Liquid Tin Corrosion and Lead Free Wave Soldering

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Abstract
Corrosion of solder pots and solder pot components in wave soldering equipment has been reduced with the introduction of corrosion resistant coatings and improved lead free solder alloys. The latest trends in protecting wave solder machine components from liquid metal corrosion by lead free solder alloys will be presented in order to provide guidelines for evaluating existing equipment as well as for purchasing new systems.

New lead free alloys are available that are less corrosive than earlier Sn/Ag and Sn/Cu alloys and can be utilized in older, unprotected equipment for a longer period of time. Cast iron, titanium alloys, and stainless steels coated with titanium nitride and Melonite QPQ are discussed and evaluated. Coatings and materials evaluations are based upon chemical, structural, and visual analysis along with field experience. Additionally, solder pot contamination sources, and tips on how to avoid contamination, are presented.

Introduction
The transition to lead free wave soldering in North America continues to increase. The European directives, China initiatives, RoHS, and competitive pressures are eliminating tin lead soldering at a fast pace. Lead free is here and wave solder process engineers must understand the process and equipment impacts to succeed in the electronics assembly market.

Figure 1 – Unprotected Stainless Steel

Background
The initial conversion to lead free in mainstream electronic assemblies began in the late 1990's. Early adopters discovered that the Sn/Cu and Sn/Ag solders caused severe corrosion of the solder pot components. Stainless steels used for soldering equipment at that time would quickly degrade with high tin (Sn) lead free alloys. Figure 1 shows the result of unprotected stainless steel running in Sn/Ag solder for approximately six months.

Alternate solder pot alloys and coatings were developed to resist Sn corrosion. Wave solder equipment manufacturers began offering a variety of solutions for new equipment and upgrades for older equipment. Melonite QPQ® [1] , gray cast iron, and titanium were found to provide good protection[2] for these early alloys and continue to remain popular for today's equipment.

Early Sn/Cu and Sn/Ag solders have been superceded by the Sn-Ag-Cu (SAC) alloys and lead free alloys containing small amounts of nickel. Some of these newer alloys are purported to reduce or eliminate the corrosion of unprotected stainless steel solder pot components.

Corrosion Protection Methods
Corrosion protections for solder pot components come in two generic types: homogenous materials and coatings. Homogenous materials are materials that naturally resist tin corrosion such as titanium and gray cast iron. Coatings are surface treatments that are applied to the base materials that imparts a level of tin corrosion resistance. Titanium nitride and

Melonite coatings are examples of surface treatments that are frequently used in soldering equipment. All of these materials exhibit good corrosion resistance to tin and have a proven track record in actual field application.

Homogeneous Materials

Gray Cast Iron – Gray cast iron has proven to be a material that resists tin corrosion and is a preferred material for solder pot construction. One way to estimate the dissolution of one material to another is through use of phase diagrams. The more soluble one material is to another (as indicated by the phase diagram), the more likely erosion or corrosion will occur. Figure 2 below shows the Sn/Fe phase diagram in the range of 99.5% to 100.0% Sn.

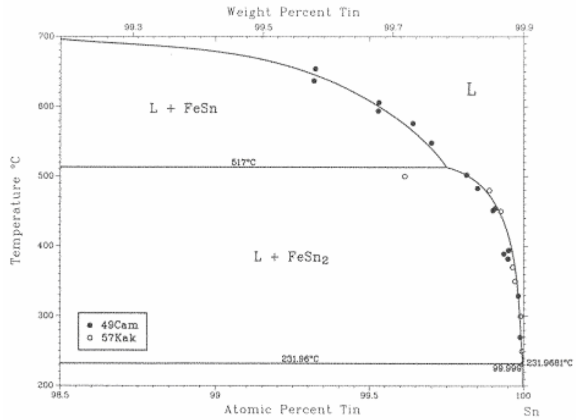


Figure 2 - Sn Rich Part of Fe-Sn Phase Diagram[2]

Per the phase diagram, Sn can only hold a maximum of 0.001% Fe in solution at 265°C (510°F). This very low amount of Fe that can be held by the molten tin is a good indicator that Fe would not be easily dissolved by molten Sn at soldering temperatures.

