TIN WHISKERS and COPPER/TIN INTERMETALLICS

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Abstract

The commercial electronics industry has been forced to change many practices in order to comply with the WEEE and ROHS directives. ROHS became effective in the European Union on July 1, 2006. One of the most significant changes to be evoked was to prohibit the use of solders containing lead(Pb).

Some industries were declared free of these regulations including military and aerospace manufacturers who were permitted to continue to use solders such as SN60 and SN62 which contain lead (Pb). The semiconductor industry was also exempted for solders used in the internal construction of components. This mainly applies to die attach solders for high power devices which often have a high lead (Pb) content.

Much research was carried out into lead (Pb) free solders and the consensus reached was that a tin/silver/copper alloy (SAC) gave the best results. This research concentrated on commercial electronic applications which generally operate in benign environments and are not expected to operate for extended periods of time. By comparison less work was undertaken on either the long term effects of lead (Pb) free solder or the use of tin(Sn) lead(Pb) solders with lead (Pb) free component termination finishes. This latter scenario appears to be unavoidable as manufacturers of “commercial” components, as opposed to “military qualified” components, have no incentive to produce components except with lead (Pb) free termination finishes. It must also be recognised that most commercial components will have copper cored lead outs.

It may surprise many readers that the mechanisms described in this paper are not new and were encountered during the early development of microelectronic components. As these phenomena were recognised, mitigation techniques were introduced and problems were averted. This was in the days when the mil/avionics industry dominated the electronic component market. Now the electronic component market is dominated by the manufacturers of games consuls, PC and mobile communications these mitigation measures are considered to be expensive and unnecessary.

This paper will review the physical phenomena which may occur with components with tin (Sn) plated copper terminations.

Introduction

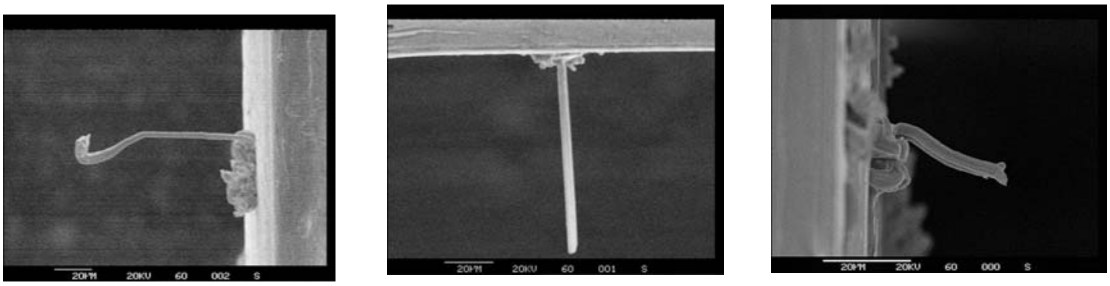
The phenomena to be considered in this paper are :-

- Tin whiskers
- Tin copper intermetallics
- Tin whisker mitigation

Spontaneous Tin Whiskers

The appearance of single crystal tin whiskers or filaments was reported inside early hermetic transistors. Tin plated headers and caps were used. Whiskers would develop inside the transistor package, often causing intermittent short circuits or permanent damage to the semiconductor element. Although the growth of the tin whiskers was effected by the bias applied to the transistors, spontaneous whisker development was also reported in unbiased components. The mitigation measures taken at this time were simple. Headers were nickel or nickel and gold plated while the transistor caps were either nickel or nickel plated. These combinations of platings and materials have remained the standard for hermetically sealed transistors ever since.

The development of whiskers in unbiased product was attributed to the stresses induced in the tin during the plating process. This is the situation that exists for many COTS (commercial of the shelf) components where pure tin (Sn) is plated onto copper.



SEM Images of Spontaneous Tin Whisker Growth

The scanning electron microscope images above show many of the common characteristics of tin whisker growth. The whiskers emerge from a larger disturbance in the surface of the tin plating. The whiskers are 100 to 200um long (much longer whiskers have been reported). The whiskers frequently exhibit sudden changes in the direction of the crystal growth.

Tin whiskers can be generated by applying physical pressure to a tin plated substrate. From this effect it may be deduced that compressive stresses drive tin whisker growth.

The situation is further complicated if the nature of the tin plating is considered. Tin plating may be:-

- Bright Tin – an acidic plating process, which includes 0.15% organic brighteners. Bright tin is more easily inspected after soldering, faster wetting and harder.

- Matte Tin – an alkaline plating process, which includes 0.015% organics. Matte tin is more difficult to inspect after soldering but generally exhibits improved soldering characteristics.

