Challenges in Attaining Lead-Free Solders

The switch to cadmium-free brazing alloys has been a little easier than finding a lead-free solder that performs similar to the one standard from the past

BY PHILIP BASKIN

Over the last 15 years, there have been many changes in the soldering and brazing industries as a result of chemical and metallurgical regulations that have changed the industrial standards for making products.

Impact of Removing Cadmium and Lead

The brazing industry in the early 1990s removed cadmium (Cd) from the BAg (boron-silver) alloys. Cadmium, a toxin, was added to lower the melting point for silver brazing filler metals. It promoted excellent flow of the filler metal, and left a clean, shiny postbraze joint. With the removal of cadmium, the melting point/flow phase increased 40°–70°F, BAg filler metal flow was slowed down, and the postbraze finish did not have the same shiny, bright finish as the Cd-bearing alloy, which had set the visual standard.

Many companies experiencing the lead (Pb)-free conversions to meet WEEE and RoHS standards are experiencing similarities with SMT and PTH assembly applications as those brazing companies that went Cd-free in the 1990s. While the term "drop-in" is used as a standard to explain the engineering required to be Pb-free, the overall manufacturing process, metallurgical evaluations, and strength/stress tests for the 'old' parts that have been produced for years have encountered more obstacles than could have been imagined. This is similar to what occurred in the brazing industry as the conversion took place to make Cd-free BAg alloys.

One of the commonalities between the Cd-free BAg alloys and the Pb-free soft solders has been the heightened meltpoint of the filler metal alloys. The eutectic of 63Sn/37Pb melts at 183°C (361°F). By replacing lead with silver, copper, and/or other alloy additions, and raising the percentage of tin to 91–99.3% of overall composition, the melting point of current conventional Pb-free solders is in the range of 217°–227°C (423°–440°F). Another factor affected by the removal of lead is the density of the alloys having been converted from a heavier 63Sn/37Pb to lighter tin-based alloy.

Due to the removal of major composition elements (Cd and Pb) from filler metals in brazing and electronics soldering applications, a more restricted flow of the respective filler metals occurred. Processes required a complete reengineering to determine changes made to the overall physical characteristics, efficiency, and durability of the newly manufactured products, as well as how to address the engineering of all the parts, the process, and long-term quality.

Improving Health and the Environment

Today, the brazing world speaks of cadmium as an element whose properties were much appreciated, but when its toxic nature was learned, it was widely agreed that it was appropriate to remove it for the long-term health and safety of brazers.

Lead is being removed from consumer electronics soldering because when it leaches into the soil from a landfill, lead is deposited into water and the soil, which is detrimental to the environment. Lead oxide is created during soldering, and the objective of removing lead is to create a safer environment. The actual amount of lead used by the electronics industry totals 0.3–0.5%[1] of the overall lead use. The battery and ammunition industries represent more than 60% of total lead use.

Common Alloys and Some Differences

While brazing and soldering employ different alloys, there are certain commonalities to the filler metal metallurgy in Pb-free solders and BAg alloys. Silver, copper, tin, zinc, and nickel are all common ingredients in solders and BAg alloys. However, the alloy percentages and the formulation are very different to meet the temperature, strength, and heating requirements for different applications.

When looking at the melting points (Table 1) of tin and lead, there is less than a 100°C difference between the two metals. The combination of these metals in a 63Sn:37Pb ratio

[1] *Source, Alpha/Fry Metals.*

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Table 1 — Melting Points of Various Alloys

Tin (Sn)	Melting Point	232°C
Lead (Pb)	Melting Point	327.4°C
Silver (Ag)	Melting Point	960.5°C
Copper (Cu)	Melting Point	1083°C
Nickel (Ni)	Melting Point	1455°C
Indium (In)	Melting Point	155°C
Bismuth (Bi)	Melting Point	271°C
Antimony (Sb)	Melting Point	630°C

Table 2 — Different Alloy Compositions in Use

96.5Sn/3.5Ag	221°C E
96.5Sn/3Ag/0.5Cu	218–220°C
96.2Sn/2.5Ag/0.8Cu/0.5Sb(a)	218°C E
95Sn/5Sb	232–240°C
91Sn/9Zn	199°C E
SnBalance/0.7Cu/0.3Ni(b)	227°C E

