

Understanding and Minimization of Tin Whiskers

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Understanding and Minimization of Tin Whiskers

Abstract

The environmental concern and marketing competition give rise to the pressure to remove lead from electronic industry. Pure tin has been thought an excellent alternative except the fear of “whiskers”, the spontaneously growing pure tin crystals on tin finish surface with nodular or filamentary shape. Tin whiskers can cause fatal reliability problems by shorting circuit or impairing mechanical properties.

By reviewing published literatures, a broad discussion is presented on various aspects of tin whiskers including the correlations between thermodynamics and kinetics studies, the origination of the formation driving force with the analysis regarding to external stress, intermetallic compound, surface oxides, inter-diffusions respectively, and the effects of plating thickness, temperature, grain structures and plating current as well. Finally, an objective evaluation is given out on three commonly used mitigation practices to prevent tin whiskers.

1 INTRODUCTION

In first and second-level microelectronic packaging, many kinds of soldering materials are used to provide interconnects. Conventionally, lead-tin alloy is the most extensively used solder due to its eutectic behavior, effectively low cost and other properties. At lead-tin eutectic point, this alloy exhibits a significantly low melting temperature, at which conductors can be mechanically and electrically connected without thermal damage. However, in recent years, environmental and public health concerns have been calling for the movement to eliminate lead. In Japan and Europe, electronic industry has been forced legislatively to consider methods of removing lead from their end products and manufacturing process. By thinking of the factors such as ease of converting existing lead-tin soldering lines, ease of manufacture and compatibility with existing assembly

methods, pure tin is seen by many in the industry as a potentially simple and cost effective alternative to lead-tin based systems.

In spite of all the benefits, pure tin encounters one big challenge when adopting it as the solution of lead-free solder: many pure tin products develop tin whiskers, pure tin crystal in nodular or filamentary shape, which cause two reliability problems for manufacturers and users. The first is electrical shorting. Whiskers can grow between adjacent conductors of different potentials and cause either a transient short as the whisker is burned open, or a permanent short. The second is potential mechanical problems with slip rings, optical devices, microelectromechanical devices (MEMS) and other similar components.

Tin whisker is not a new phenomenon. In fact, the first published reports of tin whiskers can be dated back to the 1940s and 1950s. Besides Tin, several other low melting point metals such as zinc, cadmium, indium and antimony can also grow whiskers. Historically, addition of lead was found to be an effective method of minimizing tin whisker to formation and so lead-tin alloy has been widely used in microelectronic industry. However, with the advent of lead-free movement, the risk of tin whiskers is again a significant concern.

Many scientific experiments have been performed throughout the past five decades and extensive results have been published on the subject of tin whiskers. The fundamental mechanism of whisker growth is still not understood, however, whisker growth is believed to proceed either via a dislocation mechanism or through a grain growth / recrystallization mechanism. Many theories agree that stress provides the driving force for whisker formation. Stress can exist as micro-stress (internal to the tin film itself) and

macro stress (externally applied stress). It has also been recognized that long-range mass transport of Sn is essentially attributed to the formation of very large whiskers. To date, various factors that affect the whisker growth have been observed and reported, which include crystalline structure, plating thickness, electroplating current density, substrate, temperature, humidity etc. The attributes of tin whiskers have been well documented and categorized. Furthermore, various suggestions based on different experiments and studies were brought up to minimize the growth of tin whiskers. Unfortunately, the lack of an industry standard whisker test is a significant limitation in addressing tin whiskers problems.

Critical review of existing literatures on tin whiskers is presented. The emphasis is put on the basic driving forces and the possible solutions generated from thermodynamic studies. Meanwhile, conflicts and debates are collected for further researches.

2 KINETICS VS THERMODYNAMICS

To date, most of studies on tin whiskers still focus on kinetics (how fast tin whiskers may grow and which factors may affect the growth rate), whereas investigations on the thermodynamic reasons are relatively left behind. The spontaneous formation of tin whiskers suggests a decreased Gibbs free energy from the state of pure tin electroplate to the state of tin whiskers. This negative change of Gibbs free energy is the driving force of formation of tin whiskers. If thermodynamic reasons are well understood and this driving force can be eliminated, tin whiskers problems can be expected solving more effectively and completely. At the same time, Kinetic studies can provide the means to slow down the growth of tin whiskers, which are also helpful in dealing whiskers. The relationship between kinetics and thermodynamics is presented in Figure 1.

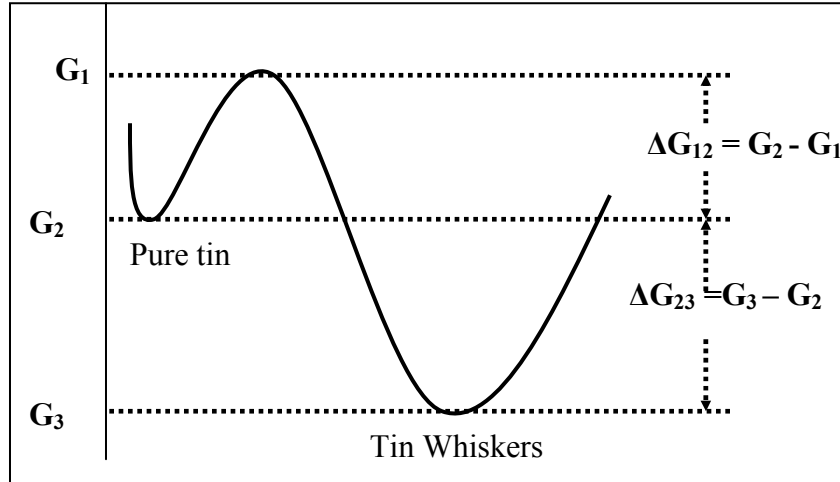


Figure 1: Relationship of Kinetics and Thermodynamics

Here, ΔG_{12} is activation energy, which is the Kinetic reason and determines the growth rate of tin whiskers, the simplified equation can be expressed as:

$$GrowthRate = N \ln\left(-\frac{\Delta G_{12}}{RT}\right)$$

In reality, the growth rate of tin whiskers is dependent on many factors, such as temperature, defects, grain size, plating thickness, diffusing coefficient, and the interactions between materials. Details will be discussed later.

ΔG_{23} is the change of Gibbs free energy, a negative value here, which defines the direction of a reaction progress. The spontaneous nature implies that the formation of tin whisker on pure tin plate is thermodynamically favorable. To date, the widely accepted driving force to form tin whiskers is the relief of compressive stress within pure tin. However, the sources of these compressive stresses are still debated.

Consequently, all solutions or suggestions to minimize tin whiskers growth can be divided into two major categories, either kinetics or thermodynamics.

3 DRIVING FORCE OF TIN WHISKER FORMATION

Tin whiskers growth is generally believed to occur in order to relieve compressive stresses that exist within the pure tin plating. In general, growth is most likely induced by stresses such as those resulting from:

- *Residual stress within the tin plating* (caused by plating chemistry and process, or mechanical working after plating)
- *Intermetallic compound formation* (the diffusions between the materials of tin plating and substrate lead to form intermetallic compounds and cause compressive stress within tin plating)
- *Diffusion* (Zinc and copper atoms from brass substrate both have high diffusivity when they diffuse into tin film)
- *External stress* (or applied stress, which can be introduced by torquing of a nut or a screw, bending or stretching of the surface, or any other inappropriate handling and probing)
- *Coefficient of thermal expansion mismatches* (between the plating materials and substrate)
- *Surface oxide* (zinc oxide and tin oxide are both possible to form on the tin surface and cause stress due to specific volume change)
- *Particle irradiation*

Among all those possible sources, residual stresses, diffusion, intermetallic compound and external stresses are most extensively investigated by industry and academia. It is noteworthy that compressive stresses may not originate from a single source. In a real case, all possible sources and their interactions need to be taken into account.

3.1 External Stress (Macro Stress)

External stresses (macro stress) are usually induced by sequent operation or handling after plating, which could be compressive stresses such as those induced by torquing of a nut or bolt assembly, bending or stretching of the surface after plating such as lead forming or crimping, and scratches, gouges in the plating and the substrate introduced by handling, probing etc (Reference 5). The correlation between external stress and tin whiskers is still under investigation. The effects of macro stress are still debated.

It has been reported applied stress could influence many aspects of tin whisker including its formation, growth rate and characteristics. For example, in *Kathlen M. Cuningham's* study, after 264h aging of pure bright tin plating, both nodular and filamentary types of tin whiskers were evident at the local point of external stress, while only filament whiskers observed at the area away from the external stress. After 408h of aging, the 90/10 tin-lead solder plated module was found to have nodular and filament types of whiskers at the mechanically stressed area, while no whiskers was evident in the area away from the mechanical stress. Similar results were obtained on hot tin dip module in a longer period of aging time (Reference 3). It has also been documented that compressively bent sample shows a higher whisker growth propensity than that no-bent samples, while the applied tensile stress decrease the whisker growth propensity (Reference 11). Moreover, in a conformal coating study, it is interesting to observe that many of the whiskers formed along a surface scratch or defect in the substrate that was not intentionally introduced. These minor defects were most possibly introduced before plating or through handling of the samples before the start of the experiment (Reference 6).

Contradictorily, it has also been concluded from other studies that external stress, tensile or compressive, has no real effect on tin whisker. There were no distinctive difference observed on the growth rate, nucleation period, density and characteristics of tin whiskers between the compressive bend region of the samples and the flat, undisturbed areas (Reference 7).

3.2 Internal Stress

Internal stress refers to the stress that exists within tin film or the interfaces between the plating and the substrates. This type of stress may inherent from the properties of the materials, production process or physical and chemical changes during storage.

3.2.1 Residual Stress (Macro Stress)

Residual stresses are directly related to electroplating process and the materials properties that inherent from other pre-treatment, hence, the factors that may increase stresses within tin plating are various. Besides the facility performing and the electroplating operation, a summery of the more salient and common factors believed to affect whisker formation is as follows:

- Electroplating current density
- Grain size and shape
- Interfacial stress level
- Substrate stress levels
- Co-deposited carbon or hydrogen

Overall, these factors may not independently influence the stress level within tin plating. The correlations among these factors can provide the key to understand the increasing of

compressive stress. Stresses fit in this category should be able to measured right after processing.

