Tin Pest: A Forgotten Issue in Lead-free Soldering?

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ABSTRACT

The phenomenon of tin pest has been known for hundreds of years. It was observed in pewter in the 18th century. There is even historic debate as to whether or not tin pest destroyed the buttons on Napoleon's army on its disastrous return from Russia in the early 19th century. Tin pest can occur in some high tin-bearing alloys at temperatures below 13°C. The "normal" white (beta) tin, with a density of 7.31 g/cm^2 , is slowly converted into gray (alpha) tin with a much lower density of 5.77 g/cm^2. This transformation and resulting expansion causes the tin to essentially crumble as shown in the photos below.

Some may argue that tin pest is not much of a concern for lead-free soldering since most electrical devices would not see such low temperatures. However, automobile electronics and cellular phone base stations could succumb to the effect.

In light of this concern, this paper will review what is known about tin pest, suggest how this information affects the lead-free assembly industry and recommend future work to clarify any remaining concerns.

Key words: Tin Pest, lead-free solder, and tin whiskers.

INTRODUCTION

Ranger Station 12, somewhere in the Afghan Mountains, 0300 GMT, Feb 21, 2010

Charles Webb, West Point Class of 2007, was cold. It seemed like it was always cold here. However, things were going well. He was just promoted to Captain only 26 months after graduation and he was going home in 6 weeks. He also really appreciated the "wireless anywhere" laptop PC that he had. His men took turns sending emails home. It made the homesickness more bearable. His 16 man team all had one hour a day with the PC on a rotating shift. No one complained when their turn was at 0300 hours (3:00 AM), it was such a treat to hear from home. The brass even liked the men using the PC since an important instant message would be immediately conveyed to Charles should one of his men be using the PC.

Oops, there it goes again! The PC had been acting up recently. Charles hoped it wasn't a major problem.

Ranger Station 12, 0305 GMT

The blast was the loudest noise that corporal Scott Adams 21 year old ears would ever hear. (Weapons experts would later state that the shock wave was likely 200 dB, mercifully only 0.001 seconds in duration). The mortar shell had hit 8.7 meters from Adams. Fortunately, a HumVee shielded him from the blast. Two weeks later Scott would be fine with a residual ringing in his ears that the docs said would likely soon go away.

The flash and thunder jolted young Captain Webb to his feet. Even though things had been quiet for several weeks, he knew they were now under attack. SOP was to immediately send a e-message to alert friendly aviation support to ID and help eliminate the enemy. As Charles sent the message on the PC the second mortar round hit. To his horror he also noticed that the PC was not responding! He tried to send another message with no success, as a third mortar round hit. He couldn't fool around with the PC anymore; he needed to lead his men.

Ranger Station 12, 0445 GMT

The fire fight was now over. The superior training of the 16 men of Ranger Station 12 enabled them to hold off 40 terrorists for nearly two hours with only minor injuries. The rising sun would reveal 11 enemy dead. Captain Charles Webb would later receive the Bronze Star for gallantly leading his men, in this difficult situation. The PC was not so lucky, it never worked again.

Army Failure Analysis Lab, 1900 hours GMT, April 1, 2010

Four of the solder joints on the PC, a civilian "ruggedized" model, were gray and powdery. A subsequent analysis with x-ray diffraction indicated that the lead-free solder in the joint had turned from beta or "normal" white tin to alpha or gray tin. This allotropic change typically turns the tin into a powder. This phenomenon has been known throughout history as "tin pest."

WHAT IS TIN PEST?

Tin is a metal that is allotropic, meaning that it has different crystal structures under varying conditions of temperature and pressure. Tin has two allotropic forms. "Normal" or white beta tin has a stable tetragonal crystal structure with a density of 7.31g/cm^3. Upon cooling below about 13.2^{o}C, beta tin turns extremely slowly into alpha tin. "Grey" or alpha tin has a cubic structure and a density of only 5.77g/cm^3 [1]. Alpha tin is also a semiconductor, not a metal. The expansion of tin from white to grey causes most tin objects to crumble.