(a) AIM Castin®.
(b) Nihon Superior SN100C.

yields a eutectic at 183°C — 49°C lower than the melting point of tin. Silver-based BAg and Cu-based BCuP alloys are standards for metal joining filler metals in the brazing industry. Today, one of the most used solders, the SAC alloys, are combinations of tin/silver/copper — all of which are components in BAg 7, 18, 21, 28, 34, 36, and 37. Naturally, the difference lies in the ratios. Again, the BAg alloys are silver-based, whereas Pb-free solder alloys are all Sn-based. However, this does not change the melting point of the silver and copper. While the melting point of the SAC alloys is higher than that of the Sn-Pb solder alloy, the addition of these very-high melting point alloys to tin still brings the solder below the 232°C melting point of tin. The true eutectic composition of a SAC alloy is 93.6Sn/4.7Ag/1.7Cu at 217°C. However, the alloy most commonly used is the SAC305, 96.5Sn/3Ag/0.5Cu. This alloy has a eutectic at 218°C, however, there is no true eutectic for this alloy, rather a plastic phase at 218°–220°C.

Still Searching for the Single Replacement

With all of the Pb-free studies that have been conducted or are planned for the future, there is still no single alloy composition that has taken the role of replacing 63Sn/37Pb. The Sn-Pb solder is a binary solder alloy; the SAC, a ternary alloy. Actually, there are many different solder alloys in use that range from binary to quintuple alloy compositions — Table 2.

Additional alloys contain tin/silver/copper and indium, bismuth, and other balance metals. With all of these choices, what makes one solder advantageous over the others?

One aspect that has been forgotten about the current conversion to Pb-free solders is that today is not the first time that Pb-free soldering has taken place. If we go back to the 1970–80s, when surface mount technology (SMT) reflow of solder paste was at its infancy, the double-sided printed circuit board (PCB) was a new method of building PCBs to place more than twice the number of chips on both sides of the PCB. This improved the overall value of PCBs by using space far more efficiently than the wave soldered plated-through holes (PTH) and taking up less placement of space where the boards were housed.

To achieve this objective, dual soldering processes were required. In step one, 96.5Sn/3.5Ag solder paste was applied to the first side of the board. With a eutectic at 221°C, this temperature was 38°C above the eutectic melting point of the Sn63/Pb37 alloy. Given this temperature difference, step two involved soldering the second side of the board with the lower melting point tin-lead solder and operating at a reflow temperature of 210°–215°C max. This prevented the silver solder side from meeting liquidus and made dual-sided reflow processes possible. To accomplish this, one of the chemical formulations incorporated for the flux medium/binder of the spherical solders was a single medium/binder that could maintain the consistency of printing, solder flow, and temperature differences the distinctly different solders required. With 96.5Sn/3.5Ag as the high-temperature solder used to ensure that the 63Sn/37Pb could be used for the lower-temperature reflow application, Sn-Ag eutectic solder powder marks the initial work in the Pb-free solder process before the term Pb-free was applied.

The Present Application Process

Today, this history of soldering is forgotten or unknown to engineers working on the Pb-free conversion. The same challenges meet today's PCBs as those that challenged PCBs more than 25 years ago:

- component and board sensitivity to being overheated
- consistent solder paste printing/screening
- semiconductors and components requiring a metallurgical consistency with the assembly solder
- consistent flow on pads and leads
- noncracking, solid joints.

Today's boards, incorporating ball grid array (BGA) components, flip chips, mini-quad flat pack (QFP) and much tighter spaces between circuit leads, pads and components, make for a more challenging solder paste application process and quality control of the soldering to the PCB, but still incorporate the same disciplined temperatures to the process as were required more than 25 years ago for the double-sided boards.

