FACT AND FICTION IN LEAD FREE SOLDERING

The electronics industry's transition to lead-free soldering has been characterised by misapprehensions about the properties that are important in a lead-free solder and about the consequences for soldering processes and solder joint reliability. In this article the realities that have emerged from the practical implementation of lead-free soldering are reviewed and their implications for alloy selection considered. Particular attention is given to the benefits of replacing tin-lead, which behaves as near perfect eutectic, with lead-free solders that also behave as a eutectic.

Misapprehensions and Misinformation

The transition from tin-lead to lead-free has been traumatic for the electronics industry both in anticipation and in implementation and perhaps as a consequence has been characterised by misapprehensions and misinformation.

The trauma is perhaps understandable given that the industry has been asked to give up the material that has been the basis for the assembly of electronic circuitry since there was such a thing as electronic circuitry. Though far from a perfect material for creating joints between the individual components of a circuit it was for the electronics industry "the devil you know" and in the many years of its use ways were found for compensating for or accommodating its weaknesses as well as taking advantage of its strengths.

It might be said in retrospect, however, that the misapprehensions and misinformation were a result of a lack of understanding of some of the important features of solders and soldering processes. It is for that reason that many people feel that the electronics industry will emerge from the transition to lead-free stronger than it went it; the change has forced the industry to look at solders and soldering processes more carefully than they have before and consequently to learn more about what is important.

It has to be acknowledged too that some of the misapprehensions and misinformation were the result of deliberate mischief on the part of those who opposed the change as just another non-tariff barrier created by European bureaucrats. It was in the interest of such people to make that change appear to be as difficult, expensive, and dangerous as possible.

By contrast, although the challenge that it faced was no less daunting, the Japanese electronics industry voluntarily decided to eliminate lead from its solders, not because of any legislation that required it but because it realised that if electronics were going to be economically recycled the presence of lead would be an expensive complication. In a country such as Japan with limited waste disposal capacity there was general support in the electronics industry for the legislation on recycling that was implemented in 2002 despite the consequent need to eliminate lead.

Some Misapprehensions

It is important that the melting point of lead-free solder be as close as possible to that of the tin-lead solder it replaces.

As the industry began to consider the challenge of finding a lead-free solder some alarm was caused by the realisation that there were no element in the Periodic Table that would reduce the melting of tin as low as did lead, i.e. from 232°C to 183°C, that did not have some undesirable complications.

Those complications include limited availability, which is reflected in cost, reduced recyclability and reduced reliability. There was really no choice for the primary constituent of lead-free solder- its relatively low melting point and its ability to form intermetallic compounds with all of the metals that the industry needed to solder made tin the obvious choice. Bismuth at the level of 57% could lower the melting point even further to 139°C but the resulting alloy is difficult to use. Zinc at the level of 9% lowers the melting point to 198°C and while there has been some successful commercial application of alloys based on this eutectic problems arise from the relatively high reactivity of that element.

The addition with least complications that produces an alloy with many properties very similar to those of tin-lead, copper reduces the melting point only a few degrees to 227°C, still 44°C higher than that of tin-lead solder. The addition of silver to tin-copper reduces the melting point a further 10°C to 217°C but that is still 34°C higher than that of tin-lead solder. According to a US EPA-sponsored study of the environmental impact of the change to lead-free that 10°C reduction in melting point comes at the expense of most of the environmental advantages of eliminating lead but variations of that tin-silver-copper alloy have been widely accepted as the preferred lead-free option. Those concerned that 217°C was still too high for a practical tin-lead replacement made further additions of elements such as bismuth and indium but these increased the cost and/or compromised other properties or the recyclability, which was one of the main reasons for elimination of lead. Practical experience has indicated however, that a melting point close to that of tin-lead was not as important as first thought.

