Fatigue Resistant Lead-Free Alloy For Under Hood Applications

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One of the key challenges to automotive electronics manufacturers is the increasingly high operating temperature, as modules are placed closer to the point of use. The move towards electronics being placed into harsher environments is being driven by the desire to reduce wiring within the vehicle, which both adds weight and is in itself a reliability hazard. While standard lead-free alloys offer higher melting points and increased peak-operating temperatures compared to tin-lead, they also show poor creep performance. We take a look at a high performance alloy designed to withstand these harsh conditions within the tough reliability requirements mandated by vehicle manufacturers.

There are a multitude of process considerations in transitioning to lead-free for any electronics manufacturer. The manufacturers of consumer electronics have developed a great deal of knowledge and expertise through their mandated move to lead-free production. This was supported by rapid developments in materials technology as well as design improvements to production equipment.

The vast majority of solder material developments focused largely on process performance improvements as well as offering economic advantages. These developments were driven by the high volume, low cost products which were covered by the EU RoHS legislation.

During this development and evolution of "standard" lead free alloys it was identified that automotive electronics operating temperatures were increasing, and the need for high reliability in the harsh environment of the vehicle engine bay was not delivered by the standard tin-silver-copper (SAC) alloys.

A working group of several companies was set up in Germany to develop an alloy which was (i) lead-free, (ii) economically viable for mass production and (iii) capable of providing reliable interconnection performance at high temperatures whilst under vibration.

Defining the alloy requirements

The development of any alloy for the high volume automotive electronics industry has to have several constraints attached, if it has any chance to be used in production in the future. The constraints placed on this development were as follows :

- Lead-Free: Although it is not mandated that all vehicle electronics should be lead-free, it was considered essential to exclude lead from this alloy.
- Operating Temperature of 150°C : This requirement alone excludes the eutectic tin-lead alloy, but also excludes standard tin-silver, tin-copper and tin-silver-copper alloys.
- 1000 thermal cycles of -55°C to +150°C with no failures.
- Acceptable cost and toxicity considerations: The alloy must have a cost within the same ballpark as the ternary eutectic tin-silver-copper system. Its toxicity must also be deemed acceptable and within the bounds of any current or potential future legislation.

Health and safety experts rated the potential candidate elements as shown in Table 1. The same list was considered from an environmental impact perspective and the order changed as seen in Table 2.

Copper	Most problem
Silver	
Lead	
Antimony	
Nickel	
Tin	
Indium	
Bismuth	Least problem

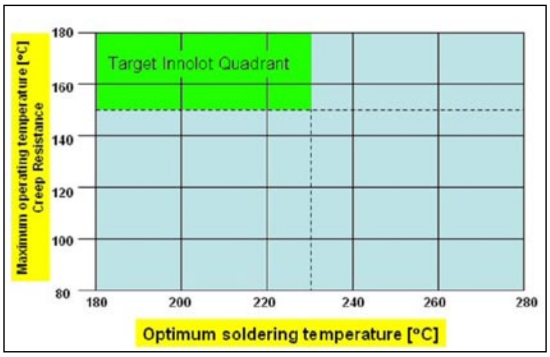
Table 1 – Environment impact ranking elements
Table 2 – Environment impact ranking of candidate elements

Copper	Most problem
Silver	
Lead	
Antimony	
Nickel	
Tin	
Indium	
Bismuth	Least problem

The alloy development needed a baseline to work from, and the following systems were considered.