Bright tin was believed to be more susceptible to tin whiskers and many O.E.M. prohibited the use of bright tin. It now seems that under certain circumstances the harder bright tin plating may be more resistant to tin whisker growth.*1

Copper Tin Intermetallics

When two metals or alloys are brought together at elevated temperatures interdiffusion and possibly nucleation and the growth of intermetallic compounds (IMC) can occur. The properties of IMC differ from the component metals often being less metallic with reduced density, reduced ductility and increased electrical resistance. Gold aluminium intermetallics are a well known problem in microelectronics and remain a major cause of the failure of COTS components.

The development of IMC is time and temperature dependent. Microstructure and compositional changes are caused by diffusion, dissolution and chemical reaction at the interfaces between the materials.

Consider soldering where two base metals are joined by a third “filler” metal or alloy with a melting point distinctly lower than the base metals. The quality of the solder joint is dependant on the “wettability” of the surfaces to be joined and the subsequent maintenance of electrical and mechanical performance through out the life time of the hardware. The life time of the hardware may be reduced by development of brittle intermetallics at the component terminatiom/solder/substrate interfaces.

With the increased use of COTS components in military aerospace and other hardware destined for harsh environments and the migration towards lead (Pb) free termination finishes copper tin IMC have become a cause for concern.

Copper and tin form two IMC phases:-

- $Cu_6Sn_5 = \eta$ phase, forms at $<170^0$C
- $Cu_3Sn = \in$ phase, forms at $>170^0$C

Experiments with pure copper tin samples have indicated that interstitial diffusion of copper (into tin) is dominant at lower temperatures ($<170^0$C) while vacancy diffusion of tin (into copper) is more predominant at higher temperatures ($>170^0$C). An atom of copper may diffuse easily into tin by the interstitial mechanism while tin diffuses into copper by a slower substitutional mechanism. It has also been shown that the $\in$ phase can develop at the expense of the η phase i.e. the η phase is consumed.

The development rate of IMC is related to the diffusion rate of the reactants. This rate is initially high when the solder is molten because a near complete mixing in liquid ensures that tin is readily available. In the solid state the rate of IMC development is typically:-

- Tamb. = 170^0C IMC Development 40um/year
- Tamb. = 100^0C IMC Development 7um/year
- Tamb. = 23^0C IMC Development 1um/year

Comparing the properties of copper, tin and the IMC:-

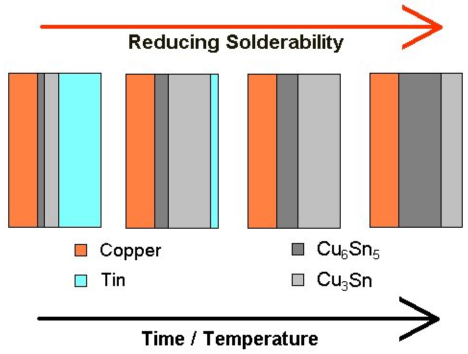
Property	**Cu**	**Sn**	**Cu_6Sn_5**	**Cu_3Sn**
Density (gm/cm^3)	8.9	7.3	8.28	8.9
Young's Modulus (Gpa)	117	41	85.56	108.3
Shear Modulus (Gpa)	46	18	50.21	42.41
Vickers Hardness (Kgm/mm^2)	30	100	378	343
Electrical Resistivity (μΩ/cm)	1.7	11.5	17.5	8.93
Thermal Conductivity (W/mK)	3.98	0.67	34.1	70.4
Specific Heat (J/Kgm.K)	0.39	0.23	286	326
Thermal Expansion (10^{-6}/K)	17.1	23	16.3	19.0

The Vickers Hardness , electrical resistivity and specific heat of the IMC are orders of magnitude greater than the component elements. This is of concern when electronic hardware encounters temperature fluctuations. The natural shear strain imposed on solder joints because of the mismatch in thermal expansion of the pcb, the solder joint and the component lead out is increased by the IMC. It is not surprising that solder joint failures occur at the IMC.

The Influence of IMC on Solderability

As described above copper/tin IMC will develop with time and temperature where ever copper and tin are used. This is the situation found in most ROHS compliant components where the terminations are copper plated tin.

Oxide forming on the tin surface might be expected to be the inhibitor of solderability but IMC may have a significant effect. The IMC at the plating termination finish will develop and eventually reach the surface of the termination. Solder will not wet to IMC.



