Lead-free Solder Products and their Properties

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Introduction

Despite the impression given by endorsements of particular alloys by industry consortia such as JEITA and NEMI there can be no certainty at this stage in the evolution of the technology that the best and final choices of lead-free alloys have been made. Those final choices will be made on the basis of the long term performance of the alloy in production and the subsequent reliability in service of assemblies made with the alloy. Because the basic metallurgy of lead-free alloys under consideration is quite different from that of tin-lead alloys their behaviour under stress is different and not directly predictable on the basis of accelerated test models developed for tin-lead solders. For that reason there has to be doubt about the usefulness of much of the currently available accelerated test data in predicting real time service reliability. Experience of mass production is, however, valid now and can be used in comparisons of lead-free solders. The Japanese electronics industry has more than five year's experience of mass production of electronic circuitry with lead-free solder and at least some of that experience might be of value to the rest of the global electronics industry as it responds to the need to deliver lead-free product to the European Community by July 1, 2006. In this paper the characteristics of some lead-free alloys will be reviewed primarily from the point of view of the Japanese experience of their performance in production soldering. It is not the intention of the authors to recommend specific alloys since, with appropriate process parameters, it is possible to get acceptable soldering with many of the alloys systems currently being considered. Rather it is the intention to consider how the various different properties of candidate alloys affect performance in production soldering processes and this can provide a guide to an appropriate selection procedure.

The Driving Force

Whether expressed in legislation or consumer preference the driving force for the move to lead-free soldering is concern about the impact of lead on the environment. Whether the negative impact on the environment of lead in the solders and finishes used in the electronics industry is sufficient to justify the cost, inconvenience and new environmental impacts associated with the change to lead-free is a matter of dispute. It is becoming clear, however, that the change will occur irrespective of the outcome of that debate. Because of the difficulty of sustaining two parallel technologies, lead-containing and lead-free, it is likely that even those sectors granted exemption will adopt lead-free once it is clear that reliability is not compromised and that lead-free assembly is not as difficult and expensive as had been feared. Whether all the implementation will proceed according to the timetables of the EC directives is far from certain. The deadline for legislation for the implementation of the directives, August 13 2004, for example, passed without any EC member country having completed the necessary action.

Lead Free Solder Alloys

As of the third quarter of 2004 about the only point on which there is practical agreement in regard to the selection of a lead-free solder is that it should contain a high percentage of tin, usually greater than 90%. While variations around the tin-silver-copper eutectic are widely cited as the preferred option in all applications Nihon Superior has data that indicate that, for example, in wave soldering a patented modification of the tin-copper eutectic is used in more than a quarter of the machines operating as lead-free. Variants of the tin-copper system containing small amounts of silver and bismuth and in some cases indium are also being used in commercial wave soldering lines.

The Role of Tin

Tin enjoys the status of the preferred primary ingredient in lead-free solder not only because of its low melting point but because of its unique ability to form intermetallic compounds with most of the metals to which soldered joints have to be made. Although, with the correct balance of surface tensions, a mechanical and electrical bond can be achieved without the formation of an intermetallic compound its presence does provide a reassurance that a true metallurgical bond with good mechanical strength has been achieved.

Alloying Additions for Tin

Although pure tin (melting point 232°C) can be used as a solder it is usually alloyed with other elements to reduce its melting point and improve its mechanical properties. With the preferred alloying addition, lead, now excluded the options for additions that are not considered toxic are limited. Tin forms a eutectic with copper at 0.7% (melting point 227°C) and silver at 3.5% (melting point 221°C) and both of these alloys have a track record of successful use as solders unrelated to issues of lead toxicity. Together at levels of around 0.5-1% and 3- 4% respectively copper and silver form a ternary eutectic with tin that has a melting point of 217°C. The high cost of silver has prompted consideration of the lowest level at which it might have some beneficial effect on properties and variants have as little as 0.3% silver as an addition to the basic Sn-0.7Cu eutectic. Of course as the silver content is reduced below the eutectic the liquidus temperature increases and a pasty range develops. At least one solder supplier is claiming that, when used in conjunction with an approximately equal amount of bismuth, a silver level as low as 0.17% silver can enhance the properties of the Sn-Cu eutectic sufficiently for its successful use in wave soldering.