3.2.1.1 Electroplating Current Density

The statement that “high current density produces higher residual stress” (Reference 5) is commonly cited by many researchers. However, by electrodepositing tin films at current density of 0.5, 1, 2, 3.5 and 4 A/dm² respectively on phosphor bronze substrate, B. -Z. LEE detected the lowest whiskers density on the tin film obtained at current density of 1 A/ dm², which is neither highest nor lowest current density in this experiment. Furthermore, it is interesting to note that the deposits obtained at 0.5, 2, and 4 A/ dm² show the smaller grain size of Tin than that obtained at 1 A/ dm² (Reference 4). Therefore, understanding how electroplating current density affects the grain size will provide us a meaningful yet practical method to minimize Tin whiskers growth.

3.2.1.2 Grain Size and Shape

Even though experimental values were not sufficient, the spontaneous development of compressive stress was thought to relate to both the diffusion of copper atoms from the substrate into the tin film and the formation of the intermetallic compound Cu₆Sn₅. Tin films with small grain size have more grain boundaries and provide diffusing species with more diffusion pathways. The amount of copper atoms diffused into tin grain boundaries per given time will increase with decreasing grain size, if given everything else same, compressive stress will build up more quickly in tin film with smaller grain and higher density of tin whiskers are expected (Figure 2). Moreover, the continuous growth of Sn whiskers must rely on grain boundary diffusion for mass supply. Large number of grain boundaries is favorable also for this long-range diffusion of Sn atoms.

Xu & Zhang verified the grain size effects on Tin whiskers formation. In their experiment, three pure tin finishes, bright tin, matte tin and satin bright tin, were electroplated on Copper substrate and stored at 50 °C for at least 4 months. Among these three pure tin finishes, bright tin has the finest grain size and is much more prone to whisker formation than the satin bright and matte finishes. For instance, after 10 month, the whisker index (a function of number n , length L , and diameter d of the whiskers) for the bright finish is about 6, 300 times higher than that for the satin bright finish (Reference 10). Similarly, in *B. -Z. LEE*'s experiment, tin film with smaller grain size presented higher whisker density than that with larger one (Reference 4).

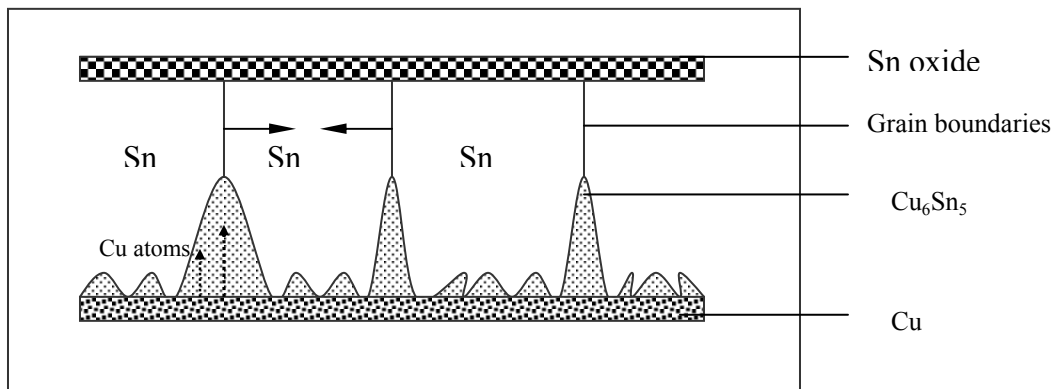


Figure 2: Cu_6Sn_5 Formed in Grain Boundaries within Tin [4]

Regarding to the shape of grains, some researcher believes that tin whiskers grow from the grains having different orientation from the major orientation of the tin film. In this situation, the tin surface oxide film can be sheared along the boundaries of the grains. To release the compressive stress in the tin film, thin whiskers grow from the grain whose surface oxide is sheared (Reference 4). On the other hand, whether high angle or low angle boundary is more favorable for diffusion is still in debate. Some believe with loosely packed grain boundaries, high angle have more dislocations to serve as diffusion paths, therefore, more prone to grow tin whiskers (Reference 11). While other concluded low angle grain boundaries are more prone to whisker growth than high angle boundaries (Reference 20).

3.2.1.3 Interfacial and substrate stress level

Unfortunately, few researches have been accomplished in this category and the related resources are relatively limited. However, it is understandable that mechanical processes used in preparation of the substrate such as cold rolling, swaging, piercing, stamping can leave the substrate in a highly stressed state prior to plating (Reference 5). Although, it is theorized that the interfacial stress caused by the high initial stress level of the hardened copper substrate combined with increased stress due to intermetallic compound formation during storage increases the stress in the tin deposit during aging, there is no direct research carried out on studying initial stress level on substrate as far as the author knows (Reference 2).

In *Rob Schetty's* model, the effects of interfacial stress between different types of electroplating materials and same substrate are demonstrated. In his experiment, deposits of pure Sn, Sn-5%Bi, Sn-Cu (1-3%) and Sn-10%Pb when electroplated over Alloy 194(a common hardened Copper lad frame industry substrate containing 2.3%Fe, 0.12%Zn, and 0.03%P, balance Cu.) all exhibit whisker growth. But the whiskers that were evident on Sn-10%Pb deposit are much fewer than that on the other three deposits. (Reference 2) *Rob Schetty* concluded that diffusion and intermetallic compound formation give rise to interfacial stresses and base materials stress level. But from other reports, it is believed that diffusion and intermetallic compound formation increase the compressive stress within tin films (Reference 4). Accordingly, some people observed whiskers originating at the interfaces between Tin deposits and substrates, while other found only within tin deposit, whiskers initiated (Reference 10).