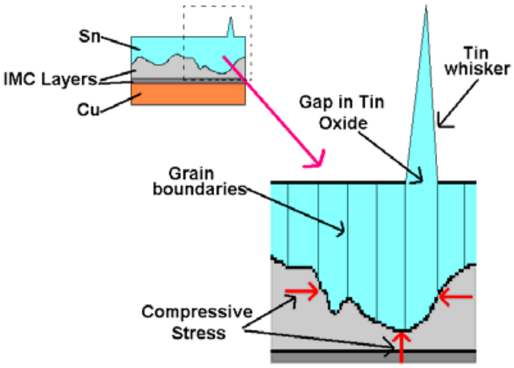
IMC development in tin plated copper terminations

IMC may also be an inhibitor to rework and repair of hardware. IMC layers may be exposed when the solder is removed around a component termination. Exposed IMC will cause a severe reduction in solderability. As the response to poor wetting is often to increase soldering temperatures, pressure and time there is an increased possibility during rework, of causing degradation to the component or the board.

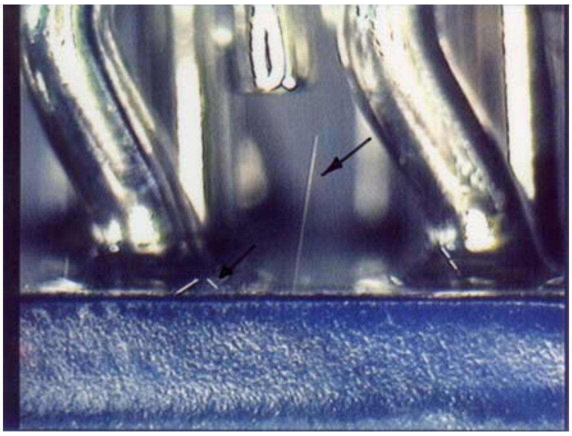
The Influence of IMC on Tin Whiskers

It might be reasonably expected that if tin whiskers are the out come of compressive stresses seen by component terminations during plating and mechanical “lead forming” then tin whiskers would only be encountered on new components. In practice tin whiskers have been observed to develop throughout the life of components indicating that other factors may also be involved. A prime candidate are IMC.

The development of Cu_6Sn_5 at the copper tin interface occupies a greater volume than that of the tin consumed in the process, thus a compressive stress is generated in the plating. This stress is relieved when tin whiskers develop. Most researchers report an association between the tin whisker and defects, mainly cracks, in the native tin oxide of the plating surface:-



Schematic of the proposed relationship between IMC and tin whiskers.



Tin whisker development on a bright tin plated relay after many months in store.

ATG Investigations into Tin Whiskers and Copper Tin Intermetallics

The SEM and optical images shown above are all from problems that ATG has found during receiving inspection and re-inspection of product held in stock. This is not the only source of data on these phenomena. ATG has been actively involved in the assessment of commercial off the shelf components (COTS) for use in mil/avionics programmes and other applications involving harsh environments.

The results from four programmes will be considered. Each programme had very different environmental and reliability (life time) requirements which are reflected in the testing performed. All of the programmes had a common factor in the use of COTS components. COTS components are of interest to this study because most have copper terminations and an increasing percentage have ROHS compliant leads i.e. lead (Pb) free.

The common factors applied to each programme were:-

- Constructional analysis of each part type before environmental testing to establish a base line assessment of the component build, quality, materials and potential reliability.
- Electrical parametric measurement before and after each environmental test.
- Acoustic microscopy (CSAM) where applicable before and after each environmental test.
- Sample destructive physical analysis (DPA) at the end of each test group

Of particular interest to this study are the DPA which included optical inspection, solderability testing and microsectional analysis of the terminations.

The environmental testing performed in each programme included:-

Programme 1 – 2000 - ongoing

Sample thermal shock of unmounted components. This programme has been running for several years during which time the test sequence has been refined. This was possible because although the quantities of components involved in the programme are large the number of part types and manufacturers is limited. Sample life testing for instance was stopped because the test was producing no failures that would not have been detected by thermal shock. This is a much simpler test to perform, although to improve confidence in the process the sample size tested was increased.

Programme 2 – 2002 to 2004

Assembly of components onto carriers using the same assembly materials and processes as the programme hardware – thermal shock.

Programme 3 – 2003 - 2008

Thermal shock, HAST (highly accelerated stress test), accelerated life test.

Programme 4 - 2007

An initial study was under taken including the constructional analysis of a range of COTS components in order to establish an appropriate series of accelerated tests. Programme 4 has not progressed beyond this study but the results are considered important because the study included passive components as well as PEMS and PEDS.

ATG Findings – Increase in Lead (Pb) Free Components

As these investigations cover the period of time when ROHS was being applied it is not surprising that the percentage of components with lead (Pb) free termination finishes increased after 2006. As will be seen from the two bar charts below Programme 4, although the smallest programme as the last to be started had the highest percentage of lead (Pb) free product.