Intermetallic Compounds and Strength

Both copper and silver have a strong tendency to form intermetallic compounds with tin (Cu_6Sn_5 and Ag_3Sn respectively) so that a characteristic that distinguishes the lead-free alloys based on tin-copper or tin-silver-copper from tin-lead is that their microstructures are dominated by intermetallic crystals dispersed in what is a nearly pure tin matrix. Tin-lead eutectic solder is essentially interleaved plates of two metallic phases, one tin with up to about 2.5% lead in solid solution and the other lead with up to 19% tin in solid solution and most of its properties of that alloy derive from the combined properties of these two phases. Although the dispersion of hard and rather brittle intermetallic crystals is the major contributor to the strength of the lead-free alloys they also reduce their capacity for compliance. Compliance, the ability of the solder to accommodate cyclical strain without degradation, is a property that can be as important in an electronic solder as absolute strength. The lower compliance of lead-free solder can result in differences in the ranking of lead-free solders with respect to tin-lead solder depending on the nature of the loading on the joint (Figure 1) and this complicates the selection of a lead-free alloy for a particular application.

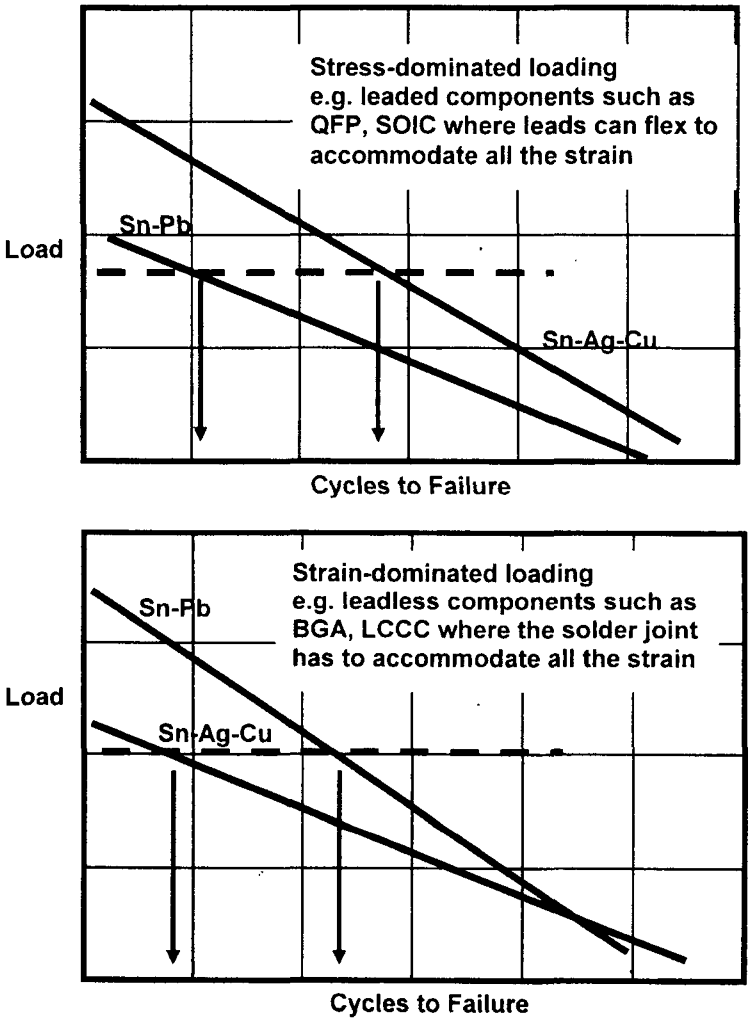
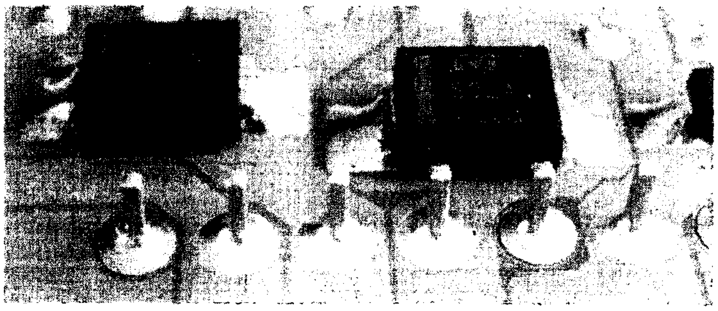


Figure 1- Schematic representation of variation with load type of strength in thermal cycling

Solid Solution Strengtheners
There is an argument that the properties of lead-free alloys based on tin, copper and silver can be enhanced by the addition of metals that dissolve in rather than form intermetallic compounds with tin. Lead was such an addition but now that it has been excluded the most popular candidates for that role are bismuth and indium. These elements can also bring the melting point of the resultant alloy down to 200-220°C range although there is not a convenient eutectic. Bismuth at a level of 57% produces a eutectic with tin with a melting point of 139°C and this alloy finds application where its melting point of 139°C makes it possible to solder temperature-sensitive components.