Graphite (carbon) flakes, found in gray cast iron, are insoluble in molten Sn. These flakes act as a barrier and reduce the possibility of erosion. Figure 3 below shows a cross section of a gray cast iron solder pot after exposure to Sn/Ag solder.[3]

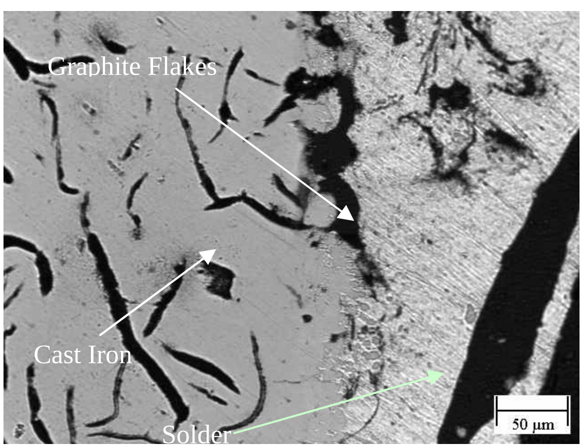


Figure 3 - Cast Iron Cross Section

Seven years of field data for cast iron operating in Sn/Ag and SAC solder indicate no noticeable erosion of the cast iron solder pot or detrimental changes to the soldering process. Advantages of gray cast iron include good corrosion resistance, an economical material, and homogeneous (non-welded) construction. A disadvantage is that it is impractical for internal solder pot components due to the tooling costs involved.

Titanium – Titanium has been utilized for solder pots, solder pot liners, hardware, and nozzle components and has been exceptional in resisting the corrosive effects of Sn based lead free solders. The common alloy used is commercially pure grades 1, 2, 3, & 4. Commercially pure grades contain 99% Titanium and show no evidence of corrosion at common wave solder temperatures.

Figure 4 shows titanium coupons, exposed to Sn/Ag solder for 8 weeks at 250°C (482°F). No evidence of liquid metal corrosion of the titanium material is exhibited[3]. In comparison, type 304 stainless steel showed evidence of wetting after two weeks exposure under these same conditions.

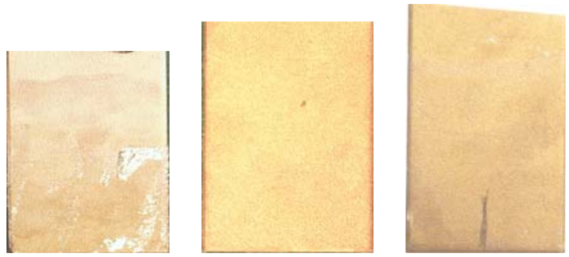


Figure 4 - Titanium Samples After Sn/Ag Exposure

Phase diagram analysis supports the field experience for titanium components. At the common soldering temperature of 265°C (510°F), less than 0.001% Ti can be held in solution with Sn. Figure 5 shows the Sn-Ti phase diagram.

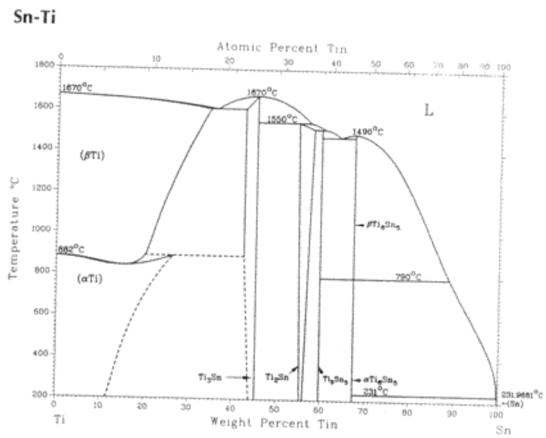


Figure 5 – Sn-Ti phase diagram[4]

As temperature increases, the amount of Ti that can be dissolved into Sn increases at faster rate than does cast iron. Utilization of titanium in solder pots for high temperature tinning applications 436°C (800°F) is not recommended. At these elevated temperatures, corrosion rates for titanium are given in the ASM Handbook of Corrosion Data[5] as 1.0 mm per year versus 0.25mm per year for cast iron.