3.2.2 Storage stress (micro stress)

Stresses in this category usually build up with storage time, which may change the initial stresses (residual stresses from plating process) i.e. from tensile stress to compressive stress. And the magnitude of the stress may alter with storage time as well. Various factors may affect the stress built-up process, such as temperature, relative humidity, defects, grain size, pre-existing external stresses. The change of storage stresses can be measured at regular intervals during a period of time, which can be months to years.

3.2.2.1 *Diffusion and Intermetallic Compound Formation*

Intermetallic compound, a substance formed between tin plating and substrates by diffusion of copper species into tin films, followed by a solid state reaction, has interested most of researchers on tin whiskers. The development of compressive stress within tin film is thought to be related to the formation of this compound. But by examining Cu-Sn phase diagram (Figure 3), it could be inferred that this intermetallic compound could either be phase ϵ or phase η with different stoichiometric range respectively. But traditionally, Cu_6Sn_5 has been used to represent this intermetallic compound formed between Cu and Sn.

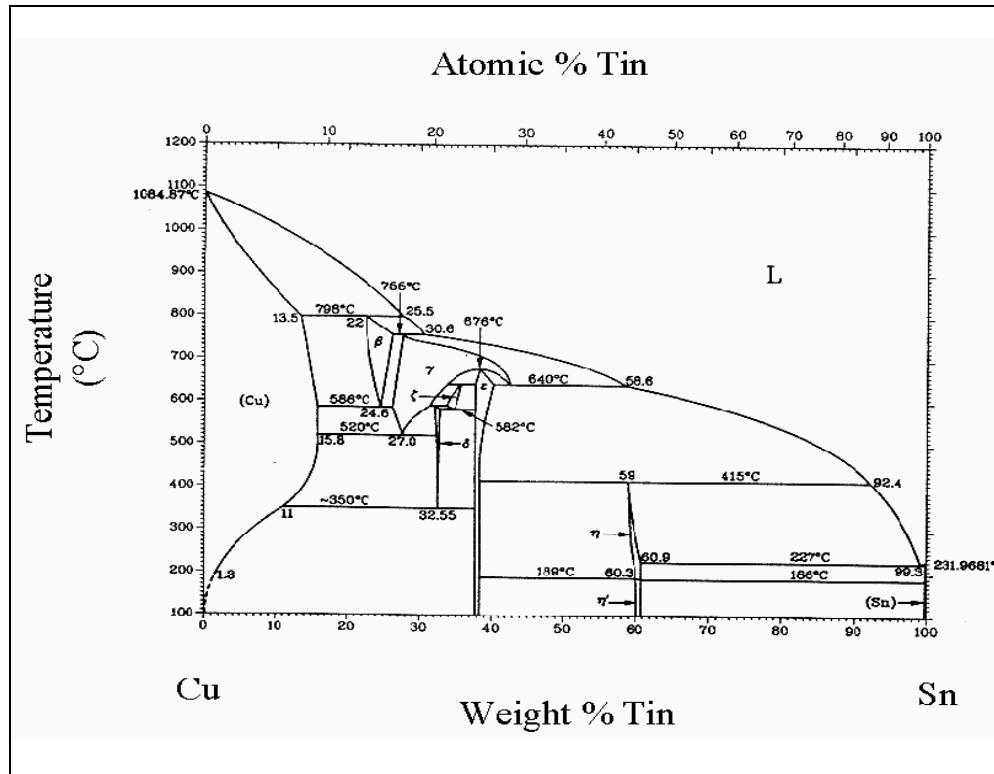


Figure 3: Phase Diagram of Cu-Sn

To study this compound, various experiments have been carried out, but the preparation of samples is similarly by depositing a layer of tin or high tin alloy over a copper-based substrate. The compressive stresses within tin plating have been proved to develop with storage time. In some case, even the initially introduced tensile stress in tin films could be eventually transferred into compressive stress in a period of testing time by the formation of intermetallic compound. In most of cases, it is discovered that compressive stresses are gradually accumulated until reach a peak, then eventually relief to a state of equilibrium by growing tin whiskers.

Xu & Zhang concluded from their research that compressive stress promotes the whisker growth and tensile stress reduces the whisker growth, the initial imposed tensile stress on the sample seems to slow down the build-up of the compressive stress (Reference 10).