Intermetallic Modifiers
Given that intermetallics are the predominant feature of the commonly recommended lead-free solders another approach to the improvement of the standard lead-free alloys which has already yielded successful commercial alloys is the use of trace level additions of certain elements specifically targeted at the intermetallic phases. These can affect the nucleation and growth of the intermetallics and refine the particle size.

Suppression of nucleation of the intermetallics should improve the fluidity of the alloy close to the melting point and this effect has been demonstrated with the addition of nickel to the tin-copper eutectic. The resultant alloy has much lower incidence of bridges (shorts) and better through-hole filling and topside fillet formation in wave soldering. The finer grain size of the intermetallic that finally forms results in joint with a surface finish comparable in smoothness and brightness and profile with joints made with tin-lead solder (Figure 2). And additions of certain transition metal elements have been found to have beneficial effects on tin-silver-copper alloys.



Sn-37Pb

Sn-0.7Cu-0.5Ni

Figure 2- Lead-free joint appearance similar to tin-lead with ternary addition to tin-copper eutectic

Trace Additions
Trace level additions (<0.01%) of a number of other elements, including rare earth elements have been found to have beneficial effects on the properties of solders including the reduction of dross rates and refinement of the grain structure and can be considered a valid part of lead-free solder metallurgy. Claims have been made of segregation of these elements to grain boundaries where it is speculated that they might have a weakening effect. No evidence of such effects has been observed and in the meantime assemblies made with alloys containing such trace additions have accumulated five years of field service without evidence of embrittlement.

Melting Points and Process Parameters

In can be seen in retrospect that the initial focus on finding lead-free alloys with a melting point as close as possible to that of tin-lead might have been misguided to the extent that the melting point is only one of the factors that determining process temperature. The early concerns that the superheats traditionally used when soldering with tin-lead alloy would have to be maintained with lead-free alloy have subsequently proved to have been unwarranted (Table 1). These lower process temperatures have been achieved by better process control and this has been made possible by improvements in equipment design that were already underway even before the adoption of lead-free solders began. In wave soldering a key requirement is a preheat system that can get the board temperature to at least within about 100°C of the melting point of the solder with minimum ΔT across components and without exceeding the permitted maximum heating rates of individual components. This is being achieved by the use of a series of several different types of preheater with different heat transfer characteristics, for example low speed and high speed forced convection, long and short wavelength infrared. And a number of other steps have to be taken in the design of wave soldering machine to ensure that temperatures are kept within the required range until after the joint has exited the solder wave. In reflow the achievement of a minimum ΔT is also the key consideration, particularly for BGA components, and this is being achieved by the use of ovens with a very high component of forced convection heating.

Alloy	Temperatures (°C)				
	MP	Wave Solder	Superheat	Reflow Solder	Superheat
Sn-Pb	183	250	67	215	32
Sn-Ag-Cu	217	255	38	235	18
Sn-Cu*	227	255	28	245	18

Table 1- Lower superheat to keep process temperatures low

The Effect of a Freezing Range

The limited range of alloying elements available for the formulation of lead-free solders and the limited number of eutectics in a suitable temperature range mean that many of the options being considered are alloys that have a freezing range. It was always considered that one of the advantages of the "63/37" tin-lead alloy was that it is a eutectic and that consideration may also have some validity for lead-containing solders. The only major exception to that rule has been in the formulation of solder pastes designed to address the phenomenon of tombstoning (complete or partial rotation to the vertical of chip components in reflow soldering) where a small pasty range (the difference between the liquidus and solidus temperatures) has been found to be one way of reducing the incidence of that defect.

A widely observed phenomenon that is a side-effect of the use of off-eutectic alloys is what have become known as "microcracks" in the fillet of solders such as the Sn-3.0Ag-0.5Cu (Figure 3). These result from shrinkage of the remaining liquid phase away from the matrix of primary tin dendrites. Whether or not these cracks present a reliability issue has yet to be finally determined but they do create a problem for manual and automatic inspection because of the difficulty of distinguishing "microcracks" from other cracks that could be detrimental to joint reliability.

