAC solder.

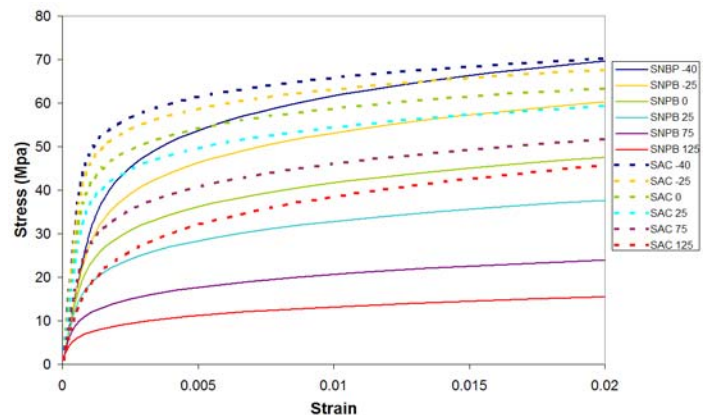


Figure 2. Stress-strain curves for SnPb and SAC305 at different temperatures.⁷

Therefore, under high strain conditions (i.e. deflection of a printed board), this additional stress is transferred to the intermetallic compound layer (IMC) or to the epoxy laminate beneath the PCB pad. Common failure locations are crack propagation through the IMC (especially with ENIG surface finish) or cratering of the pad from the PCB. A study by Roubaud (shown in Figure 3) clearly showed that SAC solder joints failed at much lower loads in a 4pt bend test.

Damage to solder joints can occur during handling or testing in manufacturing, during shipment or attachment to a chassis, or during a shock event in the field. Such damage can be undetectable at the time of incident and result in a latent failure later. One mitigating practice that can be employed is use of a partial underfill (or edge glue) to reinforce the strength of a component (especially BGAs)⁸. This recourse is often a response to a failed component after drop testing during a qualification procedure. Naturally a better practice would be to use a more compliant solder alloy that is more resistant to this failure mechanism, hence the drive for lower modulus Pb-free alloys.

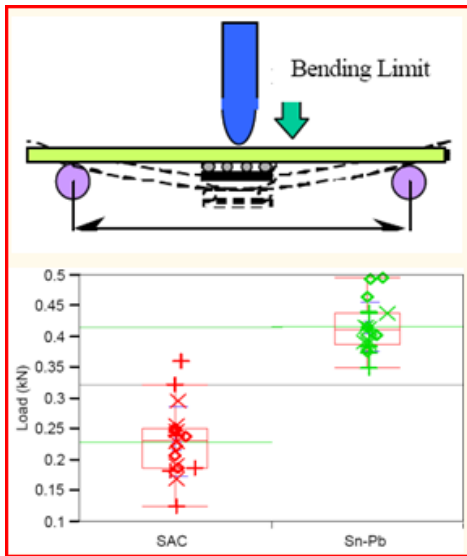


Figure 3. A 4 point bend test resulted in failures of a BGA with SAC solder joints at significantly lower bend force (lower strain) when compared to eutectic SnPb⁹.

Another aspect to keep in mind with SAC solders is the fact that they are precipitation hardened (unlike SnPb). This means that the size and density of intermetallic particles (primarily Ag_3Sn) within the joint determine the yield strength and flow properties. The rate of cooling and any subsequent aging conditions can greatly impact the particle size and thus the properties. This is why preconditioning prior to reliability testing is important, as is dwell time during thermal cycling. As the precipitates grow larger over time, the alloy becomes softer and the behavior begins to approach that of pure tin.

In addition to the alloy alone, the surface finish on the PCB plays an important role in the strength of the solder joint. Chai, et al. performed a study of drop test performance of a BGA package with SnPb and SAC305 solder with two different surface finishes (results shown in Figure 4).⁷ As expected, the failure of SAC occurred earlier than the SnPb but it was also noteworthy that there was a large reduction in

life with the combination of ENIG surface finish and SAC305 solder. This dependence on surface finish was further noted in a study by Alajoki et.al. in Figure 5. It is therefore not recommended to use ENIG on the component ball pad with SAC305.

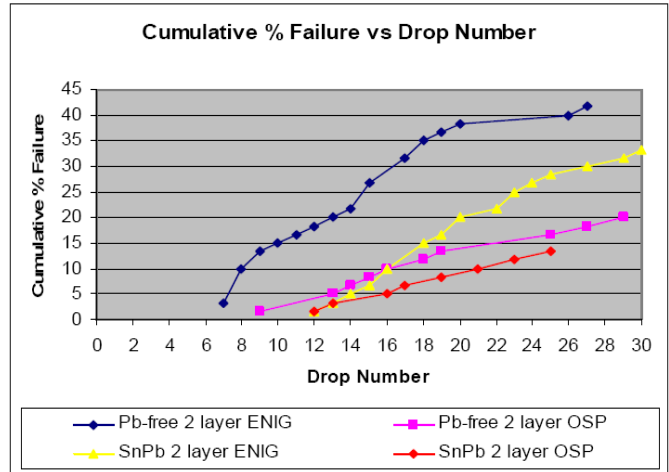


Figure 4. Drop test data for SAC and SnPb BGAs with OSP and ENIG surface finish.¹⁰