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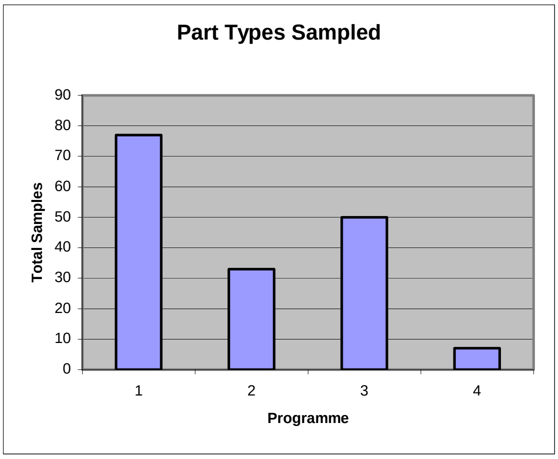
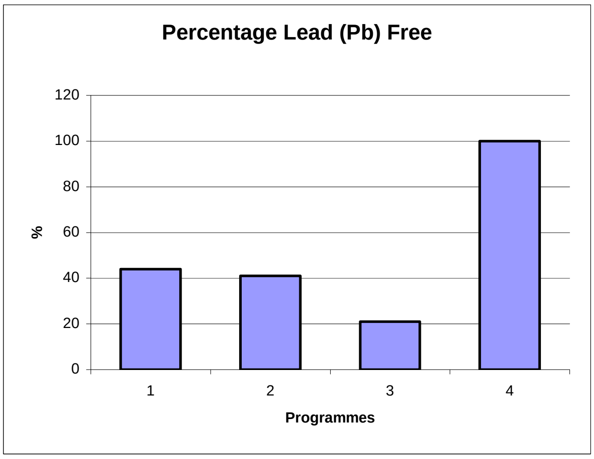
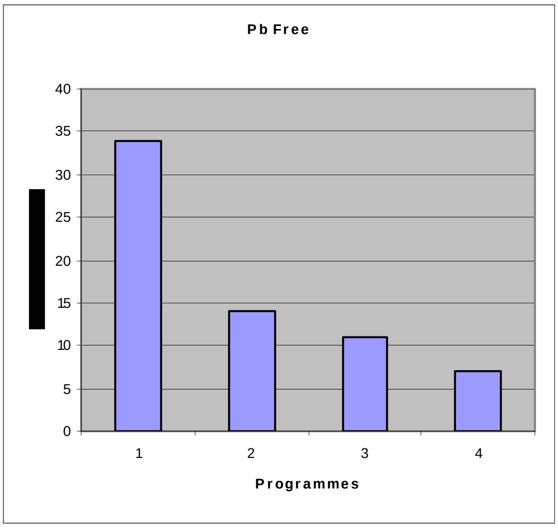
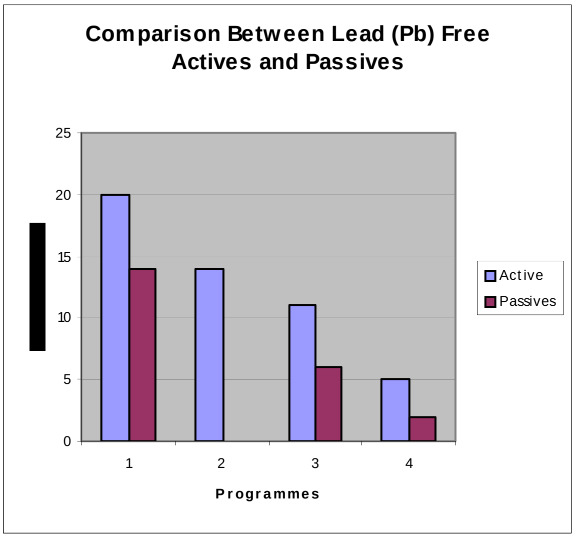




It is also worth considering the active/passive component balance. Programme 2 included no passive components while Programmes 1and 3 only included passive components towards the end of the study period. The conclusions drawn from the data below is that passive components have migrated to lead (Pb) free solder finishes more quickly than active components.





Considering the active and passive components with lead (Pb) free termination finish:-

Programme 1

- All of the active components had pure tin (Sn) plating on unpassivated copper (unpassivated = unplated).
- All of the passive components were surface mount with pure tin (Sn) plating on nickel (Ni) plating.