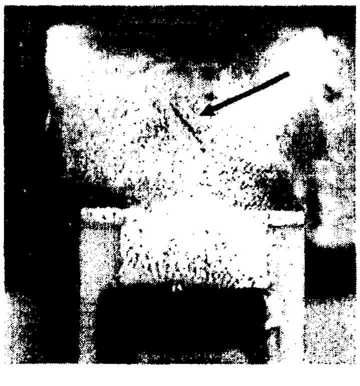


Figure: 3 Microcracking in a Sn-3.0Ag-0.5Cu alloy

Another effect of using a non-eutectic lead-free solder is the greater potential for segregation of dissolved impurity elements (Figure 4). This should not be a problem in the future when the industry has become completely lead-free but in the transition period when some components finishes still have lead-containing coatings there can be a build up of lead in the solder baths of wave soldering machines. Experience indicates that in hypoeutectic Sn-Ag-Cu dissolved lead can segregate to interfaces creating points of weakness. This segregated phase can be a factor in the phenomenon known as "fillet lift" when the solder fillet pulls away from the pad as a result of shrinkage during solidification and cooling.

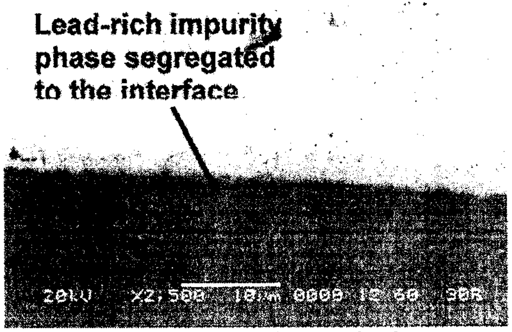


Figure: 4 Segregation of lead impurity in non-eutectic solder.

Soldering Properties of Lead-free Alloys

Although in many respects lead-free solders can provide a soldering performance comparable with that of the tin-lead alloy they are replacing there are some characteristic that have to be allowed for in soldering processes. Apart from a generally higher melting point two characteristics which have a major influence on the performance of the solder in production processes are slower wetting (Figure 5) and less spread (Figure 6).

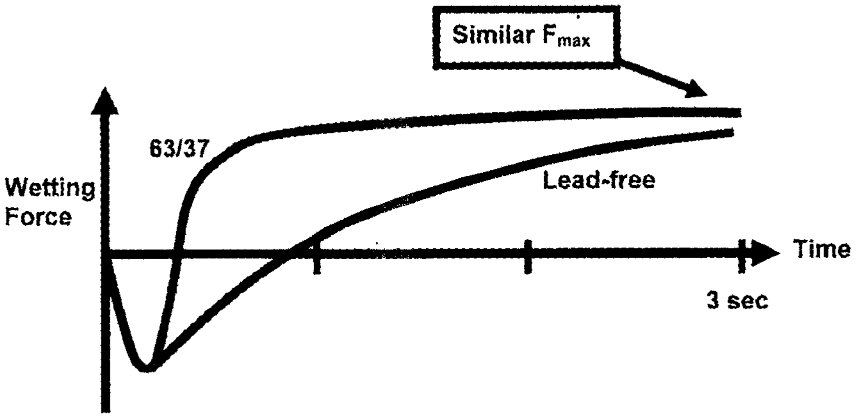


Figure 5- Schematic representation of lower wetting of lead-free solders

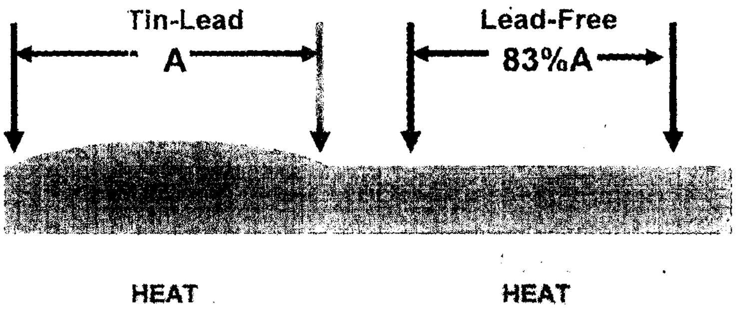


Figure 6- Lower spread of lead-free solder

The slower wetting can be allowed for by providing a longer contact time in wave soldering or a longer time above liquidus in reflow soldering. The liquid flux used in wave soldering or the solder paste flux medium should be formulated to survive the longer thermal profile required for optimum lead-fee

The lower spread can be provided for in the first instance by ensuring that printed circuit boards and components have the best possible solderability. In wave soldering flow into plated-through holes can be assisted by using maximum possible pressure in the turbulent (chip) wave and ensuring that all surfaces to be soldered are effectively fluxed. The spreading demands made on the solder in wave soldering can be reduced by reducing the area of topside pads on plated-through holes where a complete coverage by the topside fillet is required. In reflow, solder paste has to be printed to the full area of the pad.