- Tin/silver/copper (SAC): Has been shown to offer the best in process yields and is trusted by many users to provide good reliability for many

Figure 1 - Plotting the effect of single element additions



	Min Soldering Temperature	Max Operating Temperature
SAC387	235	115
+ 4Bi	228	128
+ 6Bi	219	130
+ 8Bi	212	132
+ 2.5Sb	245	130
+ 3.75Sb	245	135
+ 5.0Sb	245	150
+ 0.2Ni	240	140

Table 3 – Effect of single element additions

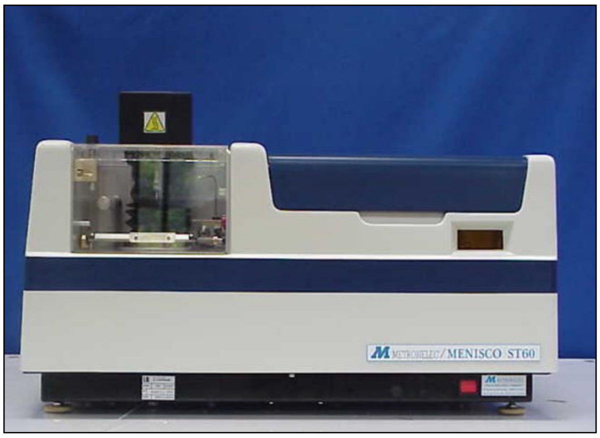


Figure 2 - Wetting balance system

applications. This alloy system has a 3-4% silver content, with the eutectic calculated at 3.8% silver and 0.7% copper.

- Tin/copper eutectic alloys: While offering a lower raw material cost than SAC alloys, the basic tin-copper alloy have been consistently shown to have inferior yield to the SAC alloys, along with reduced reliability.

Numerous studies have shown that the silver-tin intermetallic needles in the silver bearing alloys gives a considerable strength advantage to the alloy, especially when thermally cycled.

Identifying the alloying elements

The development of the alloy is done in several stages. The first evaluation criteria is to understand the limitations of the incumbent alloy and of the potential base formulation.

Firstly, the majority of existing production was with the tin-lead and tin-lead-silver alloys, which clearly fail on 2 of the foundation requirements of being lead-free and requiring an operating temperature of 150°C.

The tin-silver-copper alloy was calculated to have a maximum reliable operating temperature of 120°C using the Coffin/Manson model and calculating from the expected cycles to failure for a tin-lead alloy operating at a peak of 85°C (which is widely regarded as a safe maximum operating temperature).

The challenge then was to look to ways to take the acceptable performance of the SAC alloy in PCB assembly, and modify it within the boundaries set, whilst not compromising the original alloys in-process performance. The main target was to increase the creep resistance properties of the alloy, which would limit early life solder joint failures when operating at elevated temperatures.

The known methodology to achieve this was through solid solution strengthening and through dispersion strengthening/hardening of the alloy.

The list of the following elements were considered as additions to the tin-silver-copper matrix:

- Indium: Can lower the liquidus of the alloy however cost considerations ruled it out at an early stage
- Nickel (Ni): Provides dispersion hardening by means of intermetallic phase formation
- Bismuth (Bi): Provides solid solution hardening AND lowers the liquidus point of the tin based system
- Antimony (Sb): Provides solid solution hardening BUT increases the liquidus point of the tin based system.