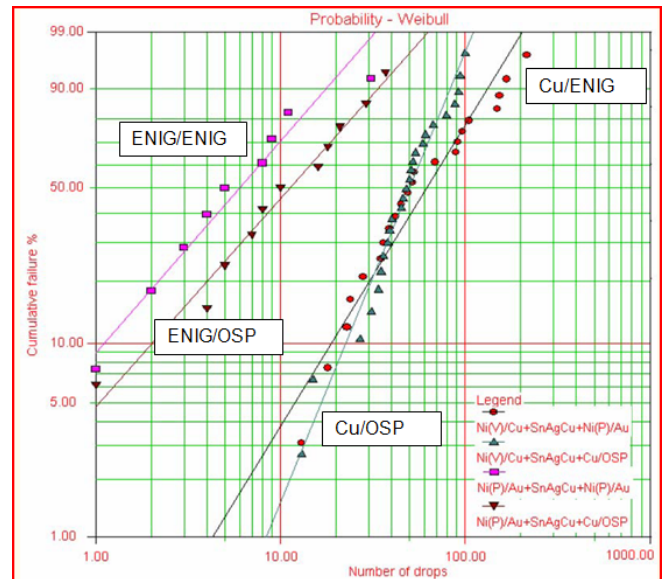


Figure 5. Drop results for SAC305 on a CSP with OSP and ENIG finish combinations on the package pad and the PCB pad (CSP/PCB)¹¹

Vibration testing performed at DfR Solutions on 2512 resistors with SAC305 and SnPb reveals that high strain cycling (low cycle fatigue) results in better performance for SnPb (testing was performed at 2400 microstrain). However, high cycle fatigue (at a strain of 1200 microstrain)

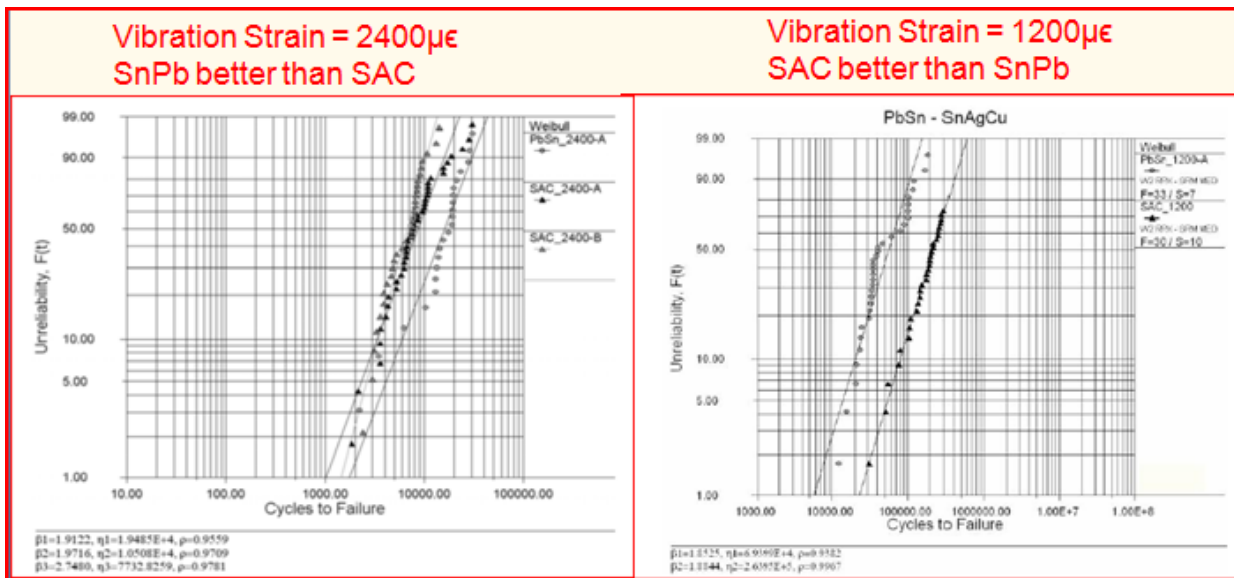


Figure 6. Vibration results of SAC and SnPb at low and high strain conditions.

resulted in better performance for SAC305.¹² This behavior is due to the higher yield strength of SAC305. When the strain is low, plasticity does not occur, thus there is little damage in which to propagate a crack.

Industry data consistently shows that SAC305 performs better in thermal cycling than SnPb for compliant components such as plastic BGAs or QFPs¹³. However, stiffer components such as resistors or QFNs perform better with SnPb. The magnitude of the change in temperature also impacts the relative reliability. Larger delta T values tend to favor SnPb while smaller delta T favors SAC.¹⁴ As a result, extrapolating thermal cycle test data to field use conditions is more complex since the same acceleration factors used for SnPb are no longer valid.