Fluxes

Given the natural tendency of lead-free solders to slower wetting and reduced spread much dependence has to be placed on the flux to achieve satisfactory soldering. However, the longer and hotter preheats and longer contact times in wave soldering and longer ramps and longer times above liquidus in reflow soldering impose heavy demands on the durability of flux activation systems. Most of the large scale production experience with lead-free wave soldering has been within the Japanese electronics industry where high-solids (>10%), halide-activated resin-based and alcohol-based fluxes are still widely used. These fluxes meet the surface insulation resistance and electromigration requirements of a no-clean flux but they have a level of residue greater than what is now considered acceptable by the American and European electronics industry. Initial trials with the types of low-solids no-clean "no-residue" fluxes that were being used in America and Europe for tin-lead soldering yielded disappointing results. However, flux suppliers soon responded with more robust low solids formulations and results obtained with these fluxes are now comparable with those obtained with tin-lead solder. For fluxes designed to work in air the solids contents are generally higher than those used for tin-lead soldering, typically around 5%. In reflow it has been found that the different chemistry of the solder powder surface requires flux media formulations that are different from those used for tin-lead solder. Again the industry has responded and results in terms of wetting, joint formation and solder balling are comparable with those obtained with tin-lead solder.

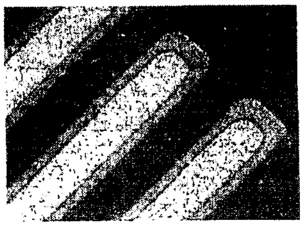
Properties Important in Production Processes

Wave Soldering

A difference between reflow and wave soldering that has implications in the selection of an alloy is that all of the stock of solder alloy in a wave soldering machine is interacting with the assemblies being soldered with the prospect of all metals on the surfaces exposed to the solder melting or dissolving into the solder bath. By contrast solder paste in discrete amounts is exposed only to the substrates in the joint area. Any elements melted or dissolved from the joint substrates remain within the confines of the joint and do not contaminate the stock of solder paste or other joints. Solder paste is not in contact with machine parts when in the molten state whereas in a wave soldering machine the solder bath, pump and wave former are exposed constantly to molten solder with implications for the solder bath materials as well as the solder. And unless a complete nitrogen atmosphere is maintained the solder is reacting with oxygen in the air to produce dross which can affect the soldering performance and the overall economics of the process.

The aggressiveness of the solder toward copper has implications both for the reliability of the assembled circuit (Figure 7) and the management of the solder bath.

Copper leaching is an issue in the management of tin-lead solder but the difference in lead-free soldering is that copper is also one of the components of the alloy rather than an impurity. The rate of erosion of copper from the board determines whether or not the copper level in the solder can be maintained within specification by the use of a low-copper replenishment alloy. If the copper content of any of the lead-free alloys increases too far the Cu_6Sn_5 intermetallic begins to precipitate at temperatures above the 227°C eutectic temperature, interfering with the flow of the alloy with a consequent increase in the incidence of shorts. The differences in the copper erosion rates for some widely used lead-free solders are apparent in Figure 8. For alloys with a relatively low copper erosion rate it is possible to keep the solder bath within specification by using a replenishment alloy that does not contain copper.



After 6 passes over a wave soldering line
105°C preheat, 256°C solder temperature 4 seconds contact time

Figure 7- Differences in copper erosion rates.