Programme 2

- 11 samples had pure tin (Sn) plating on unpassivated copper
- 1 sample had pure tin (Sn) plating on nickel plated copper (passivated)

Programme 3

- 7 samples had pure tin (Sn) plating on unpassivated copper

Comparing the number of lead (Pb) free components with the total number of components it is obvious that the Programmes were able to procure COTS components with lead (Pb) tin (Sn) terminations. Before reviewing the results of the testing under taken it is worth considering the terminations with lead (Pb) tin (Sn) finishes. This data is not readily available for Programme 1 but for Programmes 2 and 3 we have:-

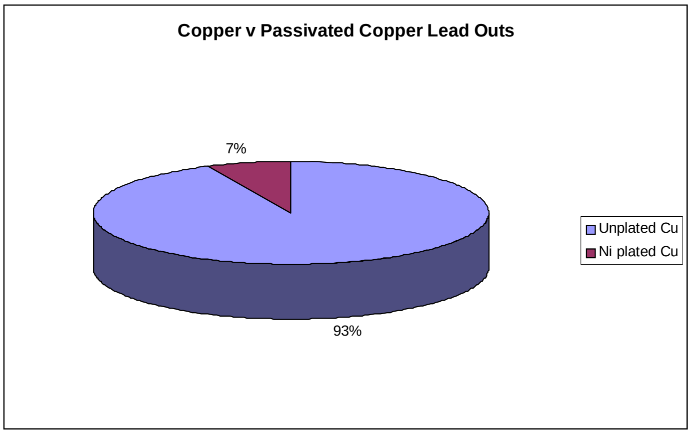
Programme 2

- 13 of the component lots had tin (Sn) lead (Pb) plating on unpassivated copper.
- 6 of the component lots had tin (Sn) lead (Pb) plating on nickel (Ni) plated copper (passivated).

Programme 3

- 21 of the component lots had tin (Sn) lead (Pb) plating on unpassivated copper
- 5 of the component lots had tin (Sn) lead (Pb) plating on nickel plated copper (passivated)
- 16 of the component lots had tin (Sn) lead (Pb) plating on nickel plated nickel iron (industrial grade hermetically sealed components).

These results also point towards a significant factor in the reliability COTS i.e. the potential for tin whisker and copper tin intermetallic development due to the preponderance of termination finishes applied to unpassivated copper:-



ATG Findings – Observation of Tin Whiskers

Despite the extensive testing performed, which included frequent optical and SEM inspection of the lead outs no instances of tin whiskers were reported.

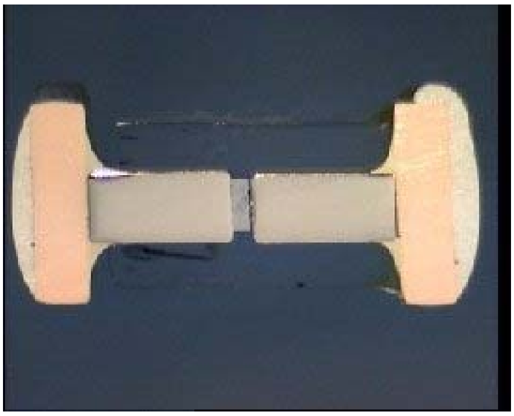
This is considered to indicate that the samples supplied were free of compressive stresses when received or these stresses were mitigated during the early phases of testing.

No tin whiskers were reported during the life tests and accelerated tests performed but this may be because of the limited development of copper tin intermetallics.

ATG Findings – Observation of Copper Tin Intermetallics

Although not taken from the four programmes detailed above, a failure in the field due to copper tin intermetallics is described below to provide an example of the problems which may be encountered.

The subject is an hermetically sealed surface mount glass diode procured to the requirements of MIL-PRF-19500



The parts had been procured for a space programme in April of 2000 and had passed all of the goods inwards inspection tests specified including sample solderability testing. Yet one year later the parts were failing optical inspection after soldering onto circuit boards due to poor wetting of the solder to the component.

A detailed metallurgical analysis of the failed parts was under taken and some variations from the norm were found:-

Element	Problem Part	Normal Part
SM Termination Finish	Pure tin (Sn)	Tin (Sn) lead (Pb)
SM Termination	Unplated Copper	Silver or Nickel Plated Copper
SM Termination Attachment	Gold Germanium Solder	Silver Copper Braze
Heatsink	Nickel Plated Tungsten	Nickel Plated Tungsten

The obvious difference is the unpassivated copper surface mount (SM) termination with a pure tin (Sn) lead finish. This would be expected to degrade with time but under the storage conditions which the parts were exposed to 1um of intermetallic development a year would be expected. The tin (Sn) plating is typically 10um thick although it is thinner on the corners of the termination. Other factors must be therefore be involved. In this case the gold germanium solder may be the culprit:-

- Gold forms a brittle intermetallic with tin which can inhibit soldering.
- The gold germanium solder had flowed onto the edges of the heat sink.
- Gold germanium solder has a melting point of 356^{0}C (82Au/12Ge). This is lower than the melting point of a silver nickel braze but it was not possible to establish the soldering time which might be a significant factor in the formation of the tin intermetallics.

There was no alternative but to scrap this diode lot. The information established after the event proves conclusively that any investigation into COTS reliability, tin whiskers and tin copper intermetallics should only be under taken when the construction and the metallurgy of the subject component are fully understood.