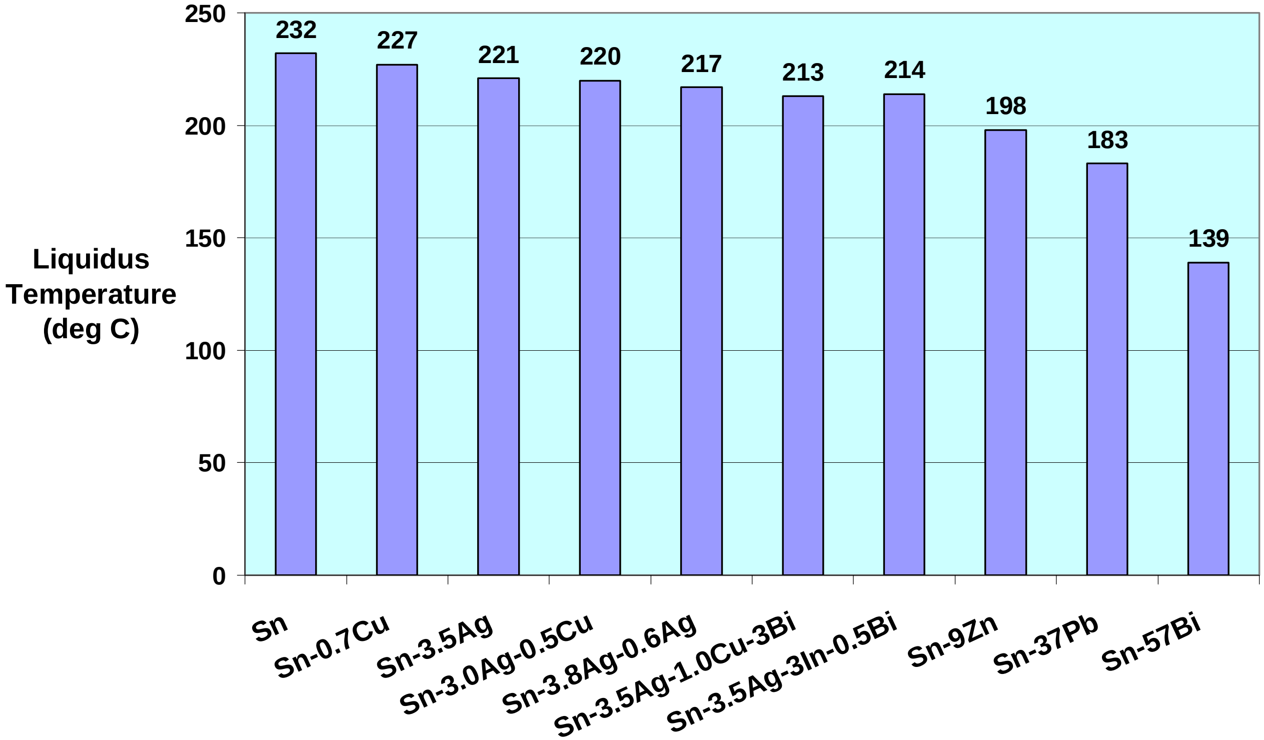


Figure 1. Liquidus Temperature of some lead-free solders compared with that of Sn63 Pb37

Process temperatures with lead-free solder will be very much higher than those used with tin-lead solder

The electronics industry gave itself a fright by applying what was thought to be a relevant calculation for the determination of the process temperatures that would be required for lead-free soldering. Noting that a typical temperature used for wave soldering with tin-lead solder has been around 255°C and that the melting point of tin-lead solder is 183°C they calculated the superheat for the process at 255-183°C = 72°C. On the assumption that a similar superheat would be required with lead-free solder they came up with expected wave solder bath temperatures of around 289°C and

299°C respectively for tin-silver-copper and tin-copper alloys. Applying a similar calculation to reflow temperatures indicated that minimum peak temperatures of 250 – 260°C would be required.

What was not realised was that there is a temperature that a metal surface has to reach before the wetting reaction required to form a joint can proceed that is not directly related to the melting point of the solder. The process temperatures used with tin-lead solder were therefore determined more by that temperature than by any concept of "superheat". Thus wave soldering with lead-free alloys can proceed at much the same temperatures as have been used with tin-lead solder, typically around 255-260°C for both tin-silver-copper and modified tin-copper alloys and reflow peak temperature are typically 10°C lower than predicted.