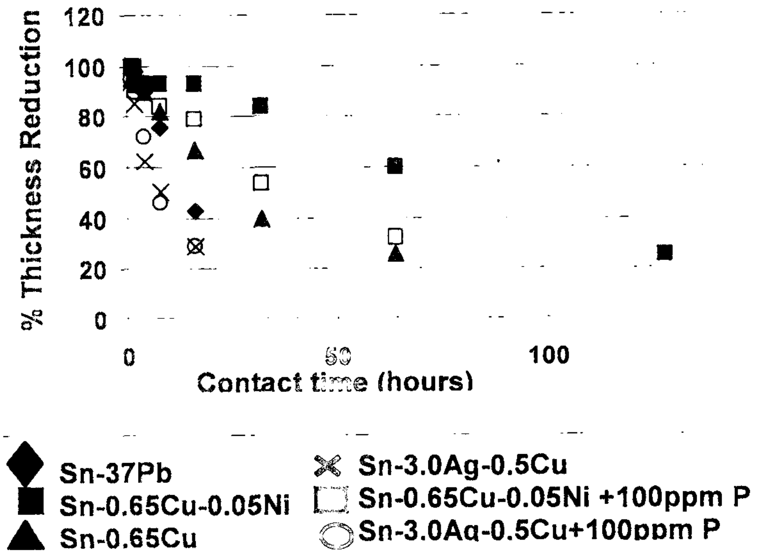


Figure 8- Rates of copper erosion for some proposed lead-free solders

Lead-free solder alloys also vary in their aggressiveness towards stainless steel. The differences lie mainly in the rate at which the alloy wets the stainless steel since after wetting has occurred the erosion rates are similar. The relative tendency of some lead-free solder alloys to wet stainless steel, in this case measured by the amount of tin left on stainless steel exposed to the molten solder after the solder is removed, is presented in Figure 9. The problem of erosion of stainless steel wave soldering machine parts has been addressed by applying special protective coatings to the stainless steel or replacing it with naturally resistant materials such as titanium. Where protective coatings are used there remains a case for using less aggressive alloys since there is always a risk of the coating suffering mechanical damage.

The combined effect of the foregoing issues of solder behavior can make a significant difference to the cost of running a wave soldering line (Figure 10)

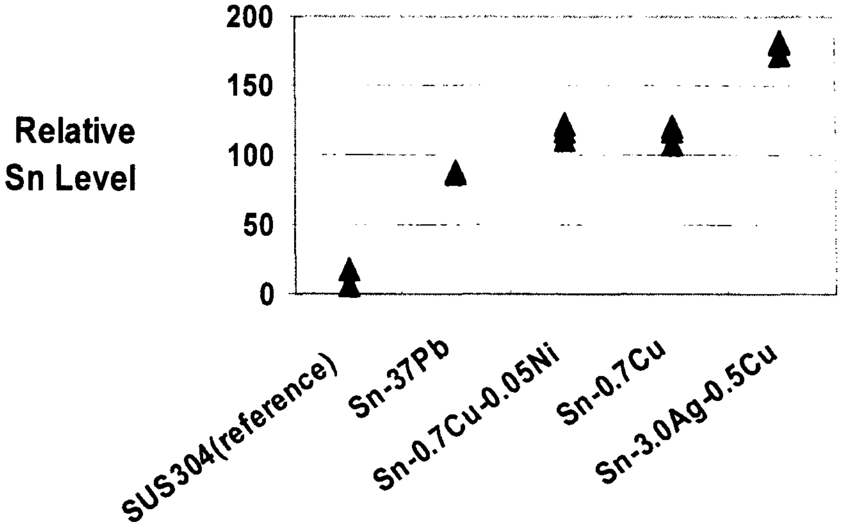


Figure 9- Relative wetting characteristics of some lead-free solders

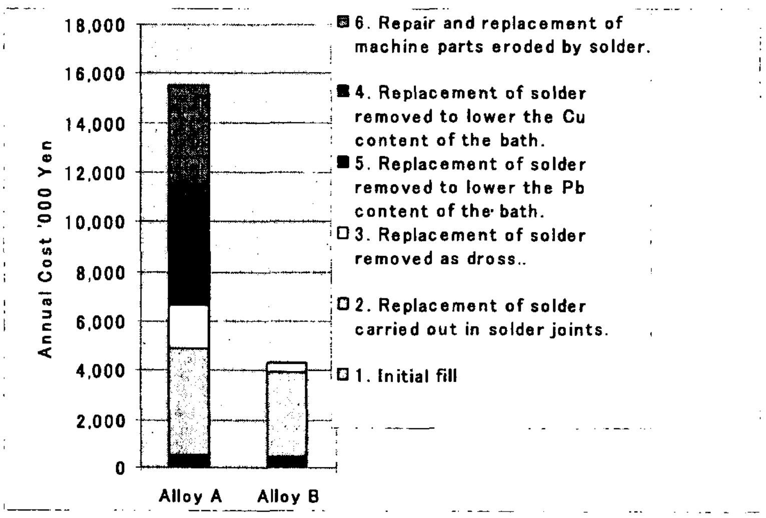


Figure 10- Factors that can affect the overall cost of running a wave soldering machine

Reflow

Issues of copper erosion occur in reflow soldering but the feature that distinguishes reflow in this context is that reactions are confined to the solder forming the joint and are thus to some extent self limiting. On the other hand the joint may be molten for more than a minute so that there is time for reactions to proceed. In such circumstances intermetallic growth is a concern since a thick layer of brittle intermetallic at the solder/substrate interface can provide a path for easy crack propagation, particularly in mechanical shock loading.