In addition to the SMT reflow using 96.5Sn/3.5Ag, there were wave solder PTH applications where a higher-temperature solder was required to meet the atmosphere and environmental heat that would have melted the 63Sn/37Pb and caused board failure in sensitive operations areas. Again, while not common, wave soldering with these Pb-free alloys was used for specialty applications on aerospace, automotive, and other control boards requiring a higher-temperature solder. Even though today it is known as a Pb-free solder, that may not have been the objective for using this specific solder. This Sn96.5/Ag3.5 binary alloy met the process requirements and helped to establish a base for what has become Pb-free solder.

Another aspect to be considered from the original days of using the Sn/Ag reflow alloy is that the standard flux formulations were rosin mildly activated (RMA) and rosin fully activated (RA) fluxes. Soldering was done using a vapor-phase process capable of incorporating a closed temperature profile for the heating and activation of the flux medium/binder to hold the spherical alloy in place on the board. This kept the component leads in place on the pads as the vapor heating process covered the board surface evenly and created consistent process parameters from board to board. Post-reflow cleaning was done in trichloroethane 1:1:1 and other CFC solvent systems that removed all rosin residues and left a very clean, shiny post-solder PCB. With the Montreal Protocol, which went into effect on January 1, 1996, all chlorofluorocarbons (CFC) were removed from the assembly process, making the overall challenge that much greater. New heating processes for SMT reflow led to convection ovens that today are accurate to ± 0.5°C.

The Lead-Free Challenge

What makes Pb-free conversion so difficult today is that we do not have the same tools available to use that we had 25 years ago. What makes it easier is that the 25-plus years of SMT reflow experience have led to the development of accurate ovens, profile tools to ensure that all temperature paths are consistent and equal, solder paste squeegee/stencils that are consistent in laying out the paste onto very small mil boards, adhesives that make double side reflow with a single alloy a standard assembly process, new x-ray inspection units for post reflow quality control of BGA and other closed components, and many more lessons learned by the hard-knocks of the early days.

An additional difference between the Cd-free BAg alloy and the Pb-free conversion are the number of factors that need to be brought together in electronics assembly compared to silver brazing. In silver brazing applications, base metals, heat sources, and fluxes remained the same. The removal of Cd in BAg filler metal was the only difference in the process changes that needed to be addressed. In electronics assembly, SMT and PTH soldering are the final steps of bringing a printed circuit board and components together. All of these elements are independently soldered or plated in Pb-free alloys and brought together in final assembly. However, the same question is asked at the final assembly process, namely, what solder will be good for all applications? That has to be answered for the PCBs, HASL, silver immersion, and other preparation activities needed to prepare the PCB for final assembly processing. The Pb-free solder or plating preparation of all semiconductors, flip chips, BGAs, passive components, and connectors that will be attached to the PCB must take place at completely different locations. For manufacturers to bring together these many different items, the Pb-free compliance of all of these items must be reviewed for the final assembly of the PCB. Given the number of different suppliers for PCBs and components, the quality control issues in the Pb-free conversion eclipse the changes that took place in the Cd-free conversion.

The Pb-free conversion is similar to the removal of Cd from the brazing BAg alloys in terms of the heightened temperature of the filler metals for all PCB assembly and the HASL/plating and component tinning/plating operations. However, the brazing process never required new fluxes to be formulated to meet the higher temperature of the Cd-free filler alloys. All AWS A5.31, AMS 3410, and 3411 specifications covered fluxes to temperatures of 1600°–1800°F respectively, and met the temperature requirements for the Cd-free filler metals that had long been in use.

The Flux Question

Prior to the Montreal Protocol, the Type RMA and RA fluxes were the standard fluxes used for a vast majority of soldering applications. In areas where the flux could be left on the PCBs, the post-solder residues were inactive and actually could be used as a protectant against moisture that could potentially cause electrical shorts, since water-white gum rosin is not water soluble. The removal of vapor-phase soldering and CFC cleaning led to a replacement and/or reformulation of rosin-based fluxes and research into what has become today's standard for no-clean and water-soluble solder pastes and fluxes.