Also, B. -Z. LEE reported that the tin deposit annealed at 150C for 1 h developed a thermal tensile stress of 14 MPa at room temp, which was relieved in one day and no whisker growth took place afterwards (Reference 4). However, it is not clear how the Cu_6Sn_5 formation could induce compressive stress in tin films. Several analyses are summarized as follows.

a. Interstitial diffusion

As proposed by some researches, interstitial diffusion of copper atoms and the formation of intermetallic compound (Cu_6Sn_5) may alter the lattice spacing in the tin plating and generate compressive strain within tin lattice (Reference 9), 5), 1). *M.Endo* studied how tin whiskers originated and grew on a brass substrate. In his research, two diffusion species were found, zinc and copper. He believes that interstitial diffusion of copper into tin forms intermetallic compound and cause stress, while zinc atoms diffused toward the tin film surface and form oxide. This zinc oxide provides whiskers with sites to grow out of tin surface (Reference 9). However, compared with diffusion along grain boundaries, interstitial diffusion is much more difficult and need much higher energy, which is not thermodynamically favorable. On the other hand, the atom sizes of copper, zinc and tin are comparable, whose atomic radii are 1.57Å, 1.53Å and 1.72Å respectively, huge strain will be created if copper or zinc “squeeze” into the small interstitial sites of tin lattice, and this is not thermodynamically favorable. It can be inferred that the interstitial diffusion of copper or zinc into tin crystals is very unlikely to occur if competing with grain boundary diffusion.

b. Volume change

The densities of copper, tin and Cu_6Sn_5 are 8.96, 7.28 and 8.27 g/cm^3 , respectively. The formation of intermetallic compound of Cu_6Sn_5 reduces the specific volume and induces compressive stress within tin film at the region near the interfaces (Figure 4) In this analysis, intermetallic compound is considered a flat layer formed between copper and tin, hence, it only give rise to compressive stress at the region near the interfaces. This hypothesis is coherent to some documented observations, where tin whiskers only initiated at the interfaces. At the same time, volume change is also thought to relate to the formation of surface oxide, SnO_x or ZnO_x .

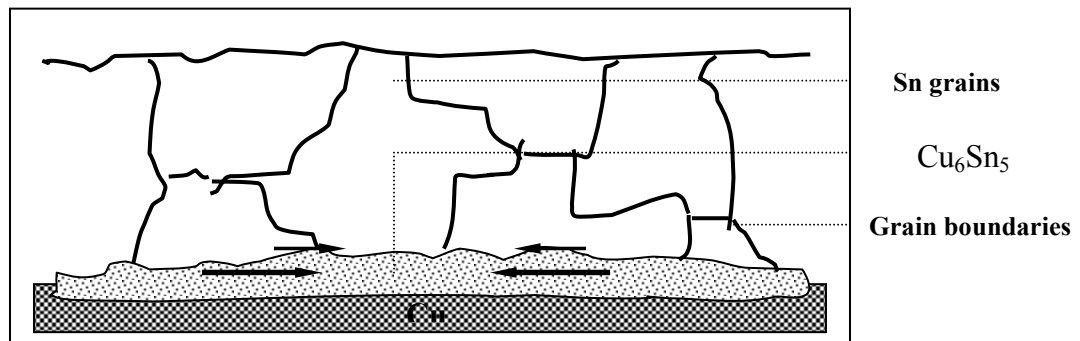


Figure 4: Intermetallic Compound Formed Between Interfaces of Sn and Cu

c. Diffusion via Grain Boundaries

If the intermetallic compound forms flatly in the interface between copper and tin, no stress will develop in the tin layer, regardless of the diffusion coefficients of species concerned. However, if the intermetallic compound layer forms in the tin grain boundaries, it will give rise to the compressive stress in the tin layer, because copper atoms are the dominant diffusing species. From above analysis, *B. Z. Lee* believes that the Cu_6Sn_5 layer is not flat and it penetrates into grain boundaries of tin film (Reference 4). (Figure 2) This hypothesis is in agreement with the observation of tin whiskers only grow within tin film other than any interfaces (Reference 10).

The diffusing coefficients of copper and zinc at room temperature are tabulate as follows (Table 1):

Table 1: Diffusing Coefficient of Selected Metals in Tin at Room Temperature

Metals	Diffusing coefficients
copper	$1.2 \times 10^{-6} \text{ cm}^2/\text{s}$
zinc	$1.1 \times 10^{-6} \text{ cm}^2/\text{s}$

3.2.2.2 Diffusion and surface oxidation

It is speculated that not only the diffusion of copper with the formation of intermetallic compound Cu_6Sn_5 , but also the diffusion of zinc with the formation of zinc oxide may cause compressive stress on tin film. (Reference 9) When tin is deposited on a brass substrate, copper and zinc atoms from this substrate can both diffuse into tin film. The difference is that copper is more prone to stay within tin film and form intermetallic compound, while zinc atoms diffuse toward the tin film surface and bind there with oxygen to form oxide. More zinc atoms on the surface were found than that inside the tin film (Reference 9). *M. Endo* proposed that the formation of copper intermetallic compound may prevent further diffusion of zinc atoms from the brass substrate (Reference 9). Another study shows that zinc atoms have higher mobility than copper and could be more easily diffuse from brass substrate to tin surface than copper. The relatively higher solubility of zinc in tin implies that zinc atoms are the dominant and faster diffusing species compared to tin. (Figure 5) In this experiment, the nodule-like whiskers present on the tin-platings made directly to brass substrate are composed mainly of tin with additions of zinc and copper, while filament whiskers growing from tin-plated brass substrates are composed mainly of tin with approximately 2% by weight of zinc, but no copper (Reference 7). *M. Endo* also proposed that the part of the built-up

compressive stress might come from the specific volume change on the tin surface due to the oxidation of zinc atoms (Reference 9).