The macro conversion of white to grey tin takes on the order of 18 months[2]. Figure 1, which is likely the most famous modern photograph of tin pest, shows the phenomenon quite clearly.

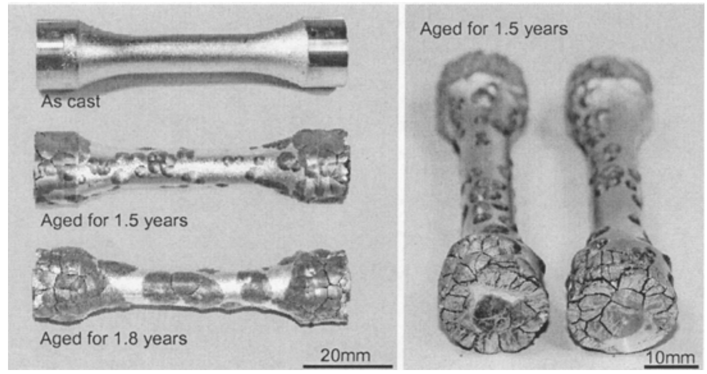

Figure 1. Transformation of Beta-Tin into Alpha-Tin in Sn-0.5Cu at T <10^{o}C from Y. Karlya, C. Gagg, and W.J. Plumbridge, "Tin pest in lead-free solders", Soldering and Surface Mount Technology, 13/1 [2000] 39-40.

This phenomenon has been known for centuries and there are many interesting, probably apocryphal, stories about tin pest. Perhaps the most famous is of the tin buttons on Napoleon's soldiers' coats disintegrating while on their retreat from Moscow. Since tin pest looks like the tin has become diseased, many in the middle-ages attributed it to Satan as many tin organ pipes in Northern European churches fell victim to the effect.

Initially, tin pest was called "tin disease" or "tin plague". I believe that the name "tin pest" came from the German translation for the word "plague" (i.e. in German plague is "pest").

To most people with a little knowledge of materials, the conversion of beta to alpha tin at colder temperatures seems counter intuitive. Usually materials shrink at colder temperatures, not expand. Although it appears that the mechanism is not completely understood, it is likely due to grey alpha tin having lower entropy than white beta tin. With the removal of heat at the lower temperatures a lower entropy state would likely be more stable.

Since the conversion to grey tin requires expansion, the tin pest will usually nucleate at an edge, corner, or surface. The nucleation can take 10s of months, but once it starts, the conversion can be rapid, causing structural failure within months.[2]

Although tin pest can form at <13.2^{o}C, most researchers believe that the kinetics are very sluggish at this temperature. There seems to be general agreement in the literature that the maximum rate of tin pest formation occurs at -30^{o}C to -40 ^{o}C. [1]

THE EFFECT OF ALLOYING ELEMENTS AND THE ENVIRONMENT ON TIN PEST

Several alloying metals retard or eliminate the formation of tin pest. The most effective tin pest retarding alloying elements are bismuth, antimony, and lead.[3] There are limited data that suggest that silver has a retarding effect on tin pest formation, however the effect appears to be moderate at best. Hence, many people assume that it is not proven that silver significantly retards the formation of tin pest, especially in field or use conditions.

A "rule of thumb" is that alloying metals that are highly soluble suppress tin pest. This effect is likely due to the decoration of dislocations or other defect sites that inhibit the required lattice expansion.[3] Elements that are not as soluble in, and that form intermetallics with tin are less likely to suppress tin pest.[3] Examples of such metals are copper and silver. Table 1 is a summary of the effect of some lead-free alloying elements on tin pest.

Alloying Metal	Tin Pest Retardant	% Concentration for effective Inhibition
Bi	Strong	0.3
Sb	Strong	0.5
Pb	Strong	5.0
Cu	None-Weak	? >> 5.0
Ag	Weak-Mod	? > 5.0

Table 1. Tin pest retarding effects of lead-free alloying metals.

Note that while bismuth and antimony will suppress tin pest at concentrations of less than 1%, about 5% by weight of lead is needed. [2,3] Silver suppresses tin pest, but at a much reduced level. Cooper is considered by most researchers to have little effect.