Field experience with commercially pure alloys indicates that Ti is a superior material for lead free equipment applications. Titanium has superior corrosion resistance at soldering temperatures and can be readily formed into various shapes. However, Ti is very costly, the material supply can be disrupted, and it is difficult to weld.

Older wave solder systems, that use a stainless steel pot, are often obsolete and replacement parts unavailable from the manufacturer. Utilizing a titanium liner in these systems can extend the life of the machine if no other choice is available.

The fit of a liner to the solder pot is extremely important to avoid solder pot heater burnout. Additionally, drain valve provisions will no longer be useful once a liner is in place.

Surface Treatments

Titanium Nitride – A TiN coating is commonly used on metal cutting tools to increase durability. In recent years it has found popularity in coating solder pot components for resistance to Sn corrosion. Titanium nitride is applied through a vacuum deposition process and has a high hardness (85 Rc) and a low coefficient of friction (0.65 against steel)[6].

Evaluation of TiN coated samples in Pb-free solders has been conducted[7]. To determine suitability for use in lead free solder, a sample solder pump impellor was coated with titanium nitride and exposed to SAC solder for six weeks at 316°C (600°F). At the conclusion of the exposure the sample was subjected to a tape adhesion test. The solder easily peeled away from the coated sample, indicating no signs of wetting to the TiN coated sample. The sample was then sectioned, polished, and examined by metallography, X-ray diffraction, Auger analysis, electron microscopy, and chemical analysis[7]. Figure 6 below shows the test sample after exposure to SAC solder.

Figure 6 – TiN coated 316 stainless steel impellor

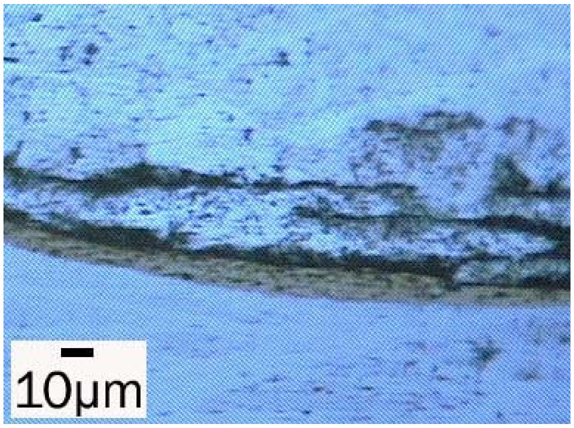


Figure 7 – Digital micrographs of areas of Titanium nitride coating on sample 1, (400X)

No TiN/Sn reaction products were observed in the digital micrographs (Figure. 7). The gold color is characteristic of TiN and X-ray diffraction indicated that the coating was TiN and not Ti_2N or other phase.

Chemical analysis was performed in a scanning electron microscope (SEM) using energy dispersive spectroscopy (EDS), with the results given in Figure 8 and Table 1.

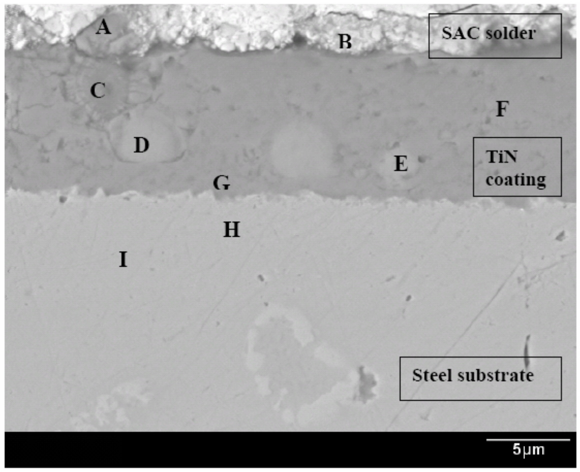


Figure 8 - Designations of areas analyzed with EDS. (3000X) EDS results in Table 1.

Table 1 - Results of Standard EDS Tests.