In addition, formation of surface tin oxide is also reported to contribute compressive stresses to the underlying tin due to the specific volume change on the surface (Reference 5)*. But the fact that satellite failed in the space due to tin whiskers problems shows that surface oxides are not necessary for whisker to form.

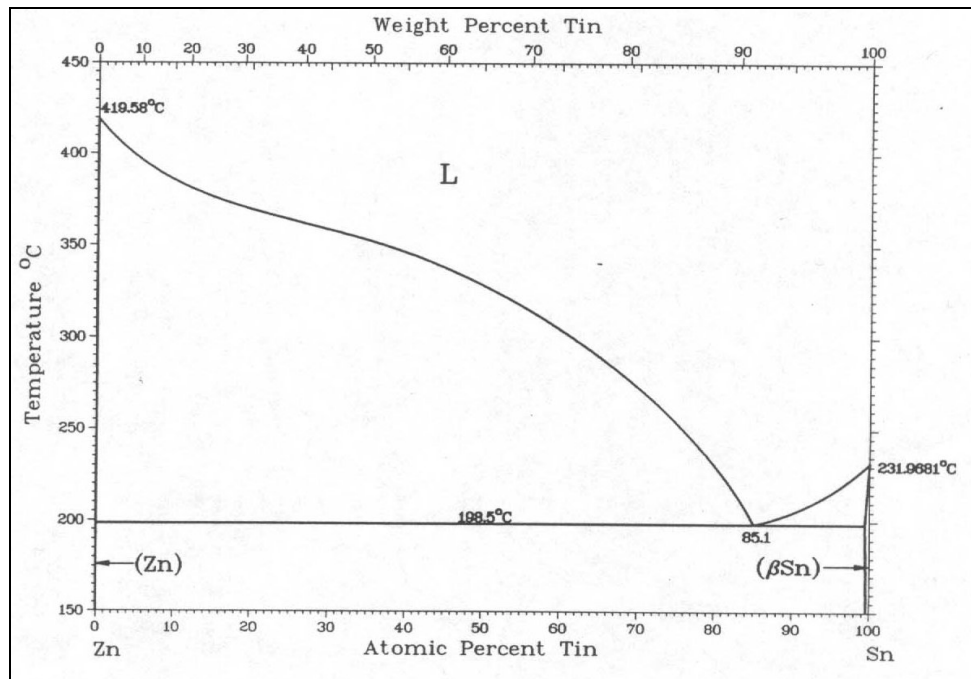


Figure 5: Phase Diagram of Zinc and Tin

3.3 Other factors

3.3.1 Plating thickness

Many researchers are still studying in this field and try to find out the safe thickness region where tin whisker growth may not be supported. Although the agreement has not yet been established, it is suggested when tin plating is over 8 μm whiskers are more resistant to grow (Reference 2), 11). Meanwhile, other recommendation has been made

that the thicknesses below 0.5 μm and above 20 μm were the relatively “safer” range, although these extremely thin or thick plates may not be feasible in applications. How plating thickness affect tin whiskers is still unknown, however, it has been hypothesized that thicker plating are more inclined to spread out the stresses evenly, especially ease off the stresses initiating at the substrate / plating interfaces (Reference 5).

Xu & Zhang compared the tin whisker formation on 3 μm and 8 μm thick Sn film respectively. It was found for thick Sn film, most of the compressive stresses were located around interface region and it distributes to entire Sn film, above all, there was almost no or very little compressive stress built up near the surface region. While for thin Sn film, surface stress was high enough for tin whisker to form after the same period of aging (Reference 11). The present of intermetallic compound layer (Cu_6Sn_5) at the interface may block the further diffusion, which, in turn, retard the formation of tin whiskers (Reference 11).

Also, if intermetallic compound Cu_6Sn_5 forms within the grain boundaries of tin film, the thickness of Cu_6Sn_5 is expected to decrease with increasing distance form the substrate/plating interface to tin surface. Hence, the local compressive stress causing by Cu_6Sn_5 will decrease toward the tin film surface. In other words, the thicker the tin film, the less compressive stress near the surface, which, in turn, will be more resistant for tin whisker formation (Reference 7)(Figure 6)

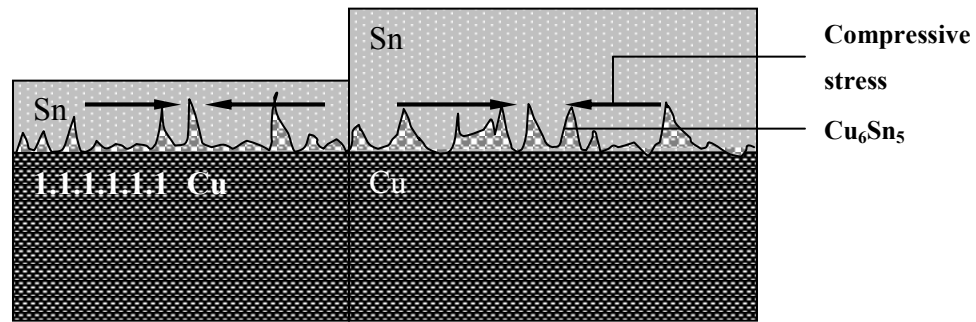


Figure 6: Comparison of thin Sn film with thick Sn film. (For thin film, stress is near surface, while for thick film, no or very little stress near surface)

3.3.2 Temperature

Elevating temperature can increase the diffusion rate of copper into tin film and aid compressive stresses to build up quickly, then, accelerates the formation of tin whiskers. However, high temperature also helps relief internal stress within tin film and consequently oppresses the formation of tin whiskers. Based on literature research, the optimum temperature for whisker to form is around 50 C°, and most of researches were conduct at this temperature. Contradictorily, in a conformal coating study, higher density of tin whiskers were observed on the samples stored under room temperature ambient conditions (25 C°) than that on samples stored at 50 C° (Reference 6).