Lead-free Solder as Printed Circuit Board and Component Finish

In the consideration of which solderable finishes will be most widely used in a lead-free electronics industry there has been a tendency to dismiss hot air solder leveling ("HASL") on the basis that the coating is too uneven and that the high temperatures that were likely to be required would damage the laminate. However, there has been strong motivation to develop a lead-free version of the finish that has for many years been the most popular in Europe and North America. The reason for the popularity is that a properly applied HASL finish can provide at least a one year solderable shelf life without the need for special storage conditions. The problems that were encountered in early trials have been largely addressed by modifications to equipment to improve temperature control during the process and, most importantly the development of an alloy that has the fluidity necessary for smooth and even flow during the hot air leveling stage. The finish is smooth and bright and has been found to have a better and more uniform thickness range than tin-lead HASL (Figure 11). The greater fluidity has also made the process suitable for fine pitch applications (Figure 12).

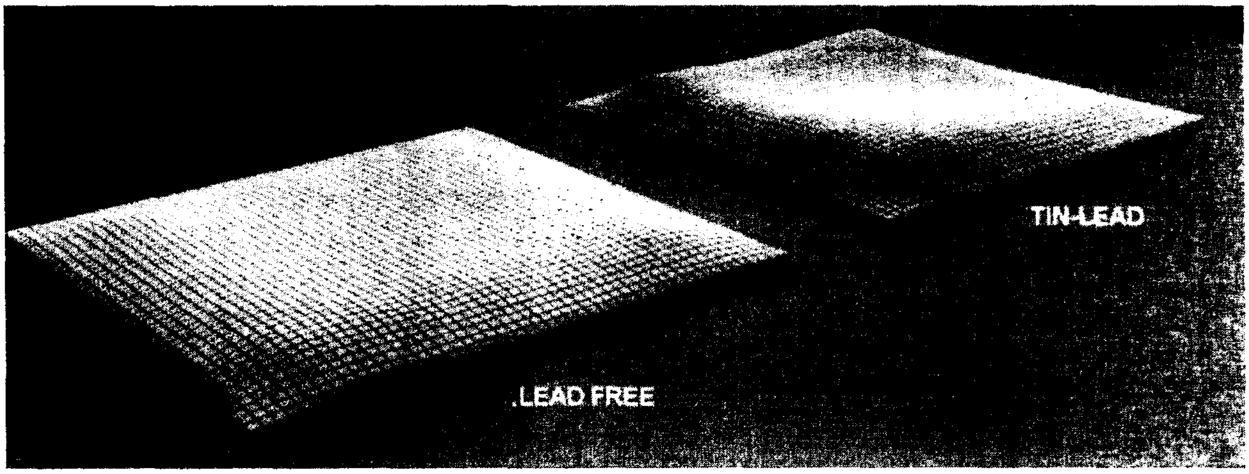


Figure 11- Greater uniformity of coating thickness with Ni-modified Sn-Cu eutectic HASL