New equipment is needed for lead-free soldering

The higher melting point of the lead-free solders is not entirely free of implications for soldering processes. The difference between the process temperature and the melting point is much smaller for lead-free solders than it has been for tin-lead solder and that means that there is a much smaller "process window" in which to operate. However, for reasons that have nothing to do with any future change to lead-free, most modern soldering equipment that had been designed for tin-lead solder already had the capability of maintaining process parameters within the narrower range required for lead-free processes. Some older equipment with limited process control capability may not be suitable but in many cases it has proved possible to run lead-free processes with simple upgrades, e.g. adding extra preheat modules to a wave soldering machine.

A controversial aspect of equipment compatibility with lead-free soldering is solder pot erosion. Molten tin will react with and dissolve most metals including the metals used for the construction of soldering equipment. The aggressiveness of tin in that regard was considerably diminished by its one third dilution with lead in conventional tin-lead solder but erosion of stainless steel could still occur if the protective oxide film is penetrated mechanically or chemically. Whether or not molten lead-free solder will erode stainless steel machine parts depends on its composition and practical experience indicates that there is a considerable difference between alloys in that regard. The presence of silver in the solder appears to disrupt the protective oxide film making these alloys more likely to cause erosion of machine parts. If, as is usually the case, the tin-silver-copper alloy also has phosphorus added as an antioxidant then the protective oxide film is quickly penetrated and damaging erosion follows. If these alloys are used then it is necessary to use equipment in which stainless steel parts exposed to molten solder are treated or coated to make them more resistant to such attack or which is line with or constructed from metals such as titanium that are more resistant to such attack.

Figure 2. Erosion of stainless steel wave

It is not important that a solder behave as a eutectic

Given that it is within the memory of many people still working in the industry that electronics manufacturers accepted an approximately 5% increase in cost to move from "60/40" (60% tin, 40% lead) to "63/37" to get an alloy that behaves like a eutectic alloy it is surprising that in the move to lead-free there was not more emphasis on finding alloys that behave as a true eutectic. Purists will point out that the true tin-lead eutectic is actually at 61.9% tin but given the tendency to lose tin by oxidation and reaction with substrates a little more quickly than lead it was found worthwhile erring a little on the high tin side.

Certainly the industry consortia in Europe and North America homed in on two alloys of nominal eutectic composition, Sn with about 0.7% Cu and Sn with around 3.8-3.9% silver and 0.7-1% copper (there being some difference of opinion about the composition of the Sn-Ag-Cu eutectic). However, in their unmodified form neither of these alloys behaves as eutectics.

To understand the consequences of non-eutectic behaviour it is necessary to consider the difference in the way eutectic and non-eutectic alloys solidify. The distinguishing feature of a eutectic is that the two or three (or more) constituent phases freeze from the melt simultaneously and isothermally in a process known as "coupled growth". Since the freezing is isothermal a eutectic behaves like a pure metal except that the solid that is forming is made up of several different phases rather than the elemental metal. From each nucleus of solid that forms within the liquid at the melting point individual solid phases grow almost in parallel with the microstructure controlled by the rate at which the elements in the liquid can separate themselves out. The classic binary eutectic is tin-lead since the lead-rich and tin-rich phases grow as closely spaced parallel plates. The gross manifestation of this eutectic microstructure is a joint with the smooth bright crack-free finish of a well made tin-lead solder joint.

When an alloy in a eutectic system is of non-eutectic composition the solidification of the eutectic is preceded by the precipitation of a primary phase which has a lower content of alloying elements than the melt from which it is solidifying. The consequence is enrichment of the remaining liquid in those elements until it reaches the eutectic composition when it freezes. The outward manifestation of the resulting microstructure is the rough grainy surface left as the eutectic shrinks away from the network of primary dendrites or intermetallic crystals. Depending on the way the solidification front moves through the solder deep shrinkage cavities can be left that have been found to be points of crack initiation in vibration testing.

