Lead- free Alloys for Wave and SMT Assembly: *Assembly with Two Alloys*

Peter Biocca
MBO Solder Inc.
Allen, Texas 2002

Abstract

Research on lead-free alternatives began over a decade ago. Starting primarily in Europe, research on lead-free solders as substitutes to the popular lead-bearing solders used today proved not as easy as initially expected by many. Over two hundred alloys have been examined and today only a select few seem to be possible choices.

The well understood tin-lead solder system used by today's electronic assemblers has been somewhat under-appreciated through the years. Today the many characteristics of traditional solders, which are well documented, are not found readily in reference to lead-free alloys and much investigative research is ongoing to determine them.

Wave soldering and SMT soldering processes, are the workhorses of reliable, high yield, defect free electronic assembly today. A switch to lead-free solders in these processes will require careful consideration, first to the alloy selection and then to the changes in process required to achieve the same results accustomed with tin-lead systems.

In the last year North America has seen increased interest in lead-free solders; this trend is expected to continue into the next decade. This paper will therefore address some of the present concerns and challenges facing the assembly industry in transitioning to lead-free for wave soldering and SMT assembly.

This paper will also examine two alloys, which have showed successful use in wave soldering and SMT assembly. The selection of these two alloys was made considering the technical and commercial issues detailed in the first sections of this paper.

This paper does address the issues encountered by transitioning to a lead-free soldering process. The commercial and technical issues discussed can be used to guide the assembler in the selection of a suitable lead-free alloy, and some time is therefore spent explaining these issues before examples of use on 99C and 96SC are had.

Alloy Selection - Technical and Commercial Considerations

When considering lead-free alloy alternatives for electronic assembly, there are several obvious technical and commercial points to consider. These points are often overlooked but they all impact the future adoption of lead-free solders as a viable option.
The present use of tin-lead solder worldwide is about 50,000 metric tons. Eliminating the lead as a source of toxicity will require replacing it and the properties provided with combinations of other elements.

Commercial considerations

Lead in solder is relatively inexpensive at about $0.40 a pound, it has remained abundant and readily available through past decades. Replacing the lead with another element will increase the cost of the raw alloy. Most metal substitutes for lead are considerably more expensive such as silver. Indium is several times more expensive than silver and therefore would be not an appropriate choice as an alternative to lead replacement.

Availability of some elements for example, bismuth, would also hinder selection. Large amounts of bismuth in the alloy would not be possible without limiting supplies. Elements currently available in quantities sufficient to satisfy the demand for 50,000 metric tons of solder are, tin, copper, silver, and antimony.

The selected lead-free alloy would have to be made available in various forms such as solder bar for wave and powder for solder paste but also solder wire for repair. Some alloys are not easily available in all forms for example: a high content of bismuth in the alloy would cause embrittlement and make drawing of solder wire very difficult. The use of zinc would promote oxidation of the alloy and require special flux systems to effectively promote wetting. Also the shelf life of a tin/zinc alloy powder would be reduced by its oxidation potential.

The recycling of the alternative lead-free alloy will have to be considered. At present all tin-lead solder in its various forms can be recycled easily. Processes for recycling tin-lead alloys into re-usable solder are proven and safe. This may not necessarily be the case for all lead-free alloys, and new recycling procedures may be required. They may also add costs to the end-user if recycling is difficult, unsafe or expensive to perform.

The key commercial factors in lead-free selection are:

- Cost of alloy
- Stability of metal costs
- Availability of elements
- Manufacture-ability into bar, wire, powder and preforms
- Availability worldwide and alloy patents
- Recycle-ability of the alloy
- Quantities of recycled materials generated by process changes

Technical considerations

Alternatives to lead-free should not require completely new flux chemistries and must be available in no-clean type fluxes, which are traditionally low in activity. No-clean fluxes have been enhanced through considerable research in the last decade with growing pains of their own; lead-free solders may require further work in this area. The present flux systems used today work well with tin-lead solders; lead-free solders do not wet and form the same types of inter-metallic bonds. With some alloys the modification required to the chemistry could be minor; in others it could mean looking for new activators or combinations of activators better suited to higher temperatures.

Some elements proposed, as lead replacements are toxic in themselves such is the case with antimony. This could limit its future use to only incremental additions in the solder.