Area	Label	Major elements (>10%)	Minor elements (<10%
SAC Solder	**A**	Sn, Ti	
	B	Sn	
TiN coating	**C**	Ti	
	D	Ti	
	E	Ti, N	
	F	Ti, N	
Steel Substrate	**G**	Ti, N, Al	
	H	Fe, Cr, Ni	Ti, Al
	I	Fe, Cr, Ni	Al

Conclusions from the TiN testing indicate that this coating withstands the corrosive effects of molten Sn extremely well. Advantages of TiN are its corrosion resistance, hardness, and low coefficient of friction. Disadvantages are cost and interior resistance and coating ability.

TiN is a costly process. Many of the parts coated are as costly as building the parts from commercially pure titanium. Also, the TiN vacuum deposition coating is not as thick through holes, tubes, and interior passages. Interiors of solder flow ducts will receive minimal to no protection.

Melonite QPQ –Originally this coating was used in small solder stations to protect the solder pot and components from early corrosive alloys used in industrial and specialty electronic soldering. With the move to lead free wave soldering it has become a mainstay for protecting solder pot components from the corrosive molten Sn lead free solder.

The coating consists of two layers: a compound layer and a diffusion layer. The compound layer consists of ε-iron nitride (Fe_3N) that is a hard, chemically stable material and is primarily responsible for the improved corrosion resistance. The diffusion layer is γ-iron nitride (Fe_4N) and is responsible for improved material fatigue strength. Figure 9 shows typical components that have been coated.

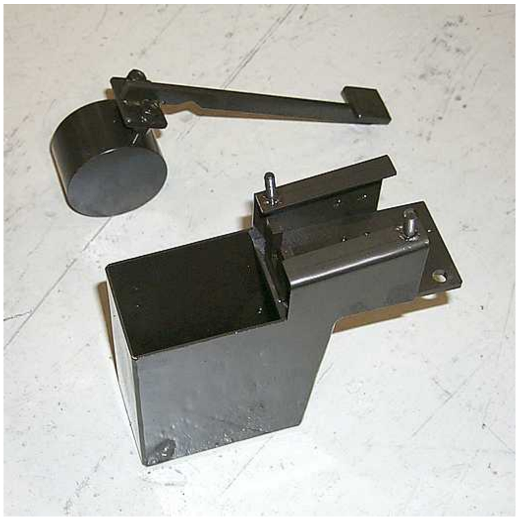


Figure 9 –Coated Components

Metallurgical testing and analysis was conducted on this coating in 2001-2002[3] which confirmed that this material would be a durable protection method for wave solder internal solder pot components.

Field experience indicates that coated components withstand Sn corrosion very well. Advantages of Melonite include good corrosion resistance, low cost, coverage of interior passages, and availability. The disadvantage is that Melonite is a coating and if damaged the underlying substrate will be exposed to the corrosive environment.

New Lead Free Alloys

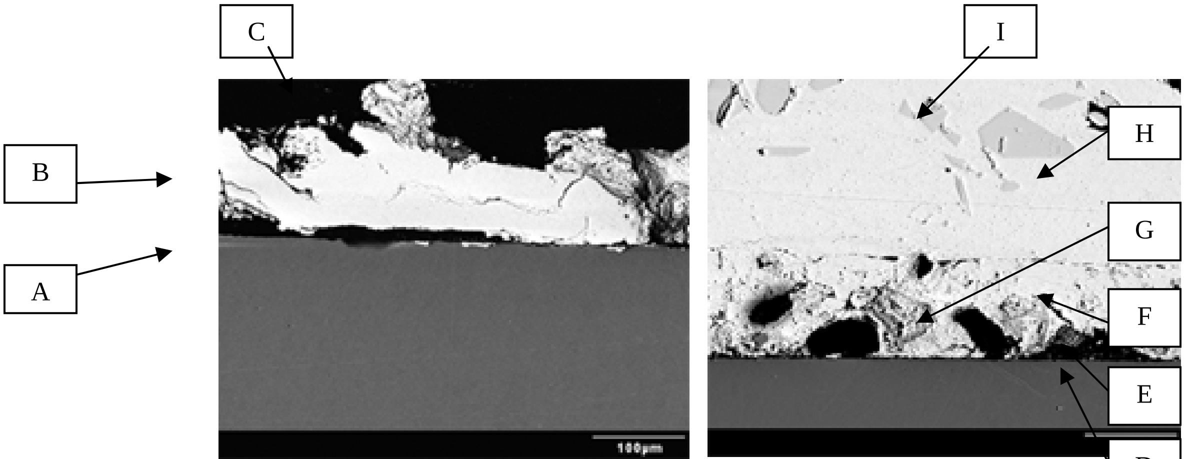
In the early days of lead free wave soldering, Sn/Ag and Sn/Cu were the commonly used alloys. Both of these alloys were very corrosive to stainless steel and thus drove the initial development of protection methods for solder pot components. As material technology has progressed, SAC alloys and alloys containing nickel replaced these early alloys due to improved solder results and costs.