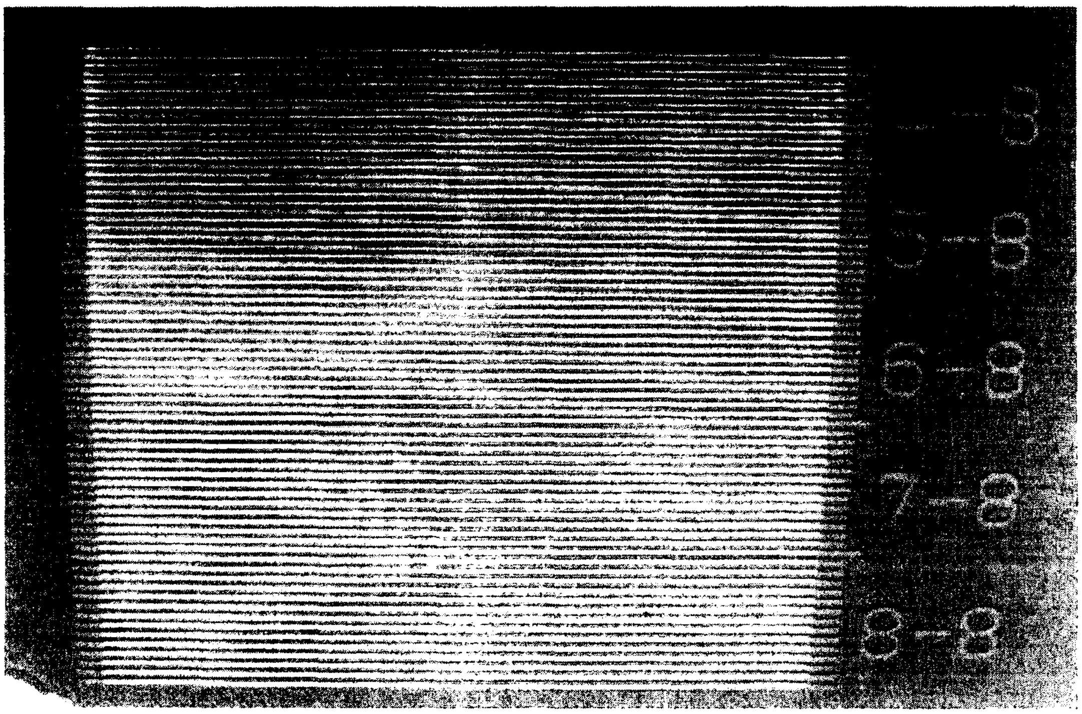


Figure 12- Fine pitch capability of lead-free HASL with Ni-modified Sn-Cu eutectic alloy

Hot dipping processes have been a popular method for applying a solderable finish to component terminations, particularly when the process also requires some soldering, e.g. the joining of transformer wire to a tag. Lead-free options for these processes have emerged and are already in widespread use. As in wave soldering a key issue is often the rate of copper erosion and the ease with which excess solder can drain from the termination. Where a high temperature is required to burn off insulating lacquer alloys with a high copper content are required to suppress copper dissolution and as in wave soldering ternary additions of nickel have found to be helpful not only in further suppressing dissolution of copper but in facilitating drainage and the formation of a smooth bright finish.

Adapting to Lead-free

As was found when there were other major changes in electronics assembly technology, e.g. the introduction of surface mount, the adoption of no-clean technologies as a result of the Montreal Protocol on the phasing out of CFC solvents, there is a "learning curve" associated with the introduction of lead-free solders. Although the challenges seem daunting there can be some confidence that, as it has before, the electronics industry will learn how to go lead-free without compromising quality and reliability. Figure 13 which tracks the experience of one particular company in phasing in lead-free wave soldering provides an example of how the industry can respond to a challenge. The encouraging point to note is that the final result was that the incidence of defects in soldered assemblies was finally lower than that which had been experienced with tin-lead solder.

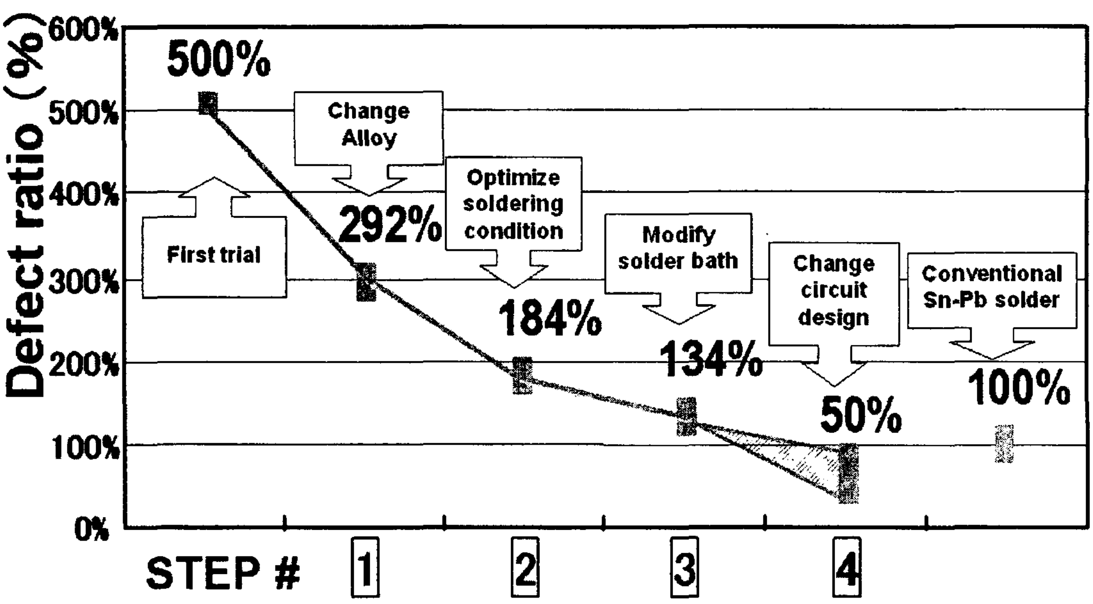


Figure 13- An example of a lead-free implementation learning curve

Conclusions

Although the results obtained so far suggest that the electronics industry will be able to move to lead-free technologies without compromising production efficiency and reliability there is much further work to be done on the development and selection of lead-free solders and the optimization of processes for their application.

Acknowledgements

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