NEMI National Electronics Manufacturing Initiative, Inc.

Annotated Tin Whisker Bibliography And Anthology

Contents

a monograph by

Dr. George T. Galyon
IBM Server Group
Chair, NEMI Tin Whisker Modeling Project

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ANNOTATED TIN WHISKER BIBLIOGRAPHY AND ANTHOLOGY

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Dr. George T. Galyon
IBM Server Group

Introduction

This document is intended as a reference for those interested in tin whisker references and related information. It was this author's intention to present the information both chronologically (the annotated bibliography) and by selected topics (the anthology). Every effort was made to make this document reportorial in nature and to minimize the natural inclination to editorialize. This document version covers the time period from 1947 thru 2003 and early 2004. Probably over 90% of the relevant English language literature is covered. There are, regrettably, some Russian/Japanese/and Chinese language documents that it was not possible to obtain. There are some references to whiskers other than tin. Cadmium, zinc, and silver are whisker forming materials, and some documentation on whisker formations in these metals is included.

Bibliography

1940s through 1950s:

A metallic whisker is a single crystalline filamentary surface eruption from a metal surface. Whiskers are usually found on relatively thin (0.5 to 50 microns) metal films that have been deposited onto some kind of substrate material. A typical whisker is one to five microns in diameter and between 1 and 500 microns in length. Whiskers can be straight, kinked, and even curved. Metallic film deposits also evidence other types of eruptions that are quite different in appearance from the whisker eruption. These eruptions are referred to in the literature as flowers, extrusions, volcanoes, etc., and they have not been of as much general interest as the much-longer whisker eruptions.

Metallic whisker formation first became of widespread interest to the scientific community immediately after WWII due to the use of cadmium (Cd) electroplating on electronic componentry. Cadmium is one of several metals that have a propensity for whisker formation. In WWII, condenser (i.e. capacitor) plates were electroplated with Cd and, over time, the Cd plating grew whiskers long enough to short out adjacent condenser plates. These observations were first reported in 1946 by H.L. Cobb [1].

In 1948 the Bell Telephone Corporation experienced failures on channel filters used to maintain frequency bands in multi-channel telephone transmission lines. Failure analysis quickly showed that Cd whisker formation was the root cause of the channel-filter failures. Bell Laboratories quickly initiated a series of long-term investigations into the general topic of whisker formation, the results of which were first reported in 1951 by K.G. Compton, A. Mendizza, and S.M. Arnold [2]. This Bell Laboratories work established that whisker formation occurred spontaneously, not only on cadmium (Cd) electroplating, but also on zinc (Zn) and tin (Sn) electroplating. It was also found that whiskers occurred on an aluminum (Al) casting alloy (Alcoa 750) as well as on silver (Ag) electroplate when exposed to hydrogen sulfide (H_2S) environments. The Bell Lab experiments studied a variety of substrate materials including copper (Cu), copper alloys, steels, and nonmetallic substrates. While the 1951 Compton, et al., paper was essentially a report in progress it made summary statements intended as a guide to future research:

1. *Whisker growths are not limited to electrodeposited coatings and may be found on solid metals as well as on surfaces metal-coated by various methods. The growths may develop in an environment in which there is relatively low humidity and, at most, only traces of organic material.*

2. *The whiskers are not compounds but are metallic filaments in the form of single crystals.*