Another deficiency of SAC is the marginal wetting behavior. It is sufficient to achieve a good solder joint, however the surface tension prevents flow on the copper surface. In situations where reflow is performed on an OSP surface finish in air with a no-clean paste (rather common conditions in the consumer electronics industry) one can expect little to no flow of the solder, resulting in exposed copper that is susceptible to future corrosion (an example in Figure 7). Achieving sufficient hole-fill with high aspect ratio vias in wave solder with this alloy has also proven to be challenging. Furthermore, the rate of copper dissolution is quite high. In a wave solder process this can result in extreme thinning of the copper at the knee of the plated through hole and in a BGA it can result in extreme thinning of the pad (especially in the event of rework). Examples are shown in Figure 8.

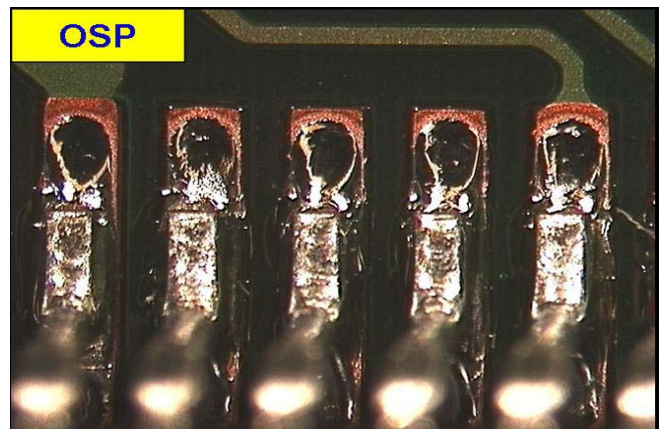


Figure 7. SAC305 paste reflowed on a QFP

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To be successful, an alternative Pb-free alloy will need to have mechanical properties closer to eutectic SnPb. The new interconnect material should be more compliant with lower flow stress, copper dissolution should be reduced, and the wetting properties increased. A lower reflow temperature would be desirable as well, but not necessary. At the same time we don't want to give up too much of the benefits of SAC 305; namely the improved thermal cycle life on the more compliant components.

Sn-Cu-Ni

As expected, Sn remains the primary constituent of most alternative Pb-free alloys being investigated. It forms a well understood intermetallic with copper and the melting temperature is favorable. The second generation alloy with the most penetration into the wave solder and rework market



Figure 8. SAC305 solder can result in unacceptable copper dissolution in wave solder and surface mount (typically becomes an issue with rework).

thus far is Nihon Superior's SN100C which is Sn0.7Cu0.05Ni+Ge. The nickel addition offers two primary advantages. It causes solidification of the alloy in many locations simultaneously thus giving a more uniform eutectic type microstructure as opposed to dendritic solidification of SAC305. The Ni also becomes a part of the Cu_6Sn_5 intermetallic layer creating a denser hexagonal close packed structure that reduces the rate of copper diffusion, thus reducing the growth rate of the IMC.¹⁵ SN100C gained a solid foothold in the wave solder process since its fluidity and wetting behavior allowed good hole-fill and reduced bridging at a lower cost than SAC305. Dissolution of copper was also considerably less, approaching that of SnPb. The use of SN100C allowed two rework attempts while SAC would hardly allow one rework before eroding an unacceptable amount of copper. Results of a good investigation on solder pot rework are shown in Figure 9.¹⁶

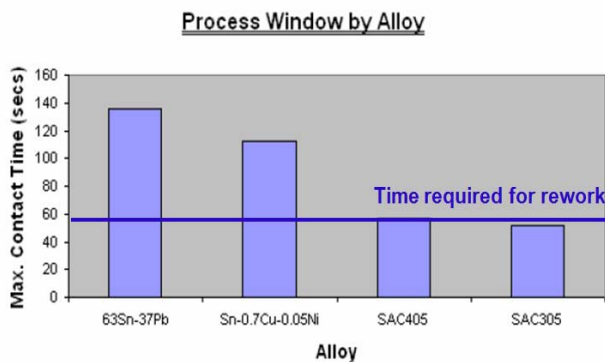


Figure 9. Maximum contact time before excessive copper dissolution takes place.

SN100C then became the primary alloy for use in Pb-free HASL finish.¹⁷ The better leveling properties and ability to control IMC thickness were beneficial properties for this application as well.

The latest push is toward use of this alloy in surface mount applications. The mechanical properties at various temperatures, shown in Figure 10, would suggest favorable results in thermal cycling, mechanical shock and vibration. However, with a melting temperature of 227°C (10°C higher than SAC305) the natural concern is that higher required oven temperatures will cause heat damage to the components. Smaller assemblies can likely withstand the added temperature and still remain below 260°C (the top temp rating of most components). Larger boards with more thermal mass will have difficulty. DfR Solutions performed reliability testing of SN100C in surface mount applications and found favorable results that tended to be intermediate between eutectic SnPb and SAC. For example vibration testing was performed on the following three different component types: 2512 resistors to represent a stiff component, TSOPs to represent a compliant leaded component (44 gull wing leads with alloy 42), and a 0.5 mm pitch CSP (96 I/O) to represent an intermediate stiffness component. Results in Figure 11 show SN100C being considerably better than SAC305 in the case of resistors and CSPs and slightly worse for the more compliant TSOPs. Since this is a high strain situation, one would expect similar mechanical shock performance relationship between the alloys.