A more subtle consequence of non-eutectic solidification is the segregation of impurities that might have found their way into the solder. When an alloy solidifies as a eutectic impurities tend to be remain evenly dispersed. However, when a primary phase freezes out first the impurities tend to be concentrated in the remaining liquid and may segregate to create lines of weakness in the joint that have been associated with the phenomenon of fillet lifting and with premature failure.

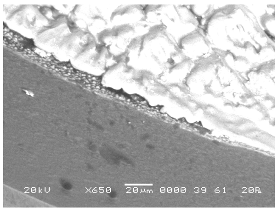


Figure 3. Fillet lift in SnAgCu joints associated with segregation of Pb

Neither of the two alloys recommended by industry consortia in Europe and America, tin-copper and tin-silver-copper freeze as true eutectics in their unmodified form and the result is the predicted grainy and often cracked finish.

There can be nothing more to lead-free solder formulation than mixing the basic constituent elements

Perhaps because tin-lead alloy worked so well as a solder without any further modification the electronics industry did not initially give consideration to the possibility that the less than ideal behaviour of the candidate lead-free solders could be improved. In the foundry industry, however, the concept of improving the performance of an alloy by trace level additions was well established and widely employed. Aluminium internal combustion engines, for example, are possible only because of successful modification of the aluminium-silicon eutectic alloy on which they are based.

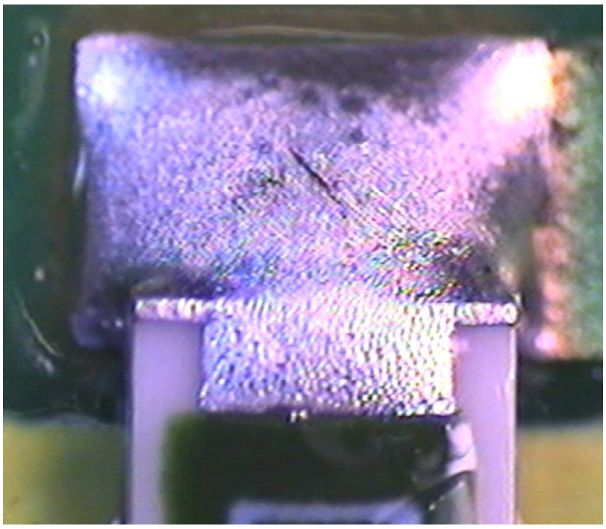
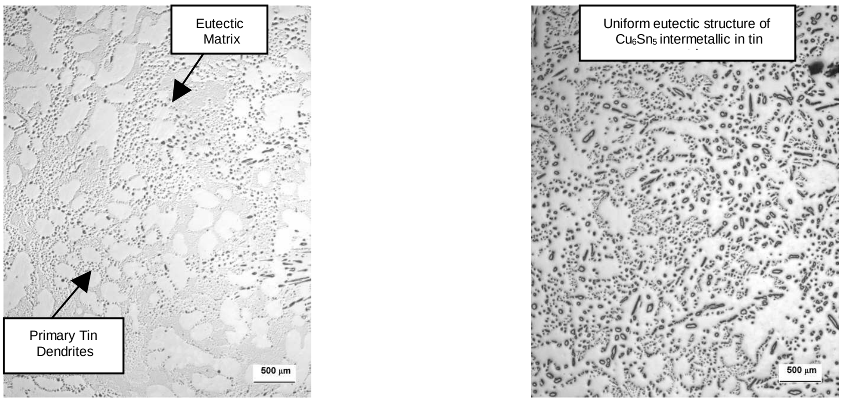