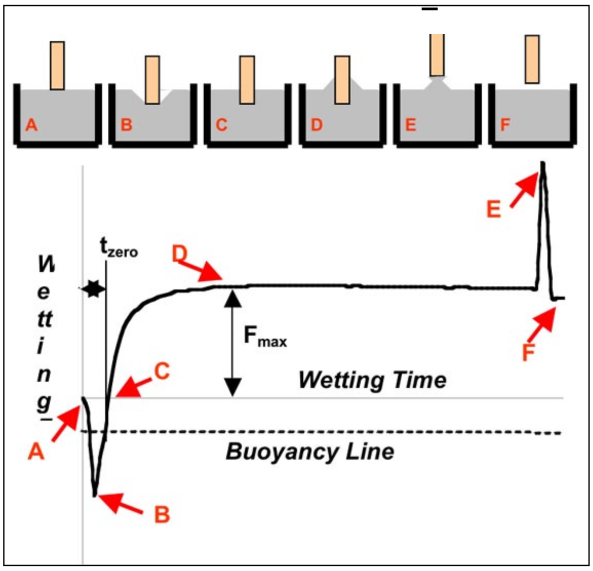
Alloy development and optimisation

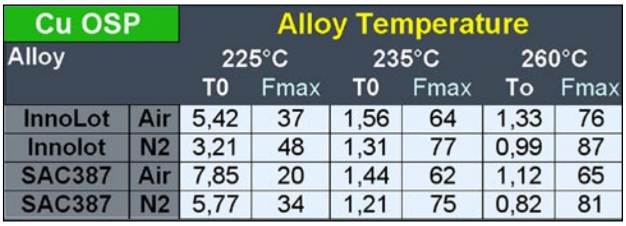
The suite of elements where now established and so alloy development and optimisation could begin. A matrix was established to evaluate the impact of various levels of single element additions of bismuth (Bi), Antimony (Sb) and Nickel (Ni) on the SAC387 system (Sn-Ag3.8-Cu0.7).

This was plotted to chart the effect of each addition on (i) the minimum soldering temperature and (ii) the maximum operating temperature based on the SnPb @ 85°C model. The calculations for various singular element additions are shown in Table 3.

It is clear that "target quadrant" from Figure 1 was unachievable

Figure 3 - The wetting curve output





Cu OSP		Alloy Temperature					
Alloy		225°C		235°C		260°C	
		T0	Fmax	T0	Fmax	To	Fmax
InnoLot	Air	5,42	37	1,56	64	1,33	76
Innolot	N2	3,21	48	1,31	77	0,99	87
SAC387	Air	7,85	20	1,44	62	1,12	65
SAC387	N2	5,77	34	1,21	75	0,82	81

Table 4 – Non-aged Cu OSP wetting tests

Cu OSP 4Hrs/155?		Alloy Temperature					
Alloy		225		235		260	
		T0	Fmax	T0	Fmax	T0	Fmax
InnoLot	Air	Abort	/	4.54	21	3.01	46
Innolot	N2	Abort	/	3.21	34	2.29	59
SAC387	Air	Abort	/	5.53	19	3.86	46
SAC387	N2	Abort	/	3.94	27	3.48	51

Table 5 – Aged Cu OSP wetting tests

with one element addition. All additions increased the alloy maximum safe operating temperature, with the strongest effect coming from the antimony additions. Both antimony and nickel had the undesired effect of raising the alloy liquidus and as a result a higher minimum soldering temperature is required. To counter this, bismuth additions into Sn based solders has an effect to decrease the solidus of the alloy which means that wetting can begin earlier. This solidus lowering effect by bismuth has been used in other alloy developments, such as for wave soldering low cost FR-2 laminates for consumer electronics.

Development of the alloy continued by combining and optimising all three dopant elements. The final alloy composition was arrived at SAC387 with 3.0% Bi, 1.4% Sb and 0.15% Ni. This combination delivered on the predicted safe operating temperature of over 150°C along with a minimum soldering temperature of 225°C.This alloy was named "InnoLot" after the project which had been initiated in Germany. The next phase is to evaluate the alloys performance.

Process performance considerations

As mentioned previously, the InnoLot alloy development was required to deliver on the tough reliability requirements mandated by engine bay or "under-hood" automotive electronics manufacturers. In addition to this it was always clear that the alloy must provide for high volume, high yield assembly processes. One of the key performance indicators for this was to understand the wetting behaviour of he alloy compared to the baseline SAC387. A wetting study was undertaken which included variations in soldering atmosphere, solder alloy temperature and surface finish, which will be described later.

Component and PCB finish considerations

As the majority of electronics assemblies have migrated to lead-free production, component manufacturers are transitioning the surface finishes of their devices. Newer component styles, like those used in miniaturisation, are being introduced in packages that will only be available in lead-free finishes.