It is widely know that high pressure hinders the formation of tin pest and tensile stress acerbates it. These phenomena make sense when one considers that anything that makes it easier to expand the lattice (e.g. tensile stress) should enhance the formation of tin pest, and anything that compresses the lattice (e.g. compressive stress) will retard tin pest formation.

It is also reported that tin oxide formation at the surface will retard tin pest formation. Several knowledgeable workers in the soldering field believe that many unknown factures such as organic contaminants probably retard tin pest also.

PRACTICAL CONCERNS FOR TIN PEST IN A LEAD-FREE ENVIRONMENT

Although it is possible for tin pest to form in cold environments in alloys without tin pest inhibitors, it is important to remember that the formation of tin pest, even in highly pure tin, is not that common.

However, since the alloy of choice for lead-free assembly is the NEMI-approved tin-silver-copper (usually referred to as SAC) it is meaningful to consider how this alloy might fare in cold environments. In these SAC alloys the silver content varies from 3.0-4.0% and the copper from 0.5-1.0%. Sadly, there are little data on the quantitative effects of silver on tin pest retardation, especially in solder joints. The fact that a strong tin pest retardant, such as lead, is required at a 5% level to eliminate tin pest suggests that 4% silver and 1 % copper will not retard tin pest in some applications. Fortunately these applications are likely rare.

In addition, contaminants in lead-free solder help retard tin pest. Consider table 2 below, results of a chemical analysis of several batches of lead-free solder. Notice the trace amounts of antimony, bismuth, and lead.

Lot#: P7027C3	
Element	**Average**
Ag	3.831
Al	.0012
Bi	.0032
Cu	.6590
Fe	.0028
In	.0028
Ni	.0010
P	.0022
Pb	.0256
Sb	.0085
Sn	95.462

Lot#: P7028A3	
Element	**Average**
Ag	3.954
Al	0.0012
Bi	0.0023
Cu	0.6487
Fe	≤.0010
In	0.0018
Ni	0.001
P	0.002
Pb	0.0277
Sb	0.0062
Sn	95.354

Lot: 7086A3	
Element	**Average**
Ag	3.718
Al	0.0012
Bi	0.0022
Cu	0.6578
Fe	≤.0010
In	0.002
Ni	0.0011
P	0.002
Pb	0.027
Sb	0.008
Sn	95.58

Table 2. Metal content analysis of three batches SAC alloys.

These trace amounts of strong tin pest retardants will contribute to retarding tin pest formation, but the levels are well below those known to inhibit tin pest formation. An additional concern being that these trace elements are uncontrolled.

Therefore, although it is unlikely that tin pest will form in SAC, there is no guarantee that it will not form in cold environments. Mission critical applications in cold environments such as military, automobile and remote base stations are applications at risk for tin pest failures.

Army Failure Analysis Lab, 1400 hours GMT, April 3, 2010

Further analysis revealed that a misguided initiative to improve solder alloy quality resulted in reduced amounts of trace contaminant levels of antimony, bismuth, lead (and other elements) in the lead-free solder. Additionally, an extremely thin protective coating was put on the solder joints to prevent oxidation of the SAC alloy. The combined effect of these harmful actions reduced the tin pest resistance of the solder in Captain Charles Webb's PC, adding risk to his team's mission.

CONCLUSIONS AND RECOMMENDATIONS

The formation of tin pest, even in pure tin metal is rare. However, it can occur in tin, exposed to temperatures below 13.2^{o}C, that does not contain inhibiting levels of metals such as bismuth, antimony, or lead. Hence, the paucity of data on tin pest formation in lead-free solder joints in field use conditions is unsettling. Mission critical applications such as those in the military, automobiles, and remote base stations have an unknown risk of experiencing tin pest.

Considering the above it is strongly recommended that the efforts of Plumbridge etal[4], Havina[5] etal, and others in understanding the risks of tin pest formation in lead-free alloys be encouraged and promoted.

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[3] Information from Tin Technology literature archive courtesy of Kay Nimmo (kay.nimmo@tintechnology.com)
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