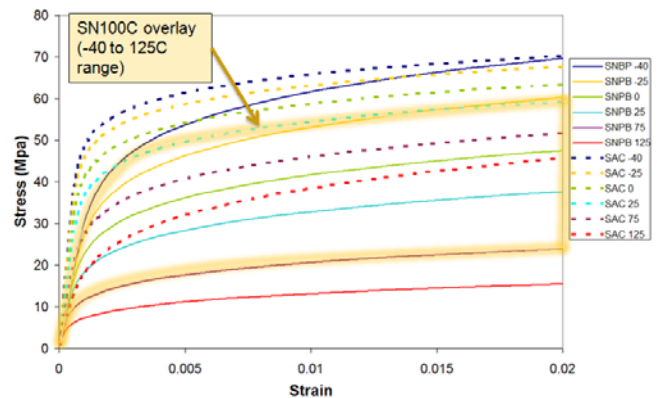


Figure 10. Mechanical properties of SN100C compared with SnPb and SAC305 from -40 to 125°C.⁵

Thermal cycle results for SN100C tend to be favorable as well. However, as mentioned earlier, the acceleration factor for each new alloy needs to be determined and used to find the true thermal cycle life expectancy under field use conditions. Many studies compare cycles to 63% failure

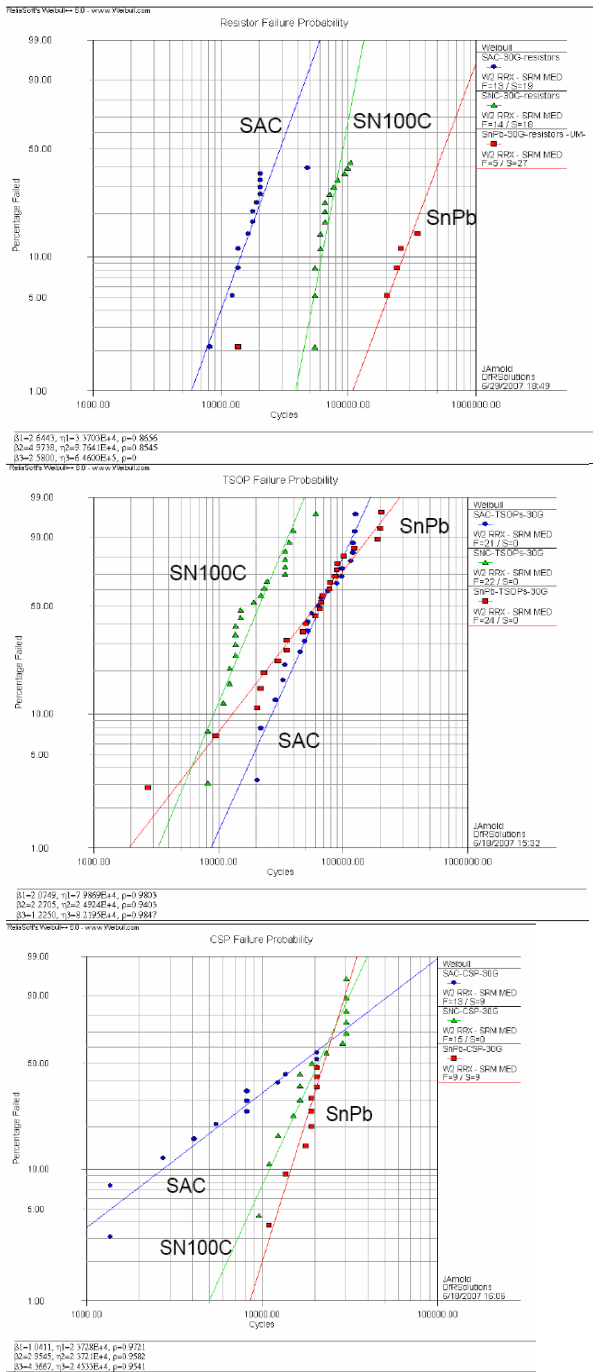


Figure 11. Vibration results at 30G (high strain) for 2512 resistors, TSOPs, and CSPs, respectively, soldered with SAC305, SN100C, and SnPb. ¹⁸

(otherwise known as the characteristic life). Of more value to reliability engineers are cycles to 1% failure of a population ($N_{1\%}$). It is helpful to base the acceleration factor on this measure and can be estimated with the modified Norris-Landzberg equation,

$$AF = \left(\frac{\Delta T_t}{\Delta T_f} \right)^n$$

Calculation can be made by testing the alloy to different delta T values, determining the $N_{1\%}$ at each, and fitting the curve to find the acceleration factor. Data was gathered for SN100C at three temperature ranges, 25-100°C, 25-125°C, and -40/125°C. This was done for 3 component types (CSP, resistor, and TSOP) and the results plotted in Figure 12.