The main PCB finishes used in the automotive electronics sector as described below:

High temperature organic solderability preservatives (OSP)

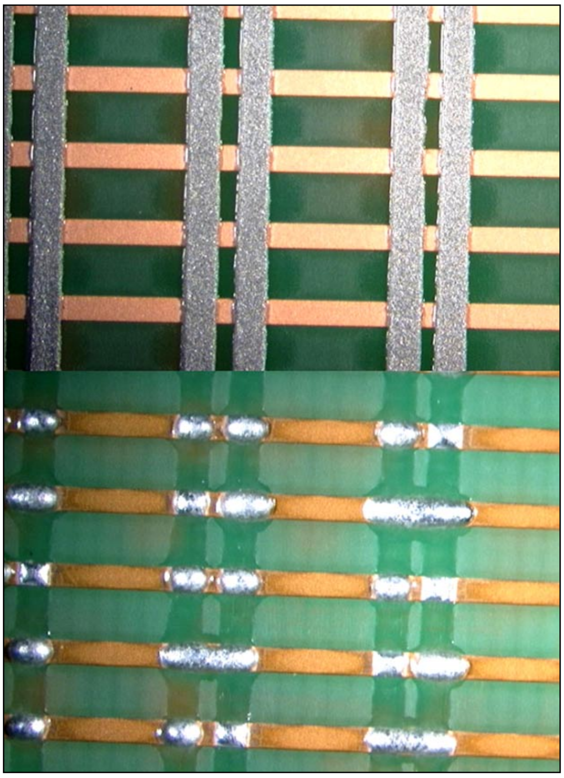
OSP is an extremely popular final finish due to its cost effectiveness and it's flat, planar surface that enables finer pitch solder paste printing. It has a good shelf life, and is even reworkable if applied poorly or stored beyond its recommended shelf life. The two downsides to OSPs are the limited hole fill that can be seen in wave soldering if the assemblies have experienced prior reflow excursions, and the lack of spread of lead-free solders pastes during reflow.

Newer generation OSPs are now available for the higher temperatures experienced in lead-free soldering processes. These high temperature products are usually completely backwards-compatible, and work very well in tin-lead processes, exceeding the performance of OSPs designed for tin-lead. In lead-free environments, high temperature OSPs perform relatively the same or slightly better than the tin-lead OSPs in tin-lead environments.

Immersion silver

Immersion silver is emerging as a choice surface finish for lead-free assembly. Some earlier forms of

Figure 4 – Cross print test method



immersion silver were associated with a failure mechanism known as planar microvoiding or "champagne" voids. These tiny voids appear in a planar form near the intermetallic region of solder joints, causing a weak spot and premature failure of the connection. There are several immersion silver options available, and planar microvoids are not associated with all immersion silver products. At this juncture it is reported that the issues of planar microvoids have been resolved in products that exhibited the problem.

Immersion silver finishes provide flat, highly printable surfaces, have very good wetting and spread properties when used with SAC alloy solder pastes, and retain very good solderability for post-reflow wave soldering. Shelf life of the surface finishes can vary, however. All immersion silver finishes are susceptible to tarnish in environments with excess sulphur.

Electroless nickel-immersion gold

Electroless nickel-immersion gold (ENIG) surface finishes are relatively common in high reliability applications. The gold provides a nearly "tarnish-proof" surface that is ideal for long term storage and solderless contacts. Its oxidation resistance gives it a very long shelf life, and even allows for bake-out if the PCBs absorb moisture during storage. The flat topography makes it ideal for stencil printing. SAC alloys spread better on ENIG than any other finish, which assists in getting full pad coverage in the reflow cycle and topside hole fill in wave soldering. It is theorized that ENIG finishes may help mitigate blow holes due to the nickel barrier that is applied to the copper.

On the downside, ENIG is the most costly final finish, "black pad" failures have been associated with it, and the surface being soldered to is nickel, not copper. Although black pad is now well understood, it still occurs, albeit rarely. Nickel can be more difficult to solder to than copper, and the joint construction will include a nickel layer in the intermetallic region. Intermetallic compounds comprised of tin and nickel are more brittle than tin-copper intermetallics.