4 RECOMMENDATIONS

Although extensive researches have been performed to date by industry and academia, there are still no effective risk mitigation practices that can be widely accepted. Some studies suggest that alloying as little as 0.9% lead with the tin dramatically reduces the density and growth rate of tin whiskers, but both nodular and filament whisker were observed at the compressively stressed area even for a 10% lead-tin finish in

Cunningham's experiment (Reference 3). In other researches, it has been theorized that the addition of Pb may delay, but not eliminate, the onset of whiskers. This theory may explain the results in *Rob Schetty's* experiments, where shorter whiskers were evident in the Sn-10%Pb sample compared to the other samples, such as pure Sn, Sn-10%Bi and Sn-1%Cu (Reference 2). Besides adding small amount of Pb, several other mitigation approaches have been suggested in the past including annealing or reflowing the plated surface with high temperature to relax internal stresses, coating the surface with a protective barrier of conformal coat, underlying Ni to block the diffusion pathway of species from substrate. But one can expect that there is still no completely solution to tin whiskers yet, all those approaches have benefits and limitations.

4.1 Conformal coating

Conformal coating refers to an insulating protective coating that conforms to the configuration of the object coated. In order to evaluate risk mitigation techniques, NASA GSFC started experiments to study the effects of Uralane 5750 (as conformal coat) on tin whisker growth. Their results show that Uralane 5750 does not prevent whisker formation, furthermore, it shortens the nucleation period of whiskers and whiskers initiate more rapidly under Uralane 5750 than that without this coating. After 2 years of the initiation of this experiment, a whisker even grew through a ¼ mil thick Uranlane 5750 coating. On the other hand, this experiment did prove that the coating retards the growth rate of whiskers, e.g. in 2 years, the longest whisker is around 2 mm long on non-coated side, while those whiskers growing under the conformal coat are around 0.05mm long. The growth rate of tin whiskers is still unknown once they grow out of the conformal coat (Reference 6).

Although growing out of the coat is possible, a whisker is very unlikely to penetrate two layers of coating, hence, conformal coating is still on the OEM mitigation guidelines and recommended to use wherever possible.

4.2 Ni barrier

If the diffusion of copper species into tin films builds up internal stress and eventually results in whisker growth, a barrier layer may be an effective method to block the diffusion pathway and prevent whiskers. *Rob Schetty* verified the effects of nickel barrier on eliminating tin whiskers. When deposited over nickel-plated copper alloy substrate, neither the pure tin coating nor the Sn-10%Pb coating exhibited whisker growth in the study. The nickel deposit is speculated to provide a lower initial stress between the interfaces and also act as an excellent barrier to copper diffusion, which hinders the formation of intermetallic compound (Reference 2).

Furthermore, according to the experiment results of *Xu & Zhang*, the application of Ni barrier layer does not only exclude compressive stress building up in Sn film, but also develops a tensile stress in Sn film. Consistent with this stress build-up process, for Sn plated over a Ni-underlayer, no whisker formation was observed after 6 months aging at 50 C°, whereas Sn plated directly over Cu shows whisker formation already after 3 month aging at 50 C° (Reference 11). *Xu & Zhang* also evaluated the effects of plating Sn on various Ni layers with pre-existing internal stress, which varied from tensile stress to compressive stress with different magnitude. A noteworthy result shows that the magnitude of the tensile stress in Sn is independent of the stress in the Ni-layer and most likely related to interfacial diffusion between Sn and Ni (Reference 11).

To understand the correlations between the interfacial diffusions and internal stress built-up process, diffusion mechanisms between specific elements, i.e. Sn with Cu, Sn with Zn, and Sn with Ni, need to be carefully examined. It is noteworthy when deposited on the barrier layer of Ni, the atoms from Sn film become dominant and faster diffusing species compared to Ni atoms. By examining the phase diagram of Ni-Sn (Figure 7), it can be clearly found out the solubility of Ni in Sn is less than 0.005at. % Ni, whereas the solubility limit of Sn in Ni is 11.0 at. %. The significant difference of the solubility implies that it is more easily for Sn to dissolve into Ni than for Ni to dissolve into Sn. Accordingly, the faster diffusion of Sn atoms leads to material deficiency (Kirkendall effects) on the Sn film side adjacent to Ni layer and gradually build up tensile stress within Sn film. (Reference 10) (Figure 8)