Along with the improved results, these later alloys tend to be less corrosive to stainless steel than the previous Sn/Ag and Sn/Cu alloys. Specifically, the alloys containing nickel have shown positive results in terms of minimizing the corrosion of stainless steel solder components. For wave solder equipment that cannot be upgraded with the newer corrosion resistant materials, the Sn based solder alloys that contain nickel provide a viable alternative in extending the life of this older equipment.

Laboratory testing was conducted on Type 304 stainless steel samples by exposing them to SN100C solder at 260°C (500°F) for two and four weeks. After exposure the samples were sectioned and examined by several methods including; tape test, SEM analysis, EDS analysis, and AES analysis.

Tape test results indicated that the solder easily peeled away, with no wetting or reaction products observed. Sectioning was performed and backscatter electron imaging was conducted.

Figure 10 shows backscatter electron (BSE) images of the stainless steel strips. Table 2 lists elements detected by EDS at selected locations. Very limited wetting of the surface was observed on the samples, because BSE images did not show any form of a reaction product on the stainless steel (SST). The solder layer separated from the surfaces of the SST strips. EDS of the specimen showed Fe was the major constituent with Ni and Cr as minor elements.



A. #01 SST, 2wk exposure (200X) **B. #02 SST, 4wk exposure (200X)**

Figure 10 - BSE images of SST-solder cross sections for #01 and #02 (20kV). A separation of SST and solder is seen on the left side of Fig. 10A.

Table 2 - Elements Detected in Selected Locations of #01 & #02 Cross Sections Refer to Figure 10 for locations.

Sample	Location	Flag in BSE Image	Elements Detected
#01	304 SST	A	Fe, Ni, Cr
	Solder (light gray)	B	Sn, Cu
	Solder (rough gray)	C	Sn, Cu
#02	304 SST	D	Fe, Ni, Cr
	Solder (rough gray close to SST)	E	Sn, Cu, Fe (trace)
	Solder (rough gray away from SST)	F	Sn
	Solder (black phase)	G	Si
	Solder (light gray)	H	Sn
	Solder (dark gray)	I	Sn, Fe, Cu

There was some Fe, Cu and possibly Ni detected in the solder layers. The presence of Fe in the SN100C solder suggests that a small amount of erosion of the SST surface was possible. In comparison, the same testing conducted on stainless steel samples exposed to Sn/Ag solder exhibited observable wetting and erosion after two week exposure. These results indicate a material that is many times less corrosive to stainless steel than the Sn/Ag and Sn/Cu alloys.

Material and Alloys Summary

It is important for equipment suppliers and wave solder process engineers to recognize that there is not one material or alloy that is suitable for every application. Wave solder equipment manufacturers must work with their customers and evaluate each lead free conversion opportunity and select the best solution. Safety, cost, desired equipment life, and process requirements will drive the material selection.

A solder pot made from a coated material must be inspected for degradation much more frequently than a solder pot made from a material that is naturally resistant to lead free solders, such as cast iron. As coatings can become damaged, catastrophic failure can occur if this damage remains unnoticed and the entire contents of molten solder leak onto the floor of the factory.

An equipment purchaser who desires equipment to run trouble free for 10 years or more should consider commercially pure titanium for the interior components. On the other hand, if purchasing equipment for a specific contract, capital equipment costs can be reduced by utilizing coated solder nozzles. Utilizing coated components, however, requires more care be taken during maintenance activities to avoid damage to the coatings.

To assist the process engineer with the selection of wave solder machine components and materials, the following table is provided as a guideline for choosing materials and verifying their performance.