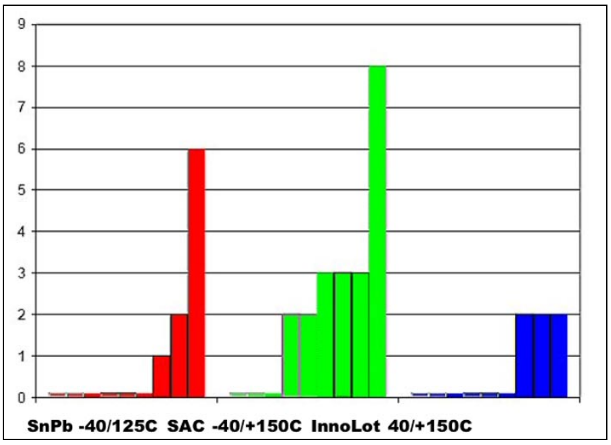


Figure 5 – Cycles to failure in 250 cycle blocks

There is no "perfect" surface finish for PCBs. The automotive assembler should consider the advantages and disadvantages of each, and make the best possible choice for the performance of their product.

Wetting behaviour characterisation

Wetting balance tests have been generally used to measure the solderability of components and as an aid to developing and testing fluxes. However if test variables are kept constant then this can be used as a relative measure of the alloy performance. Wetting tests were carried out on a wetting balance tester as shown in Figure 2.

The system was modified so that the testing could be carried out in both an air and nitrogen atmosphere. A standard test flux was used and several surface finishes were evaluated.

For each surface finish testing was carried out using 2 atmospheres (air and nitrogen), with three solder temperatures (225°C, 235°C and 260°C). Two aggregate measurements were taken from each trace which were maximum wetting force (F_{max}) and Time to zero wetting force (T_{zero}). Fmax is shown by position "D" on the following diagram, and T_{zero} is shown as point "C". The key requirement for the alloy development was to perform as well as the standard SAC alloy.

Evaluation focused on several component and PCB finishes, and one of the key indicators was determined to be OSP copper which would be tested in its virgin state and after thermal ageing. The results for the copper OSP surface is shown in Table 4. Note that the development InnoLot alloy shows faster wetting speed than SAC387 at the lower solder temperature, but equal speeds at higher temperatures. It is believed that this performance difference is facilitated by the bismuth inclusion in the alloy.

Also note the impact of nitrogen atmosphere on both the wetting speed and force. This result was important as it showed that the development alloy was capable of air and nitrogen reflow, and that the wetting capability below 230°C had been realised, albeit with less then optimal results due to a slow wetting speed. The wetting speed will always appear to be slow on these systems when the alloy is only a small delta from its liquidus point, as there is inadequate pre-heating of the sample. For this reason the InnoLot material was tested against SAC387 on a reflow test PCB using a technique described later on.

The results of aged OSP PCBs are shown below. The ageing process was achieved by baking the PCBs to 155°C for 4 hours. The results show marginally better wetting performance by InnoLot than SAC387, although the 225°C test had to be aborted with both alloys, due to no wetting during the cycle. It could be argued that the stand-

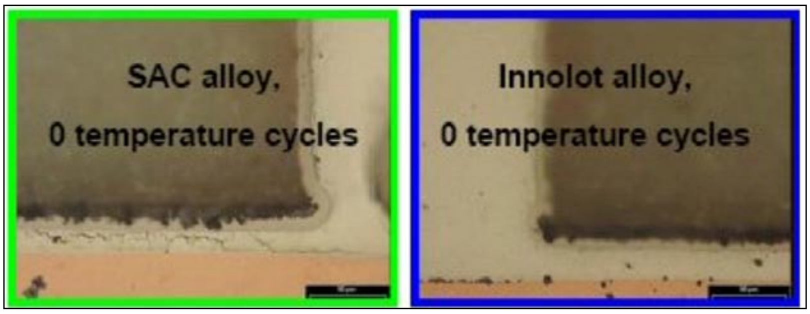
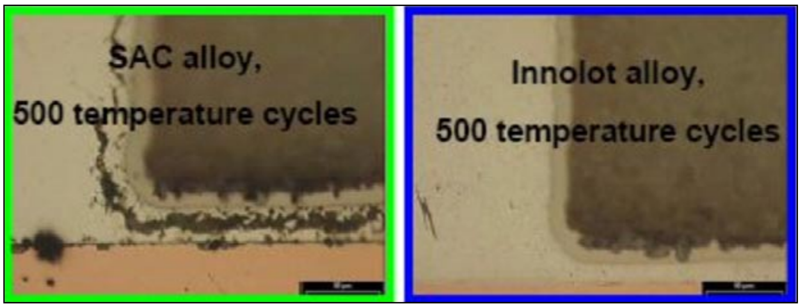