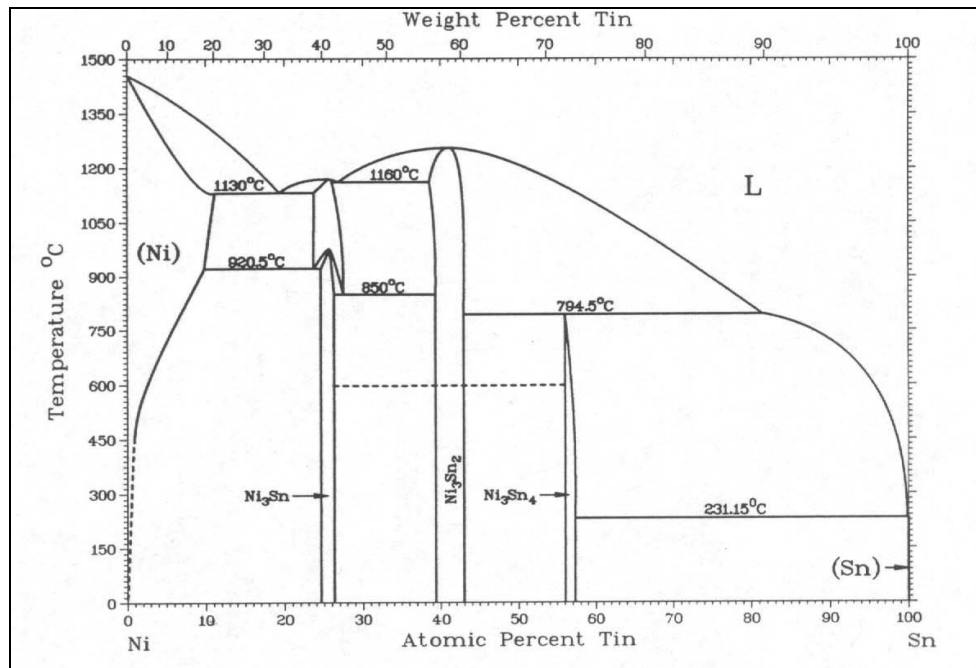


Figure 7: Phase diagram of Ni and Sn

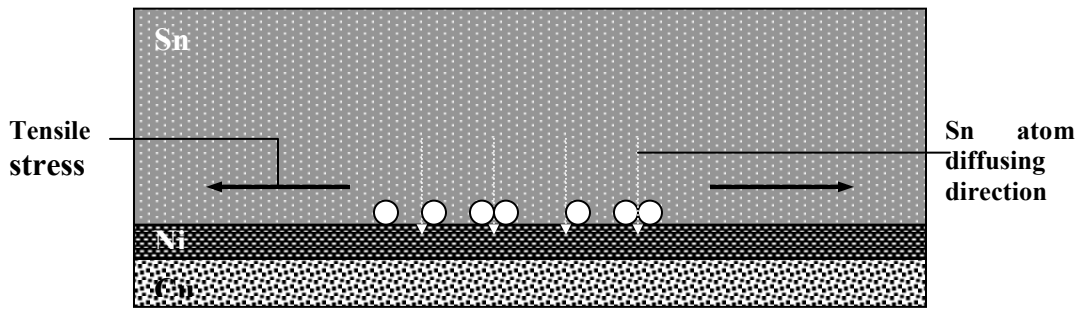


Figure 8: Tensile Stress Built up in Sn Film by Diffusion of Sn Atoms into Ni Layer

Although general benefits of nickel barrier have been proved by some researchers, tin whiskers have also been observed on passive components utilizing a nickel barrier layer construction such as those used in MLCCs and connectors (Reference 19).

4.3 Reflow

Two major beneficial effects can be obtained by reflowing or fusing tin-plated parts after manufacturing and testing: one is to relieve the inherent internal stress, the other is to help grain growth. It is believed that tin film with large grain size is less prone to grow whiskers than that with small grain size (see section “grain size and shape”). Further study shows after reflowing, there is no compressive stress built up again in Sn film even after a long period of aging, e.g. 18 months, hence, no whisker growth observed (Reference 11). However, research also found that reflow could not fuse back existing whiskers into Sn film, long filament whisker just bent down when the sample was reflowed at 260 for 70 seconds (Reference 11), which leads to high risks of short circuit for fine-pitch components. Surface layer of Sn oxide is suspected to hinder tin whiskers melting down since Sn oxide does not melt at this reflowing temperature. Therefore, it is highly recommended to reflow tin-plated parts before any formation of tin whiskers.

5 CONCLUSIONS

Compressive stresses are widely accepted as the driving force to form tin whiskers. However, the origination of compressive stresses within tin films is still under extensive studies. The internal stresses resulted from diffusion of copper or zinc from substrate, formation of intermetallic compound and surface oxides are thought to be the cause of tin whiskers. On the other hand, whether external stresses play the same role on driving tin to form whiskers are debated. Kinetically, many factors are directly related to the growth rate of tin whiskers including plating thickness, plating current density, grain size and shape, and temperature etc. To minimize to harm of tin whiskers, many mitigation practices have been proposed, but none of them are able to eliminate tin whiskers effectively to date. There are still many puzzles remained, such as where tin whiskers initiate, how diffusing species interact with one another, and whether intermetallic compound form flatly between interfaces or penetrate into grain boundaries. To fully understand tin whisker phenomena and put it in control, further studies are in need.

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