The example described above raises two important questions:-

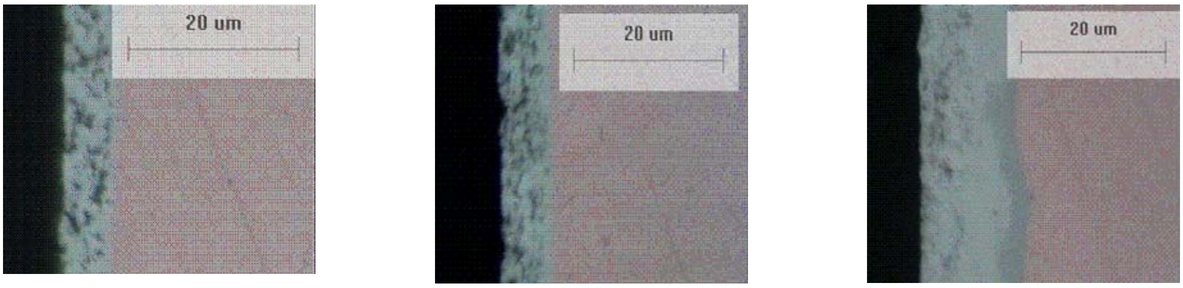
- How fast do copper tin intermetallics develop in practise?
- How much variation in the rate of development could be expected?

Programme 3 had components which could be subjected to sample microsectional analysis:-

- Which had been retained as control samples.
- Which had been subjected to HAST at 125^{0}C.
- Which had been subjected to Accelerated Life Test at150^{0}C.

Although most of the components on this programme had tin (Sn) lead (Pb) coatings on copper, tin copper intermetallics are as prevalent as in pure tin (Sn) finishes on copper. This is because tin (Sn) lead (Pb) solder the lead (Pb) appears as “precipitates” in the tin (Sn). This is very obvious in the images below where the dark regions are the lead (Pb) and tin (Sn) can be seen in close contact with the copper of the lead out.

Microsections Through Tin (Sn) Lead (Pb) Plated Unpassivated Copper Lead Outs



Control Sample. 25°C

HAST Sample
96 hours at
+125°C, 100% RH .

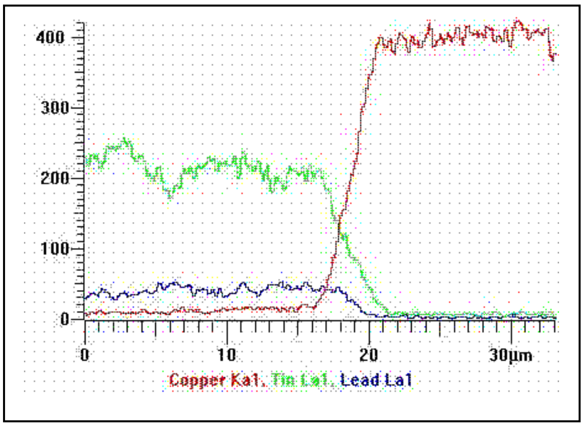
AcceleratedLife Test
Sample
2418 hours at 150°C

In the images above:-

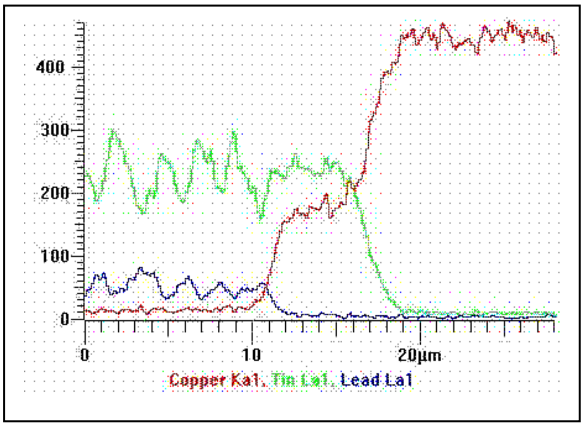
- A very thin line of line of intermetallic can be seen at the interface between the copper and the solder of the ex-control sample.
- The line of intermetallic was more obvious on the ex-HAST sample.
- A thick line of intermetallic was evident on the ex-Accelerated Life Test sample.

This may be better illustrated by looking at the energy dispersive x-ray spectra of the samples. The graphs below show the position of the elements on a line taken through microsectioned ex- HAST and ex-Accelerated Life Test samples.

Intermetallic Thicknesses in ex-HAST & ex-Accelerated Life Test Samples



HAST resulting in a 4 micron intermetallic layer



Accelerated L.T. resulting in a 9 micron intermetallic layer.