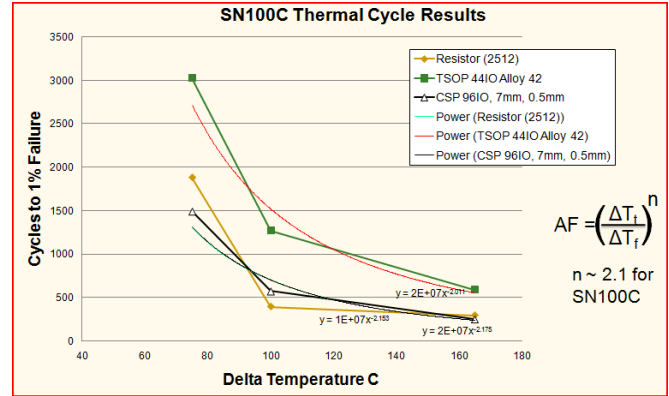


Figure 12. Weibull plots were used to determine 1% failure at 3 different delta T values. Regardless of component type the exponent n in the acceleration factor was near 2.1 for SN100C.

Thermal cycle data at different delta T values were taken from Syed¹⁹ and Qi²⁰ to determine the exponent n value at 1% failure for SAC and SnPb (shown in Figure 13). SAC had an n-value of 1.9 for a resistor solder joint and 1.75 for a BGA while SnPb had an n-value of 1.7 for a resistor and 1.55 for a BGA. Note that other investigations in the literature can show larger n-values for SAC, however they usually base these off characteristic life values.

Thermal cycle testing of various component types was then performed at -40/125°C and the $N_{1\%}$ value determined. The data for a CSP is shown in Figure 14. Similar data was gathered for a 2512 resistor. The newly found n-value and acceleration factor was used to extrapolate the life expectancy at reduced temperature ranges and the results shown in Figure 15 for both CSPs and resistors.

It can be seen that the n-value in the acceleration factor makes a large impact on the expected life when extrapolated from the test conditions. These results appear to show that SN100C performs very well in surface mount applications when compared to SAC305 for both stiff components and more compliant components. More work will be required to overcome the larger reflow temperature required for SN100C. For assemblies that can manage this increased thermal exposure, the reliability should be quite good.

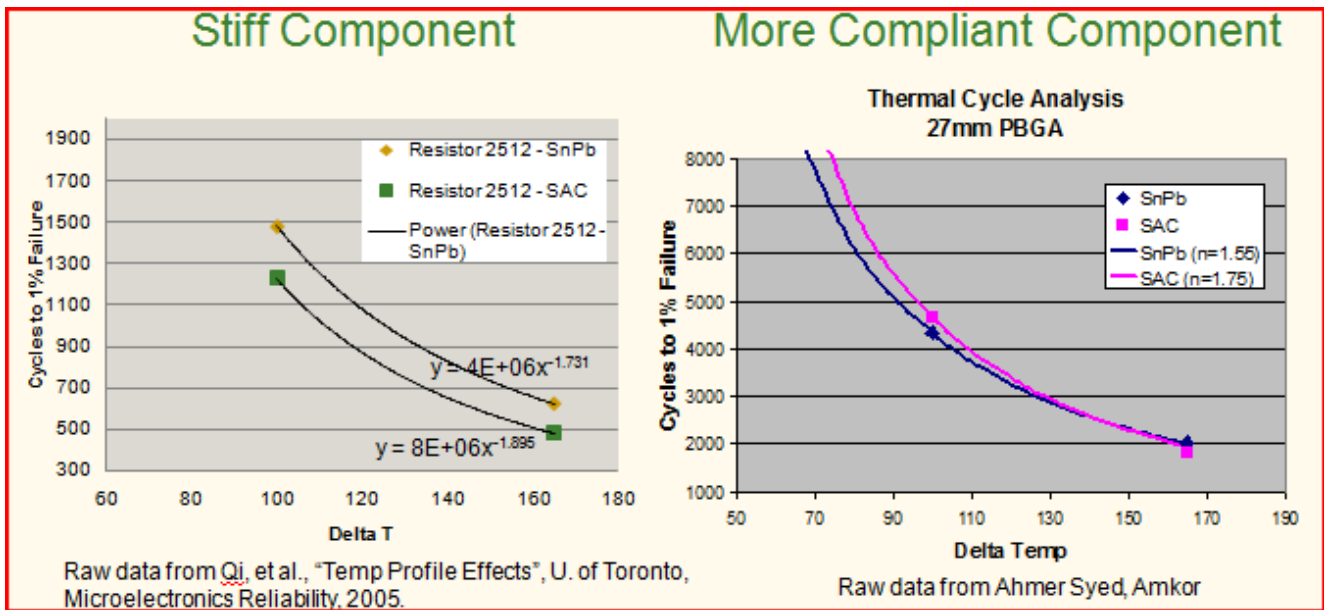


Figure 13. Cycles to 1% failure data for SAC and SnPb. Best fit to data showed exponent n-values for each solder type.