Mechanical properties of these alternatives are also different and will require careful selection to suit the final assembly and its intended use. The melting point will also change, traditional Sn63 and Sn62, melt respectively at 183 and 179 Centigrade, many of the choices available today melt at substantially higher temperatures in excess of 200 Centigrade. Process changes will be required and component life under these process conditions verified for long term reliability.

Board and component finishes will have to be chosen to be compatible with the lead-free solder. Lead on component finishes and HASL boards can create low melting phases in the reflowed solder, phases that melt at lower temperatures than the alloy itself. An example of this, is the Bi-Pb phase formed with tin-bismuth solders and lead found on component or HASL finishes which melts at 97 degrees Centigrade.

Also to be considered during any implementation process are the changes to internal quality standards that may occur, many of these alloys have different surface tensions and also the surface finish may not be typical of traditional solders. Interpretation of solder joint quality will be different and require re-training of quality personnel.

To be noted is the fact that impurity levels and their effects on lead-free alloys is not completely known. This will create some concerns at the solder manufacturers level but especially to solder wave users where contamination of the solder will occur and require proper monitoring and eventual disposition of the solder if contamination increases, when to replace is not known completely.

Lead-free alloys may offer benefits such as increased temperature resistance, higher mechanical strength, and higher fatigue strengths. This could be a reason other than lead toxicity for a switch over to these newer alloys.

Also notable is that at the present time few alloys exist to eliminate high lead alloy use in component manufacturing. Therefore completely lead-free assemblies are not possible. Substantial lead reduction is possible however with the soldering process.

<u>The key technical factors in lead-free selection are:</u>

- Board/component finish compatibility
- Melting point of the alloy
- Mechanical properties of the alloy and inter-metallic bond
- Flux chemistry compatibility
- Production process change requirements
- Quality control process changes
- Training for soldering personnel.
- Impurity limits for new alloy
- Reclamation of impure alloys, especially wave

Rework and Repair with Lead-free Solders

Regardless if assembly is done using a wave solder system, reflow oven, repair and rework including parts that need hand assembly, there will be a continuing requirement for flux cored solder. At present three lead-free alloys are readily available. These are the traditional Sn96, SnAgCu, and 99C. These alloys may be drawn and as such can be available in no-clean, water-soluble and rosin cored solder wire configurations of differing diameters to include finer gauges.

In the IDEALS project, a European consortium on lead-free work, it was found that both the SnAg3.5 and the SnAg3.8Cu0.7 flux cored wires showed no particular problems. Soldering temperatures had to be maintained above 360 Centigrade to achieve wetting. The wetting of solder on copper was found to be less than when 60/40 tin-lead was used. Flux spattering at these higher soldering temperatures was also noted.

If a lead-free, no-clean flux cored solder is used, it is recommended to use the most active flux systems allowable in the type of assembly being manufactured. One should also consider flux percentages that are slightly higher in the range from 2-3 %. The additional flux will assist in better wetting of the lead-free solder.

Water soluble flux systems will offer better wetting with these lead-free alloys due to their higher activity attributed to halide additions.

In hot gas repair work, the use of nitrogen will permit better wetting. The nitrogen will reduce the oxidation of the flux system and enable the flux to sufficiently reduce the surface tension of the lead free alloys. Poorer results can be expected without the use of nitrogen.

Pull tests done under the European IDEALS program, demonstrated adequate pull strengths for both Sn96 and the SnAgCu alloy. The results were comparable to traditional 60/40 tin-lead solder on bare copper boards and Sn/Ag coated QFP leads.

99C is another alloy that has been available in the market place as a lead-free alternative for over five years. The melting temperature of this alloy is 227 Centigrade and therefore good, higher solder tip temperature is essential for good wetting. Solder joint formation time is however likely to take longer than with traditional leaded alloys due to the fact that the wire take a longer time to reach the melt temperature.

When it comes to choice with lead-free wire solder it is to a great extent limited, any of the above can however be adapted to a lead-free soldering process with minor changes to the process.

Key variables in lead-free repair and rework:

- Solder melting temperature
- Soldering temperature requirement
- Flux type - no-clean/rosin/water soluble
- Flux concentration - 1, 2, 3 %
- Flux volatility/spatter
- Nitrogen assistance requirement

Solder Waving with Lead-free Solders

Limited work has been done with lead-free in wave soldering applications. The traditional tin-lead alloy Sn63 is well understood in wave soldering applications.
The methods of fluxing a board, preheat it to activate the flux and solder wave dynamics are all understood.