Most of the research since the 1951Compton paper focused on Sn electroplated onto a variety of substrates. Sn and Sn alloy electroplates became one of several platings of choice for electronic componentry due to a favorable combination of contact resistance, corrosion resistance, and solderability. In I952, Herring and Galt [3] described the mechanical properties of thin whiskers of Sn, and inferred that whiskers were single crystals. In 1953, Peach [4] proposed the first dislocation mechanism for whisker growth, which stated that Sn whiskers grew from Sn atoms migrating through a screw dislocation at the center of the whisker. These migrating Sn atoms subsequently deposited themselves at the whisker tip. Shortly after Peach's 1953 publication, Koonce and Arnold [5], from Bell Laboratories, published the first electron microscope micrographs of Sn whiskers and concluded that whiskers grew from the whisker base, thereby voiding the Peach hypothesis. All subsequent investigations have been in agreement with the Koonce-Arnold observation that Sn whiskers grow from the base and not from Sn atoms deposited at the tip of the growing whisker. That same year, F.C. Frank [6] and J.D. Eshelby [7] independently proposed that whiskers grew from dislocations located at the whisker base that operated through a diffusion-limited mechanism, thereby leading to a whisker growth event. The Eshelby mechanism involved Frank-Read dislocation sources emitting loops that expanded by climb to a boundary. These dislocation loops then glided to the surface and deposited their half plane of extra atoms at that surface. The Frank mechanism involved a rotating edge dislocation pinned to a screw dislocation that was at right angles to the surface. This rotating edge dislocation was claimed to stay in the same plane after each revolution, and for each revolution an additional layer of Sn atoms was added to the whisker base. The stated driving force for the Frank and Eshelby mechanisms was surface oxidation that created a negative surface tension in the region where the whisker ultimately formed. This negative surface tension factor was the driving force for the dislocation motions deemed necessary for whisker growth.

In 1954, Koonce and Arnold [8] published additional electron microscope micrographs showing that the Sn whiskers could be kinked. Also in 1954, Fisher, Darken, and Carroll of U.S. Steel published the first full-fledged journal article on whisker formation and growth [9] in *Acta Metallurgica* titled "Accelerated Growth of Tin Whiskers." This article emanated from a chance observation that Sn-plated steel mounted tightly in a metallographic clamp grew a pronounced number of Sn filaments (whiskers) after only a few days. A ring clamp was developed and growth-rate measurements were made as a function of clamp pressure and time. The data showed that the induction period (i.e., delay time) for initiation of whisker growth would approach zero as clamping pressure increased. Furthermore, whisker growth rates were determined to be essentially linear and, at some point in time, went to zero (i.e., the whisker stopped growing). The maximum growth rate, reported at a clamping pressure of 7500 psi, was about 10,000 Angstroms/sec. Fisher, et al., pointed out that growth rates for spontaneous Sn whisker growth had been reported (private communication — not referenced) as being about 0.1 to 1.0 Angstrom/sec. In this landmark article we see for the first time the proposition that Sn atoms move from a region of high compressive stress to a region of lower stress. Furthermore, Fisher et al., attempted to unify all of the observations made as of that date (1954) in previously published reports. In addition, for the first time, the presence of non-whisker "extrusions" was noted. Whiskers were observed to grow "*not from this extruded tin, but from the vicinity thereof.*" Fisher, et al., summarized with a list of propositions that all Sn whisker growth models should meet:

1. *The mechanism must produce a single crystal.*
2. *The mechanism must explain a linear growth rate.*
3. *The mechanism must rationalize the observed induction periods for spontaneous growth.*
4. *The mechanism should be capable of rationalizing the sudden termination of whisker growth at the end of a period of extremely high and constant growth rate.*

The importance of the Fisher, et al., article was that it established compressive stress gradients as the driving force for whisker growth. The majority of all subsequent proposed whisker growth models have acknowledged this observation by Fisher, et al.

The first whisker commentary published after the Fisher, Darken, and Carroll paper was a 1955 article by Hasiguti [10], which stated that the thermodynamic approach of Fisher, et al., could not rationalize the magnitude of observed whisker growth rates. Hasiguti proposed that the stress in the whisker-growing medium was relieved by whisker growth when it "*cannot be relieved by extrusion, the stress in the medium can ...be considered to exist right up to the surface.*" Secondly, Hasiguti proposed that a concentration of vacancies at the root of the whisker was maintained at a constant level by the absorption of vacancies at edge dislocations situated at the end of the stress gradient. Using these assumptions, Hasiguti showed that a linear relation should exist between the growth rate and the applied pressure (as reported in Fisher, Darken, and Carroll). However, the growth rates predicted by Hasiguti were still at least an order of magnitude smaller than the measured growth rates shown in the Fisher, et al., paper.

In 1955, G.W. Sears published an article [11] for Zn, Cd, Ag, and CdS (cadmium sulfide). This article has often been referenced in subsequent tin whisker articles, but the subject matter is not relevant to whisker growth from an electrodeposited film.