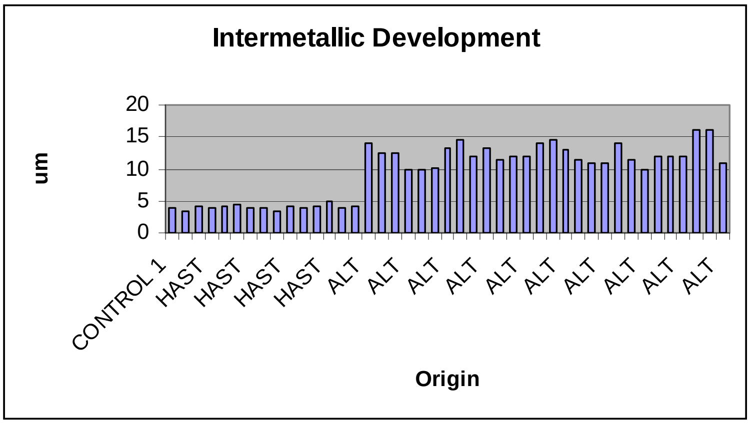
In the graphs above:-

- The brown line indicates where copper is present.
- The green line indicates where tin (Sn) is present.
- The blue line indicates where lead (Pb) is present.

The differences between the HAST and Accelerated L.T. graphs to note are:-

- The interface between tin and copper has moved to the left.
- The presence of copper is now detected around the 10um line indicating that the copper has defused left wards into the tin (Sn).
- Where the copper and tin (Sn) lines overlap intermetallics exist.
- The lead (Pb) in the solder has been displaced to the left by the intermetallic development indicative of a stress in the material.

A total of fourteen ex-HAST, twenty eight ex- Accelerated L.T and two control samples were available. The combined results for these samples are shown below:-



As might be expected there is a considerable difference between the HAST and ALT results. What was unexpected was the variation within each apparently homogenic sample group:-

- HAST samples had an intermetallic thickness range of 3.5 to 5um
- ALT samples had an intermetallic thicknes range of 10 to 16um

Two control samples and fourteen further samples from each group were subjected to a solderability test to the procedure defined in MIL STD 883 Method 2003 and were then subjected to microsectional analysis:-

- Ex-control samples – the solderability test result was acceptable.
- Ex- HAST samples - the solderability test result was acceptable.
- Ex-ALT samples - the solderability test result was unacceptable.

When the intermetallic thicknesses were measured:-

- Ex-control samples – average thickness = 2.6um - (before solderability - average = 2.7um.
- Ex- HAST samples - average thickness = 2.7um - (before solderability - average = 4.2um).
- .Ex-ALT samples - average thickness = 10.2um - (before solderability - average =12.7um.

The general pattern of the distribution of intermetallics had remained the same but there was a marked reduction in intermetallic thickness after solderability testing:-

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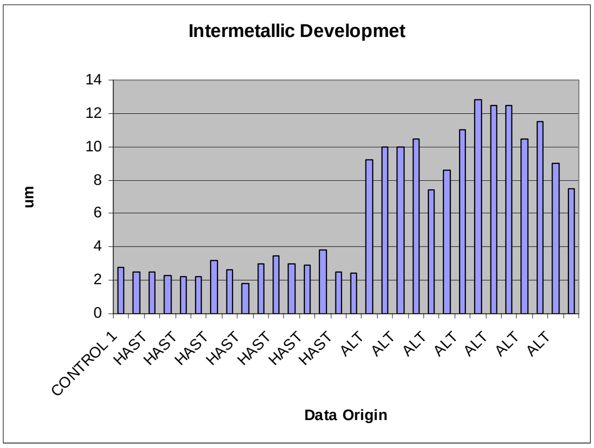
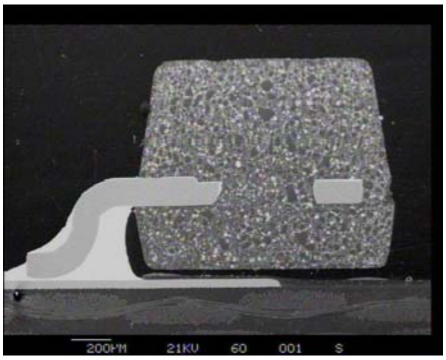


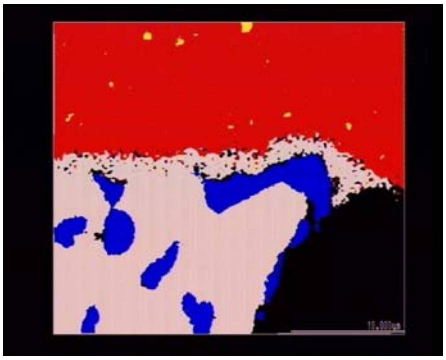
This is considered to be happening because the Cu_6Sn_5 is being broken down and dispersed into the solder bath (T=245^0C). The ALT sample solderability failures are considered to be due to the Cu_3Sn intermetallic layer.