When lead-free solder is introduced to the wave soldering process many new variables are added to the process. Many of the ternary alloys suitable for solder paste use can complicate this process.

Tin-lead solder was easy to control, the drossing characteristics are well known and the effect of the contaminants is well understood. This is not the case with lead-free.

The traditional solder pot temperature of around 250 Centigrade does not apply as most of the lead-free substitutes will require higher temperatures, up to 265 Centigrade in order to offer good fluidity and reduction of the surface tensions. These higher temperatures will cause higher drossing possibilities, at the same time the metals do not oxidise at the same rate; this could lead to concentration variations in the alloy. The Sn63 solder alloy tends to reach equilibrium in a true process, and adjustments can be made after a metal analysis by the addition of pure tin bars. Ternary alloys such as SnAgCu, are more difficult to adjust and maintain at the required elemental concentration limits.

Due to the slower wetting times resulting in the use of lead-free alloys, as can be demonstrated in wetting analysis evaluations using the wetting balance tests, nitrogen may have to be used in an attempt to improve performance. This would also reduce the oxidation of the lead-free solder, simplifying the control process somewhat.

Nortel, for example, has run the 99C alloy in their wave solder process. This alloy was run at a temperature of around 250 – 255 Centigrade using nitrogen inerting with success. The 99C alloy offers the advantage of being a binary alloy, containing 99.3% tin and 0.7% copper with a melting

temperature of 227 Centigrade. It is easier to control, if the tin content goes down during use since pure tin bars can be added should the level of copper increase. Pot skimming or partial removal with the addition of fresh solder can restore the alloy's operational limits.

Nortel was able to successfully use a halide free no-clean flux with low solids in range of 2-3 %. The boards used by Nortel were of bare copper OSP types, and component leads were tinned.

An independent test laboratory using the same alloy without the introduction of nitrogen has also conducted evaluations. Again a low residue halide free flux was used, based on adipic acid as its primary activator; the wetting was found to be acceptable and hole fill was as per existing acceptance standards. However, it was found that not all no-clean fluxes gave good results. Fluxes containing more volatile or more readily decomposed activators packages fared less favorably in reference to hole-fill and wetting. Flux selection and amount applied will play an important role in the successful implementation of a lead-free wave process.

Due to the sluggish wetting characteristics of some lead-free solder alloys changes in the soldering process may be required. Some of these changes may include the application rate of additional flux to the underside of the circuit board, reduction of conveyor speeds and increases in solder contact time at the solder wave. These will all assist the wetting process. Water soluble fluxes due to their higher level of acidity, should fare better in the promotion of good plated through hole fill. Also of concern is the potential for higher bridging defects due to the sluggish nature and higher surface tension of many lead-free alloys.

Board and component finish is critical, to avoid the formation of lower melting phases.
Lower melting phases and contraction properties of these phases within the solder joint, has lead to pad or land fillet lifting.

The relative cost of lead-free alloys must also be considered. Considering the cost of the Sn63 alloy, removing the element of lead and replacing it with more expensive tin, copper or silver will significantly increase the of cost of both the Sn95.5Ag3.8Cu0.7 and Sn99.3Cu0.7 alloys with the end result that a lead-free process will cost more than a tin-lead process. The use of nitrogen inerting in a wave will also add further cost to the process.

Key variables in a lead-free solder wave process are:

- Alloy cost
- Solder pot temperature
- Drossing characteristics of the alloy
- Nitrogen inerting or air atmosphere
- Flux selection and activator package
- Flux application system and volume
- Alloy contaminant effects
- Alloy elemental concentration control
- Recycling of spent solder
- Board / lead finishes
- Process control changes
- Quality acceptance requirement changes

SMT and Lead-Free Solders

More investigative work has been done in the use of lead-free solder pastes at this time.
Some binary, ternary, and quaternary alloys have been used by various O.E.M.'s around the world.

Nortel successfully ran 99C RMA no-clean solder paste in nitrogen inerted ovens, while Nokia has documented work done with the ternary alloy SnAg3.8Cu0.7. Panasonic has manufactured consumer electronic products using SnAg3Bi. These are only a few of the options investigated, numerous other alloys are also available.