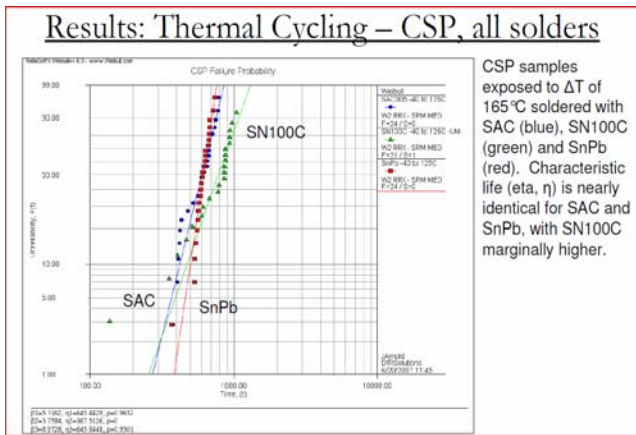


Figure 14. Thermal cycle results (-40/125°C) for a CSP soldered with SAC305, SnPb, and SN100C. Note cycles to 1% failure are similar (300-400 cycles).²¹

SAC105

When the issue with shock deficiency of SAC305 surfaced, the first improvement was to reduce the elastic modulus and the flow stress of the alloy through reduction in silver content (note Figure 1). SAC105 became a popular solder ball choice for BGAs that went into consumer electronic applications where drop/shock performance was important. However, the shock improvement came at a price. The melting temperature of SAC105 was nearly 227°C and resulted in head-in-pillow defects if the assembly temperature was insufficient. Additionally, the thermal cycle performance declined and components did not always pass reliability test requirements. Instances occurred where component manufacturers had to change solder ball alloys for customers depending on what reliability requirement was being stressed. Some reports show that

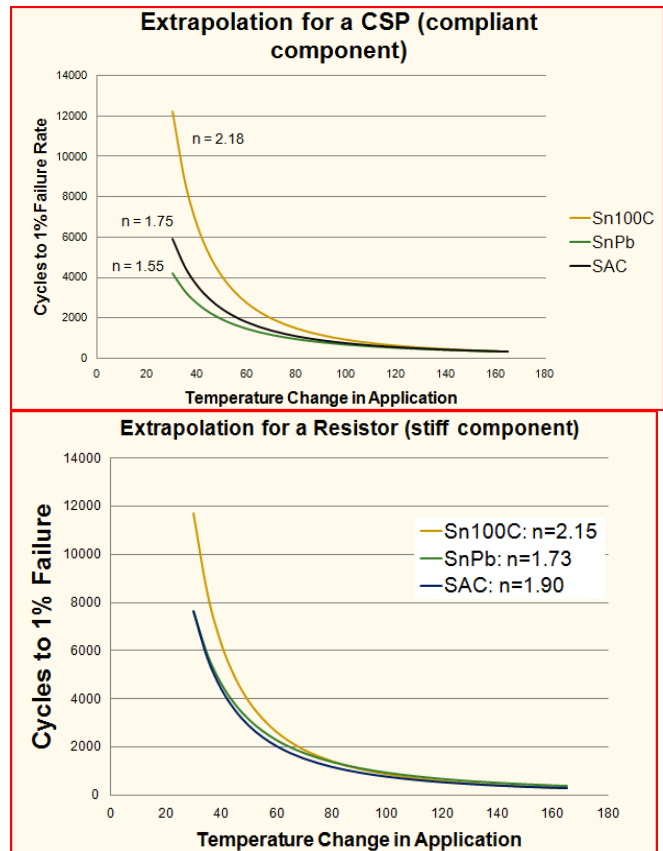


Figure 15. Extrapolation from test conditions with a delta T of 165°C to smaller delta T ranges that would be more typical for field use applications. Results shown for a CSP and a 2512 resistor.

shock performance of SAC105 depends greatly on the surface finish (as did SAC305). For example a study by Unovis showed the SAC105 on ENIG had even lower shock

Drop Test Results of As-Reflowed Samples (Min, Max, 2X-StDev)