The source for determining what is the definition of liquid no-clean flux was instituted by Bell Corp. Research, the Bellcore 000078. This standard established chemical tests to ensure that no halide was present in the flux formula, that copper mirror corrosion would not occur over a 24-h period in an environmentally controlled atmosphere, and that surface insulation resistance (SIR) values would exceed 10^8 at 100 ohms for 168 to 500 h. These standards were adopted and incorporated into the IPC ANSI-J-STD Standard 004 and 005 flux and solder paste definitions.

When comparing liquid RMA fluxes (solids content: 15–50%) to no-clean fluxes (solids content: 2–5%) the activity level was not only much less than the RMAs', the small operational envelope available with no-clean fluxes forced all engineering to 1) strictly ensure all PCBs met prestuffing cleanliness and coating specifications, 2) apply the flux consistently for each different PCB, 3) incorporate a disciplined wave soldering preheat profile for top-side temperature for each different PCB, and 4) produce consistent solder joint finish and quality to meet the consistency requirements for mass production of PCBs. These are just four main factors to wave soldering with the changes of the Montreal Protocol for wave soldering.

Solder Bath Differences

While it is commonly stated that new Pb-free solders are a "drop-in," the process factors described here are only part of the challenge. While Pb is considered an improper solder metal, the high Sn-content products are also very aggressive alloys that can eat-up stainless steel. In the solder baths of the Sn-Pb wave solder machines, cast iron or steel were commonly used for a solder bath that ranged from 200–2000 lb of solder. However, the switch to the Pb-free alloys is commonly being dealt with by adding titanium (Ti) form fittings into solder baths. Titanium is a neutral metal that develops its own oxide, which does not react to tin when it is heated to soldering temperature. In reflow applications, this factor will not play a role since no solder bath is being used.

Another factor that is widely different in solder bath applications is the development of dross. In the old days when Sn-Pb solder was used, one could watch the top of the solder bath to see what color the surface reflected. If the surface maintained a silvery finish, the solder was clean. However, if there was a copper/brass finish, the copper content could be growing too high in the bath. To remove the copper, one would set the temperature to bring the copper to the surface as the heavy solder would sink and the light dross and metallic free-floats would rise to be removed. This cannot be done in the Pb-free solders. The lesser density of the Pb-free solders and the incorporation of copper into a number of the alloys used for wave soldering require all operations to monitor the copper levels and compensate for the buildup of copper. Excess copper can lead to tin whiskers, and other defects such as joint cracking, lack of connection yielding peelable components, cosmetic shortcomings of cloudy, pitted joints, and other quality control issues established by a manufacturer.

In terms of the solder pastes definition of no-clean, there is a great difference between the no-clean liquid fluxes with a solvent base of 95–98% vs. a solder paste that has a spherical powder content of 85–91%. Since the solder pastes must endure a preheating profile that does not degas the solvents in the flux medium/binder that hold the solder and lead in place over and on the pad, a rosin/resin is used to achieve the reflow requirements of the solder paste. This results in a postsolder residue of 2–8% that meets the no-clean standards of the IPC ANSI-J-STD 005. Additionally, this residue must be pin-testable — meaning that all individual joints can be electrically tested to ensure they meet electric/electronics operations and specifications. Today, SMT boards use much more densely packed, smaller components that have experienced an exponential growth over the PCBs of 25 years ago. However, the vapor phase solder process of 25 years ago that worked so well with the Sn-Ag alloy is no longer available, and the complete process analysis for the Pb-free conversion continues.

No Equivalent to 63Sn/37Pb

To date, a Pb-free equivalent to 63Sn/37Pb has yet to be announced. Long-term life tests are being conducted, and more trace metal additions in parts/million to a Sn-based multialloy solder are being evaluated to address the joint cracking, tin whisker, ductility, and other common factors Pb-free alloys continue to encounter.

Broad descriptions in this article describe the assembly processes of SMT reflow and PTH wave soldering, but only briefly touch upon the major factors that must be analyzed in the Pb-free conversion, such as 1) the finish of the PCBs where all components are attached, and 2) the semiconductor and component leads and what is the solder or plating that is used on the surface. In both cases, the elements that are provided to the final PCB assembly are critical to the conversion of Pb-free since the small amount of Pb in both the PCBs and components will cause a board that was thought to be Pb-free to fail the RoHS requirements. This is leading to the manufacture of all components with a Pb-free finish, and a similar movement in PC fabrication.