99C as an alloy for solder paste requires higher reflow temperatures, its melting point being 227 Centigrade. Consideration to board and component integrity after reflow can be a concern. At the very least board discoloration can result should peak temperatures of 240+ Centigrade are used for extended periods.

The SnAgCu eutectic alloy, melting temperature 217 Centigrade, used by Nokia showed good results at a peak temperature of 232 Centigrade. The atmosphere used was air, the board type was Nickel/Gold FR4 double sided reflow process. The lead-free alloy was therefore used as a drop-in replacement to their existing process.

In the above SMT build process the flux system was a traditional no-clean flux system with about 65% solids in the flux, designed for high speed printing at about 150 mm/second. The flux activation levels were able to withstand the higher peak temperatures with no added discoloration effects and few solder balls.

ALT showed the assemblies to be fully functional after test conditions of 1000 thermal cycles from -25 to +125 Centigrade with a dwell time of 15 minutes at the lower and higher temperatures plus a 15 minute dwell at ambient.

Panasonic builds were done at a peak reflow temperature of around 230 Centigrade, the alloy melting temperature was around 210 Centigrade. Much more work is ongoing here with different alloys.

In SMT applications the flux system will need to be robust enough to work effectively at higher preheat and peak reflow temperatures. The potential for micro-solder balls increases if the flux system is not designed for these higher operating temperatures. Higher preheat temperatures will promote slumping and spread of solder paste also more rapid deactivation of the activators will only aggravate the phenomena.

More active flux systems, including water-soluble halide activated flux systems should solder better in air atmospheres.

The concern over board and lead coatings remains the same, avoiding lower melting phases within the solder joint and the formation of large intermetallics concentrates due to higher reflow temperatures. The higher dissolution rates of certain finishes can also add to the phenomena. An example here is copper, copper will dissolve more readily into lead-free solder and cause copper/tin intermetallics that can affect joint mechanical properties and cosmetics.

If cleaning after soldering is required, the higher temperatures seen by the flux may also render the flux residues more difficult to remove in the existing process.

Key variables in a lead-free SMT process are:

- Melting temperature of the alloy
- Flux chemistry - activation, temperature effects
- Wetting and surface tension properties of the alloy
- Process changes
- Quality inspection criteria changes
- Solder ball and bridging potential increases
- Cosmetic effects of flux at higher reflow temperatures
- Component and board reliability at higher reflow temperatures
- Compatible repair and rework alloy
- Compatible wave process
- Residue cleaning / removal process

Conclusion

Although great strides have been made in the investigation of lead-free solders, much more remains to be done. While some alloys are showing promise as drop-in alternatives to Wave, SMT and Rework processes, component / board effects remain an area of concern. If high reliability is too be maintained work will be required to determine the effects of the higher temperatures required to properly reflow these higher melting alloys on components and boards.

Changes to quality standards will inevitably occur, and with this re-training will be required. Lead-free alloys behave differently mechanically and cosmetically when compared to traditional tin-lead systems.

It is unlikely that only one lead-free alloy will prevail. There will be a need for a lead-free alloy in wave soldering, 99C looks like a good candidate, and several lead-free alloys for SMT assembly, to take care of thermal limitations of components and circuit material types.

Further work will need to done on flux chemistries, the present flux systems were designed to work well in tin-lead processes. New fluxes will have to be developed which will safeguard the present defect levels to which we are accustomed.

With pressures coming from Europe and Asia, the switch to lead-free is inevitable on a global basis in the near future, July 2006 !

Acknowledgements

Implementing Lead-free Soldering-European Consortium Research by Dr M Warwick,
Journal of Surface Mount Technology, October 1999.

Panasonic Disk Player Turning a New Leaf, by Tom Baggio,
IPC Proceedings, Conference October 1999.

Lead-free Nortel Experience by Ken Snowdon,
IPC Proceedings, Conference October 1999.

Validation of a Lead-Free Process by Tommi Laine and Atso Forsten,
Proceedings Georgia Institute of Technology 1997.

Lead-free: Don't Fight a Fact by Phil Zarrow,
Circuit Assembly August 1999.

For further information and assistance on how to successfully implement a lead-free soldering process, please contact MBO.

MBO Inc. 2002