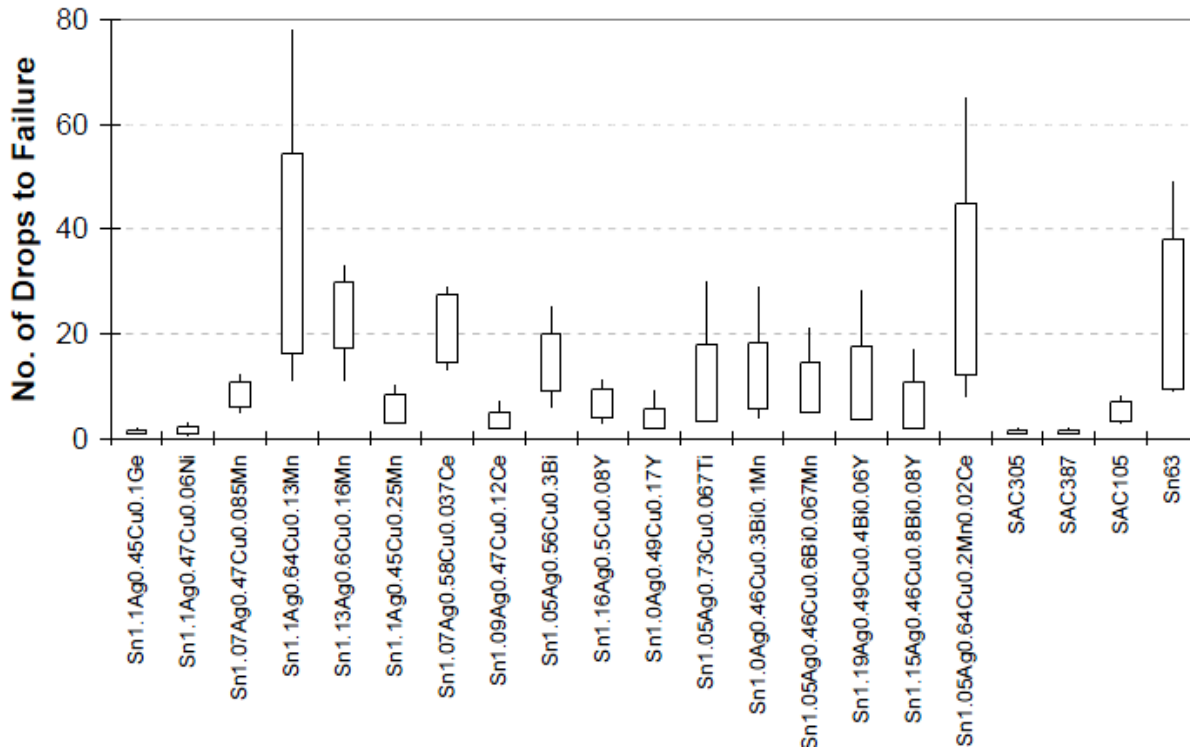
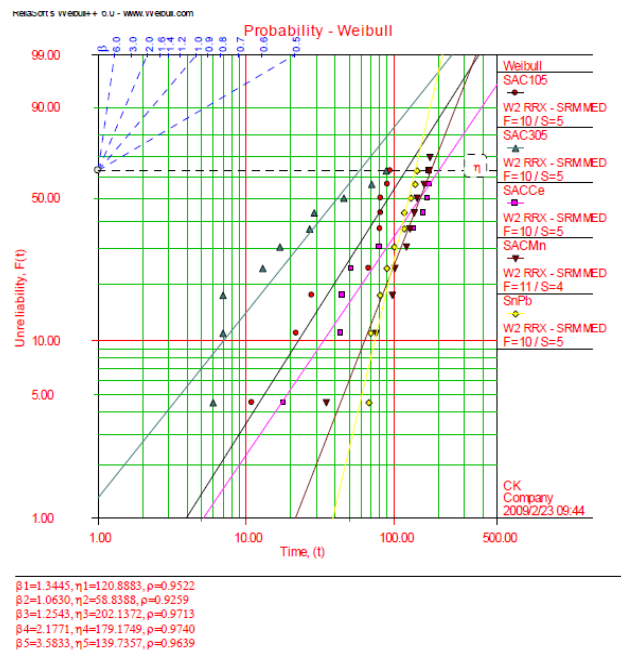


Figure 16. Drop test results for alloys near SAC105 in composition but with other elements added.²²

performance than SAC305 on ENIG, whereas SAC105 on OSP was best.²³

Work did not stop with SAC105. In 2006 a comprehensive study was performed at Indium to show drop test results for SAC105X alloys (alloys with other additions). Results are shown in Figure 16. SAC105 is indeed an improvement over SAC305, but is far short of previous industry standard eutectic SnPb. Small additions of cerium, titanium, and manganese seemed to result in large improvements in shock performance. The development efforts at Indium have been most focused on the Ce and Mn additions with the most recent results showing great potential.²⁴ Alloys investigated were SACC (Sn-1Ag-0.5Cu-0.02Ce) and SACM (Sn-1Ag-0.5Cu-0.05Mn). Drop test results are shown in Figure 17 and thermal cycle results in Figure 18. Drop test results similar to SnPb are attained without sacrificing thermal cycle performance, which remains as good as SAC305 for a BGA device. Dynamic bend test results were also better than SAC305. The trace additions were credited with suppressing intermetallic growth (especially on Ni) and reducing coarsening of the precipitates in the matrix – which in turn also helped prevent grain growth.



SACM ≥ SnPb ≥ SACC > SAC105 > SAC305

Figure 17. Drop test results for a 244I/O BGA (0.5mm pitch). Ni/Au on package and OSP on board. 250 thermal cycles as a precondition.

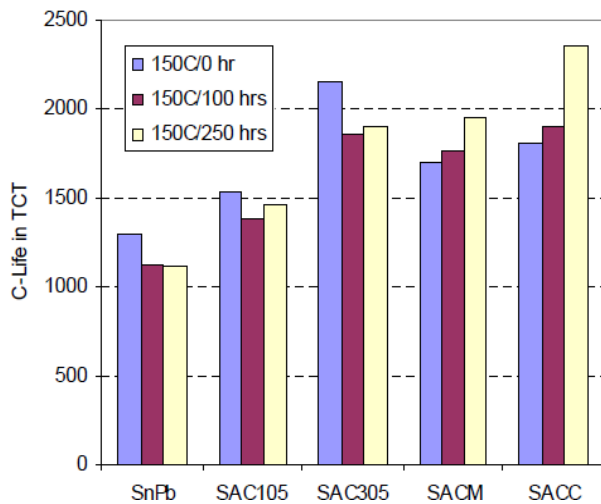


Figure 18. Characteristic life when thermal cycled (-40/125°C) for a 244I/O BGA (0.5mm pitch). Before and after preconditioning as shown. SACM and SACC perform similar to SAC305.²⁴

Pandher et.al. investigated a SAC105 + Cr + Ni additions and found good improvement to shock performance.²⁵ They also investigated additions of Bi and found similar improvements (shown in Figure 19). Thermal cycle testing showed no improvement with the Ni+Cr additions but significant improvement was observed with the Bi addition (a version of this alloy is referred to as SACX by Cookson).