Figure 4. Surface appearance of eutectic and non-eutectic solder joints

To understand how candidate lead-free alloys could be modified to improve their performance as solders it is necessary to look more closely at how they differ from tin-lead solder. A significant difference between these lead-free solders and tin-lead in that the other phases in their eutectics are intermetallic compounds rather than simple metallic solid solutions. Although the tin-rich and lead-rich phases in the tin-lead eutectic are crystalline they do not grow in a form that is recognisable as crystalline. By contrast the intermetallic compounds in the Sn-Cu and Sn-Ag-Cu systems, Cu_6Sn_5 and Ag_3Sn grow in a faceted manner to form structures that are distinctly crystalline in appearance, needles in the former case and plates in the latter. Probably because that faceted growth is difficult to nucleate the coupled growth that is characteristic of a eutectic does not normally occur. Instead the alloy behaves as it had a lower alloying content and precipitation of primary dendrites occurs until the build up of alloying elements in the remaining liquid is sufficient to trigger eutectic solidification.



(a) (b)

Figure 5. (a) Non eutectic microstructure of unmodified Sn 0.7Cu
(b) Eutectic microstructure of Sn0.7Cu modified with controlled addition of Ni.

For those looking for ways to make the tin-copper and tin-silver-copper eutectic behave more like tin-lead solder this difference provided a clue. If the a way could be found to make it easier for the intermetallic component of the eutectic to nucleate and grow more readily that alloy might freeze as the eutectic it was supposed to be. Systematic studies of ternary additions to the tin-copper system in the late 1990's identified nickel as the element that if added to the alloy at a very low but precisely controlled level had the desired affect and an alloy based on that patented discovery is now one of the most widely used lead-free solders.

The nickel works by replacing some of the copper atoms in the Cu_6Sn_5 intermetallic. Since the nickel atom is slightly smaller than the copper atom it replaces the structure is distorted and it is believed that this makes it easier to nucleate so that its coupled growth with tin in a eutectic is facilitated. Whatever the mechanism the result is an alloy that in behaviour as a solder as well as microstructure and appearance is much more like tin-lead than the unmodified tin-copper.

For solder it is always a case of "the stronger the better"

Electronics circuitry is an assembly of a wide range of materials with different coefficients of thermal expansion so that as the assembly goes through temperature cycles resulting from changes in the temperature of the environment in which it operates or the heating and cooling as it is switched on and off there are relative displacements between the various parts of the assembly. And much electronics, particularly that in automotive, aerospace as well as industrial and even domestic applications is subjected to accelerations that result in loads being applied to the solder joints. When the accelerations are cyclical, i.e. vibrations, joints can be subjected to accumulated strain.

If there are flexible terminations that can accommodate that strain then a strong solder can be an advantage. One of the features of modern componentry, however, is that such flexible leads are replaced by direct solder connections, e.g. in BGA packages. The strain has to be taken up either by the body of the component of by deformation of the solder. If the former is the case then the component may be overstressed and fail by cracking. In the latter case the consequences depend on the characteristics of the solder.

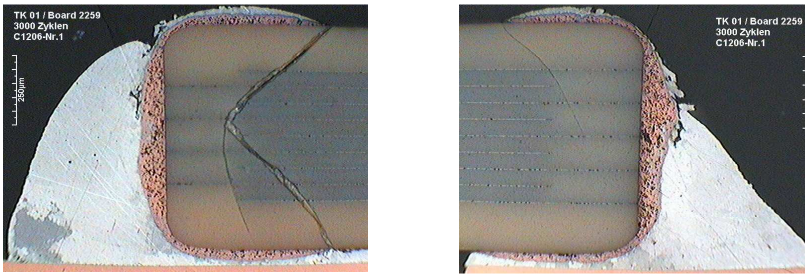


Figure 6. Chip capacity cracked by unrelieved stress resulting from differential strain in thermal cycling