Table 3 – Summary of Material Recommendations

Material	Pros	Cons	Recommended Uses	Inspection Frequency
Commercially Pure Titanium	Extremely resistant to effects of Tin at lead free soldering temperatures.	Very expensive. Impractical to manufacture many components. Welding difficult. Not suitable for high temp soldering > 350°C	Areas subject to frequent maintenance or cleaning. Internal solder module components where long life is required.	Inspect for degradation every two years.
Melonite Coated Stainless Steel	Inexpensive and good corrosion resistance. Dip coating process. Interior channels can be coated and protected.	Will degrade if damaged.	Internal solder module components. Not recommended for solder pot.	Inspect Quarterly.
TiN Coated Stainless Steel	Good corrosion resistance.	Expensive. Will degrade if damaged. Inability to coat interiors of ducts and tubes.	Internal Solder module components. Nozzles, impellors, pump shafts. Not recommended for solder pot.	Inspect Quarterly.
Gray Cast Iron	Inexpensive. Excellent Resistance to Tin-rich solder. Resistant at high soldering temperatures.	Each component must have tooling produced.	Safety critical components (main solder pot).	Inspect annually.
Low Corrosion Lead Free Solders	Very little to no corrosiveness to stainless steel.	As with all lead free alloys acceptable defect rate must be verified.	Obsolete equipment with unprotected stainless steel components.	Inspect Quarterly.

Lead Free Alloy Contamination

With the cost of lead free solder constantly increasing in price, understanding how to avoid metallic contaminates in the lead free solder has become an important topic. Upon discovering that a particular contaminant is increasing in the solder alloy, the common reaction is that it must be coming from the equipment. However, metallic contaminates come from unexpected sources and sometimes the PCB itself. The following are tips on the likely causes of an undesired element in the solder alloy. These tips derive from process experiences over the past several years.

Anti-Seize Compound – Wave solder machines utilize anti-seize on threaded fasteners for the solder pot and solder pot components. This compound comes in a variety of formulas containing different metallic particles to prevent threaded fasteners from "seizing" under high temperatures. The proper compound should not contain metallic particles that are considered contaminates to lead free solder. If copper-based or nickel-based anti-seize compounds are used during maintenance of the wave solder machine, these will get into the solder bath.

PCB/Pallet Hardware – Assemblies with metallic hardware on the bottom of the PCB or pallets that have exposed hardware that passes through the wave have caused a gradual contamination of the solder bath. Nickel-plated hardware running through the solder wave has caused problems at several facilities around the world.

PCB substrate and components – Lead free solder readily dissolves copper and nickel from the circuit traces and component leads as soldering occurs. Frequent monitoring of the solder pot metallurgy, early corrective action to the alloy, and optimizing for the minimum solder dwell time in the wave can reduce this type of contamination.

Tools/hardware dropped in solder pot – Stainless steel has a higher density than the common lead free alloys and will sink to the bottom of a solder pot. Over time, these tools will degrade releasing Nickel and Chromium into the solder.

Damaged or non-protected solder pot components – Older equipment that has not been upgraded with the newer coated type nozzle components will corrode with many of the lead free alloys. Also, coated nozzles in which the coating has been damaged will release unwanted metals into the solder bath.

Wrong alloy – It is key to have a material control program in place to segregate solder alloys and reduce the likelihood of an operator accidentally putting the wrong solder in the machine. Many instances of lead contamination are because the lead solder has not been properly controlled. New triangle shaped lead free solder bars and "poke yoke" type bar feeders have reduced this problem but it is key to have process in place to segregate and control solder bar in a facility.

Conclusions

Lead free solder can be used in pre-existing and new wave solder machines if appropriate materials are used in the construction of the soldering unit. Solder pots should be made of gray cast iron or other naturally corrosion-resistant material. When coated materials must be used for solder pot construction, care must be taken to inspect for possible degradation. Melonite QPQ and TiN coated materials are good solutions for the internal solder pot components and have proven resistive to Sn corrosion in the field. Lead free alloys containing nickel exhibit minimal corrosion when used with unprotected stainless steel and can be a good solution to extend the life of older machines. Contamination of lead free solder can be caused by many factors and ,in most cases, is not equipment related. All possible sources of contamination should be considered and evaluated to fully understand this problem.

Acknowledgements

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