Figure 6 – Vibration effect : zero T cycles
Figure 7 – Vibration effect: 500 T cycles



ard test flux is too weak to cope with an aged OSP finish.

Wetting tests on OSP copper in an air reflow system, with the alloy in a ROL0 solder paste system, showed acceptable wetting performance with a peak surface temperature of 225°C. This was repeated with a peak surface temperature of 235°C. The test pattern employed was a "cross print" test pattern which has evenly spaced horizontal copper strips, overprinted by pairs of vertical paste strips which have an increasing gap between each pair. The alloy wetting performance can then be quantitatively compared to another test condition by logging how many of the gaps are bridged after reflow. The cross print test method is depicted in Figure 4, and the gaps range from 0.1mm to 0.8mm.

The results for this more practical test are designed to show qualitative comparative rankings, by means of a quantitative method of counting "bridges" as described above. It should be noted however that there are some very key differences to the analytical testing method of wetting balance testing as follows: (i) The alloy is produced in a powder format and mixes with a fully activated commercial lead free solder paste flux system and (ii) the samples have been a full preheating cycle which will help to prepare even the aged copper surfaces.

The results showed that the Innolot alloy is capable of wetting an aged copper surface in a process with a surface peak temperature of 225°C. With SAC387 the result was marginal under the same conditions, which highlighted the importance of the lower solidus of the InnoLot alloy on its lower temperature performance requirement. Further testing was carried out on several surface finishes but will not be covered in this article.

Reliability testing

After confirmation that the soldering properties of the alloy had met their design criteria, the next phase was to start the mechanical reliability testing of the InnoLot alloy, compared to its baseline SAC387 alloy.

Initial thermal cycling was carried out and rigid devices from RC0402s to RC2512s were monitored and the number of failures plotted every 250 cycles up to 2000 cycles. This is shown in Figure 5.

SAC387 showed significant failures after 750 cycles whereas Innolot did not show any until after 1500 cycles.

The next phase was high speed shear strength testing after various thermal cycling regimes. This showed that the Innolot alloy had equivalent results after a -40/+150 1000 cycle regime as SAC387 after a -40/+125 100 cycle regime. Beyond 1000 cycles with the -40/+125°C test the performance gap between the alloys widens considerably.

The final phase of reliability screening was to thermally cycle the test boards, and add the vibration component. At this phase of testing the SAC387 alloy really does perform poorly. Vibration without thermal cycles on SAC387 starts to show cracks at the alloy PCB interface on rigid devices. There is no evidence of this with the InnoLot alloy. This can be seen in Figure 6.

After thermal cycling with the vibration component added, SAC387 suffers from gross failures while InnoLot alloy remains intact. This can be seen in Figure 7.

Conclusion

This development of the InnoLot alloy has provided a potential solution for electronics which are subject to continual vibration and high temperatures. The majority of work to date has focused on the SMT reflow process. This is a more controlled process than wave soldering from an alloy perspective, as dissolution of surface elements from the PCB and components is limited to each individual joint. In the reflow process the alloy behaves in a very similar manner to the standard SAC alloy, from which it was developed.

Trials in wave soldering with the alloy were carried out during its development and performance was as good as a SAC alloy. However, a long term trial with this 6 element alloy has not been embarked upon to date, and so the effects of increasing levels of contaminants is not understood at this stage.