DISCUSSION

For wave solder applications the trend has been away from SnCu and SAC305 toward alloys such as SN100C and SACX due to improved fluidity and hole fill with a reduction in copper dissolution. Since a wave solder pot typically operates in the range of 255-265°C, the higher melting temperature of these alloys are insignificant. In fact, by providing improved wetting one could argue that the boards can be run with lower preheat resulting in less chance for damage to components.

For surface mount applications the reflow temperature is more critical since the PCB and all the components will have to survive the higher required temperature. All of these promising new alloys discussed (SN100C, SACM, SACC, and SACX) have a melting temperature near 227°C and so may need to be assembled at up to 10°C higher than SAC305. Since the switch to Pb-free several years ago, suppliers of components and PCBs have made improvements that have made components more resistant to heat damage. However, it remains to be seen if the added temperature requirements of these alloys will cause other reliability problems that offset the gain achieved with the better solder properties. An increase in head-in-pillow

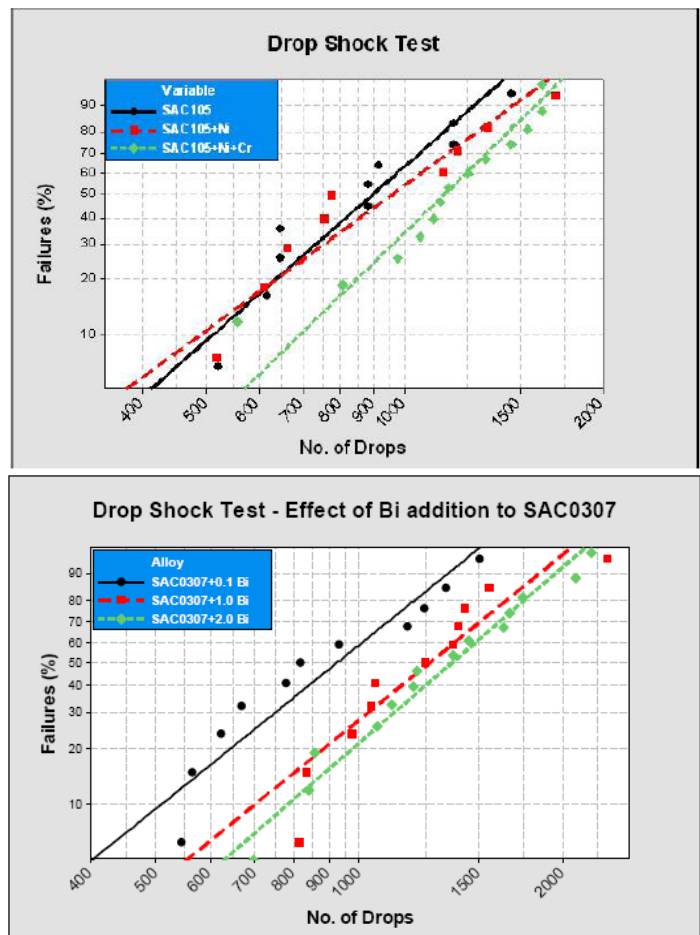


Figure 19. Drop test results for SAC105+Ni+Cr and SAC0307 + Bi. Both additions improve shock performance of the base alloy.

defects is one example. For smaller assemblies with less thermal mass, reaching solder joint temperature of 235 or more without damaging components should be achievable. This is less clear for larger assemblies.

Some of these alloys may also require further data to determine the acceleration factor (preferably to 1% failure as was demonstrated with SN100C). Users would then be better equipped to extrapolate their thermal cycle test data to their particular use application. As mentioned earlier, pad cratering at high strain has been a problem with SAC305. Measurement of strain limits for various component types compared to SAC305 and SnPb would be highly desirable data for these newer alloys.

Another challenge may be in proving process capability for adding trace elements in the necessary amounts in a mass production environment. Some of the additions to these alloys are so small as to sometimes be thought of as impurity levels.

SUMMARY

The transition from SnPb to Pb-free has been fast and furious for an industry where it can take a decade or more to gather the necessary reliability data. SAC305 was introduced as the Pb-free alloy for surface mount applications and many would argue has been rather successful considering the tight timescale. Deficiencies have since been identified and a transition has begun to newer alloys. For handheld products the first change was to SAC105 for improved shock resistance. It was then recognized that the loss in thermal cycle resistance was not acceptable for other applications. The next push will be to achieve improvements in shock and thermal cycle behavior. Sn-Cu-Ni, SAC105C, SAC105M, and SACX show promise but all require higher process temperatures. It is likely that one or more of these alloys will become popular for BGA balls and surface mount applications in the future. It is also possible, but less likely, that a lower melting temperature alloy such as SnAgBi could be brought back to the table after the threat of Pb contamination has subsided. In any case, we should be prepared for a period of transition that will be a challenge for both BGA component suppliers and electronic manufacturers.

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