One of the underappreciated advantages of tin-lead solder was not its strength but its compliance, i.e. its ability to absorb a lot of strain without hardening and cracking. By contrast the tin-silver-copper solders that have been most widely promoted as THE alternative to tin-lead harden quickly as they are obliged to accommodate strain with consequent crack initiation. On the other hand, solders based on the tin-copper system are much more like tin-lead in their ability to absorb strain without embrittlement and consequently yield higher reliability in applications where the joint itself is obliged to accommodate substantial cumulative strain. Jean-Paul Clech has summarised the results of numerous reliability tests on Sn-Pb, Sn-Cu and Sn-Ag-Cu in the plot in Figure x. This indicates that while at low strain Sn-Ag-Cu alloy joints survive more thermal cycles than either Sn-Pb or Sn-Cu, when the joint has to accommodate substantial strain the reverse is the case. In the lead-free program of the US military/aerospace Joint Group on Pollution Prevention it has been found that the modified tin-copper eutectic outperforms tin-silver-copper in vibration testing.

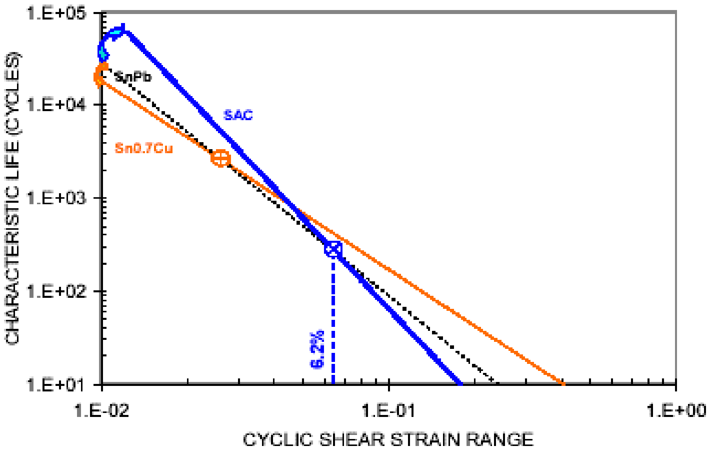


Figure 8. Strain dependence of solder reliability

HASL will be only a minor printed circuit board finish in the lead-free era.

Since it first became clear that the electronics industry would have to become lead-free the conclusion of nearly every panel discussion on printed circuit board finishes has been that HASL, the finish that has for many years been on 80 – 90% of printed circuit boards used in Europe and North America would largely disappear. HASL, Hot Air Solder Levelling, is the process of a applying a solderable finish to the tracks and pads of a printed circuit board by fluxing the board and immersing it for a few seconds in molten solder before drawing it out through hot air knives which squeegee off excess solder to leave a smooth, bright solderable finish. The prediction, perhaps reflecting the hope of their proponents, was that HASL would be largely replaced by alternative lead-free finishes. The finishes widely promoted as the most likely lead-free alternatives have been immersion silver and immersion tin with OSP for lower end consumer applications and ENIG (Electroless Nickel/Immersion Gold) for higher end technical applications. In fact lead-free HASL was confirmed as a viable commercial process in 2002 and there are now several hundred lines in commercial operation around the world.

The expectation that lead-free HASL would not survive into the lead-free era was probably based on early experience with alloys that were not really suitable for the process. Their effective fluidity was low and to get anything like acceptable results it was necessary to use a process temperature so high that the laminate was degraded and interconnect integrity compromised. However, the modified tin-copper eutectic alloy that had been developed for wave soldering was found to work well in the HASL process at temperatures around 260°C, only a little higher than has been used with tin-lead. With the viability of the process confirmed it now seems likely that HASL will continue to be the most popular printed circuit board finish in the lead-free era.

The Reality

There are more misapprehensions that could be discussed, e.g. that all lead-free materials are vulnerable to whisker growth, that they are vulnerable to "tin pest", that defect rates will always be higher than they were with tin-lead solder and that, if the sky does not actually fall in then planes that rely on lead-free electronics will be falling out of the sky. Without in any way diminishing the challenge that has been imposed on the electronics industry by the EU RoHS directive the reality that seems to be emerging is that the electronics industry will survive the change to lead-free and probably emerge from it in a stronger position than it entered. Certainly the industry will understand probably better than it ever has what is important about solders and the processes in which they are applied.