The results described above for Programme 3 are considered to vindicate the theories about intermetallics made at the start of this paper except for the intermetallic providing the compressive stress to instigate tin whisker growth. Some unexpected phenomena were however experienced during Programme 2:-

Soldering of PEM with pure tin (Sn) plated lead outs to a PCB with Sn60 solder found no difference in reliability when compared to PEM with tin (Sn) lead (Pb) solder treated in the same way. NB, this programme was using thermal shock as the main evaluation tool. However when microsectional and materials analysis was undertaken a tin(Sn) rich layer was found between the solder and the copper:-



SEM Image of a microsection
through aPEM soldered onto a PCB
using Sn60 solder.



ED Spectroscopy derived image of a
solder copper lead out interface:-
Red = copper
White = tin (Sn)
Blue = lead (Pb)

This tin rich layer was also found when samples from the same lot were subjected to the routine solderabilty test. Because the samples tested had met the Programmes requirements no further work on this phenomena could be under taken.

Tin Whisker Mitigation

It is now generally accepted that tin whiskers are the result of compressive stress in the tin plating.

The stresses induced during the plating process can be relived by baking the part at high temperature. This is not a new idea. Harris Semiconductors adopted pure tin (Sn) plating on MIL product in the 1990s and mitigated for tin whiskers by baking at 150^0C. No problems were reported with product delivered to ATG.

What must be remembered was that the Harris Semiconductor product had nickel plated nickel iron alloy cored lead outs. As has been illustrated above most COTS parts have unpassivated copper lead outs and any exposure to high temperature will accelerate the development of copper tin intermetallics. Simply, baking may alleviate plating stresses whilst at the same time instigating or accelerating a mechanism which will generate further stresses in the tin (Sn) plating.

Considerable time and effort has been expended studying the effects of conformal coatings on tin whiskers*2 to 4. It is generally accepted that conformal coatings will not prevent the growth of tin whiskers. Conformal coatings will however trap the whiskers that are shorter than the conformal coating thickness and limit the potential for free particles of tin to develop.

Some success has been reported with coatings containing a high proportion of filler but this type of coating is only practical in a limited number of applications*5.

Passivating the copper lead out inhibits tin whisker development but it is unlikely that a COTS manufacture would incur the additional costs involved.

There are lead (Pb) free alternatives to pure tin (Sn). TI have used a nickel/palladium/gold plating for some years. ATG has upscreened COTS parts with this lead finish and has not experienced problems nor have there been any field failures.

For the MIL/Aerospace community there is also the option of refinishing the lead outs.

The lead (Pb) in tin (Sn) lead (Pb) solder will inhibit tin whisker growth. Lead (Pb) slows the diffusion of intermetallics. The soft lead (Pb) regions of the solder provide relief for the stresses which can cause tin (Sn) whisker growth.

Dipping gold plated lead outs in molten solder (de-golding) has been standard process for many years. This processing was under taken to eliminate gold tin intermetallics which develop during the soldering process. Also in degolding it is important to dip the component twice in two different solder baths. The first dip removes the gold plating while the second dip in fresh solder ensures that any intermetallics are removed. This is necessary because the gold which has been removed will alloy with the solder only until a saturated solution is formed. This occurs with >2% by volume of gold in SN60. De-golding was only performed on the parts of the lead out which were to be soldered. It was not necessary to dip the leads to the component body.

The situation for pure tin (Sn) plated lead outs is different. Ideally all of the tin (Sn) should be removed and replaced with tin (Sn) lead (Pb) solder. This process is being offered commercially in the USA and the UK. ATG has evaluated a range of COTS components which have been processed in this fashion. This evaluation has found no degradation of the electrical performance or the inherent reliability resulting from this process. There are however concerns about the ability of the process to completely eliminate pure tin (from) the area where the lead out enters the encapsulation. It is suspected that the temperature of the solder dipping process will alleviate any stresses in any remaining pure tin (Sn) plating particularly if the component can be dipped twice.

Of course when the component is dipped the lead out temperature is ramped up and down and there must be a period of time when the lead out is not immersed in molten solder and copper tin intermetallics will continue to develop.

It is possible to strip tin chemically and replate the lead outs but ATG have bad experiences of this process. The chemicals used will etch the base materials of the lead outs, reducing thickness and strength, and may degrade the component encapsulation.

Conclusions

Tin whiskers are a potential reliability hazard to all electronic systems. Limited mitigation is possible but with our current understanding predicting where and when tin whiskers will develop is not possible.*6

If COTS components are used there is a high probability that the parts will have unpassivated copper terminations. The use of such components in high temperature environments and in systems demanding very long operating life will bring the risk of copper tin intermetallic development which may in turn lead to solder joint failure.

References

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