Which Alloys Are Available?

There are many Pb-free alloys available, but there is no single alloy that has become an equivalent to the 63Sn/37Pb. Additionally, at this date, the IPC has not yet released test parameters for the ANSI-J-STD standards of the Pb-free solder(s) and fluxes, which will be the guideline for industry standards. As a result, the choice of alloy(s) must be made by manufacturers upon their own research into a specific alloy, upon the end-users specification, and/or upon cost.

When breaking down the solders by application, we find that there are certain Pb-free solders that work well in one application, but are not necessarily the choice for a second application. With wave soldering and SMT reflow as the main assembly processes incorporated in board building, a Sn-Cu alloy, the Nihon Superior SN100C, is an excellent choice for wave soldering in terms of flow, joint strength, and a bright, shiny finish. With a eutectic of 227°C, this allows the solder to be operated at a temperature of 245°–260°C, which is a similar temperature range used for 63Sn/37Pb solder. However, this temperature may not be preferred for SMT reflow due to the higher melting point of this alloy vs. other Pb-free solders. But this does not eliminate this solder, by any means, as a possible all-around solder.

For reflow soldering, SAC 305 alloy is used for the majority of SMT reflow applications due to the melting point of this solder being in the 218°–220°C range, the stress tests that have been conducted on this alloy in a wide array of solder tests, and due to many companies specifying this alloy to contract manufacturers or subcontractors providing boards for the overall chain on controls on an assembly. Given this solder's ability to be used as a wave soldering alloy, the SAC305, to date, is the closest choice to being the new 63/37 solder. However, recent increases in the price of silver have made the cost of this solder for wave solder applications reach a point where manufacturers are looking for an alternative that is less expensive and has compatibility with the SAC305 reflow alloy.

Additional research has Sn-Ag-Cu ratios other than the SAC305 being used for both wave soldering and reflow soldering. Furthermore, there are quad and quintuple alloy combinations that are being sold and proposed that use (or will use) bismuth, indium, and other trace element stability alloys to lower the temperature. The overall study time frame for these alloys is still too early to provide sufficient information for them to become the new 63/37 solder.

A final alloy that is being used is binary 96.5Sn/3.5Ag solder. It is the only Pb-free alloy with military specifications, which lends proof to its overall reliability of as a Pb-free alloy. The simplicity of this binary alloy, with a eutectic melting point of 221°C, does not make this solder radically different from the other solders being used, except its volume of Ag is 0.5% higher than SAC305, and the cost of Ag has increased.

One alloy that has taken no hold in North America, but is being looked at overseas, is 91Sn/9Zn. The Sn-Zn alloy has a eutectic at 199°C, which is only 16°C higher than the eutectic of 63Sn/37Pb. However, Sn-Zn solders are known as an aluminum soldering alloy with no connection to PCB assembly. Cosmetics and flow are major issues for this alloy, however, the potential for different chemical reactions with its 9% Zn is the primary reason this solder is not being given serious consideration as a Pb-free solder.

The Search Will Continue

In conclusion, there is no hard and fast drop-in solution for the Pb-free conversion. While we have met and passed the date when this change should have been incorporated globally as an easy conversion to make, the wide variety of different solders that have been introduced and new alloys being evaluated indicate that this conversion is very difficult and still in a state of flux.

In the brazing industry, the Cd-free conversion was very tedious from the assembly angle, but was capable of being achieved using and refining the same tools, heating methods, and process steps that had been in place for many years. However, in electronics assembly, many of the assembly and cleaning tools that were available prior to 1996 are no longer in place. While technology is certainly available for this conversion, there are still a great many time consuming, equipment investment, and initial steps that need to be implemented and understood for the Pb-free conversion to take place.

In the coming years, more metallurgical assessments of Pb-free solders will be made to ensure strength, ductility, uniformity, and other requirements for long-term stability. In this regard, the Pb-free and Cd-free conversions share a great many characteristics that require time, testing, evaluation, and many aspirin.◆

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