The next relevant commentary published after Hasiguti's 1955 article was a 1956 letter to the editor by J. Franks [12] that described a dislocation glide mechanism dependent on self-diffusion of Sn, which Franks believed met the first three of the four propositions outlined in the Fisher, et al., paper. Franks then elaborated on his model in a 1958 *Acta Metallurgica* article [13] based on data from Sn films electroplated onto a steel substrate. Franks proposed a dislocation mechanism whereby whisker-generating dislocations are pinned due to lattice faults, and thereafter acted as dislocation sources under the influence of either an applied or internal stress field. The main feature of Franks' model was pinned dislocations that moved by glide to grow whiskers, with material for the whisker being supplied by a rate-controlling diffusion mechanism. Franks accounted for the difficult proposition #4 of Fisher, et al., (i.e., the observation that whisker growth suddenly stopped at some seemingly fixed end point regardless of the growth rate or applied pressure) by surmising that dislocation sources eventually became fixed (i.e., the dislocations become incapable of generating new dislocations) due to faults introduced into the "*region by the constant addition of material to the region at the base of the whisker...eventually locking the whisker generating dislocations*".

In 1957, Amelinckx, et al. [14], published an article on a helical dislocation model for whisker formation and growth. Helical dislocations are spiral prismatic dislocations that can move to a surface by a climb mechanism and add a burgers vector thickness of material to that surface for each complete loop of the spiral that reaches the surface,. Amelinckx claimed that his model was consistent with the Koonce-Arnold observation.

G.S. Baker in 1957 [15] studied the distribution of angular bends in whiskers for zinc (Zn), cadmium (Cd), and tin (Sn) coatings. Baker found that the bend angle distribution had peaks at angles corresponding to the angles between low-indices planes in the crystalline lattice. Baker commented on the relevance of his observations relative to the dislocation mechanism theories proposed by others, thusly;

1. *The conclusion from this is that whiskers do not grow with a root coherent with the base material, but are separated by an incoherent interface from the base material. The bend is then formed by a change in direction of growth at the base of the whisker, the parts of the whisker already formed reorienting in space to give a constant orientation of the growing face".*

Baker concluded that his observations were not consistent or compatible with dislocation mechanisms of whisker growth.

The whisker growth rates reported by Fisher, Darken, and Carroll have been generally, but not specifically, reproduced in subsequent reported research in the intervening years. V. K. Glazunova in a 1962 paper [16] reported on clamp pressure experiments for Sn coated brass and steel plates at pressures of 150 kg/cm^2 that resulted in whisker growth rates of only 2.3 Angstroms/sec (as compared to the reported 10,000 Angstroms/sec in the Fisher, Darken, and Carroll paper). In a little known, and never heretofore referenced, 1964 publication [17], Pitt and Henning reported on Sn-plated steel clamp pressure experiments where the highest whisker growth achieved at clamp pressures of 8000 psi. was 593 Angstroms/sec. Pitt and Henning also reported that whisker growth rates decreased with time, which was in stark contrast to the linear with time growth rates reported by Fisher, et al [9]. Pitt and Henning did show that whisker growth eventually ceased, as did Fisher, et al. Pitt and Henning also commented about clamp-pressure experiments done with hot-dipped tin and 50%Sn-50%Pb (lead) deposited onto copper and steel substrates. While whisker densities decreased with increasing lead (Pb) content, considerable whisker growth did occur at high (several thousand psi.) clamp pressures for the 50%Sn-50%Pb plating. Pitt and Henning also observed that hot-dip coating on Cu substrates produced considerably fewer (about half) whiskers in comparison to hot-dip coatings on steel substrates. These observations by Pitt and Henning complicated the four propositions of the Fisher paper because it was now necessary for whisker growth models to explain both linear and nonlinear growth rates. There have been no known published commentaries on whisker growth rates since the 1964 article by Pitt and Henning.

S.M. Arnold of Bell Laboratories published three monographs on whisker topics over a ten-year period starting in 1956. The first publication [18] was a review article that compiled all the Bell Laboratories experimental observations made up to 1956. This 1956 article by Arnold was the first discussion in the published literature on mitigation strategies. Arnold commented that all the experimental factors studied (temperature, relative humidity, applied pressure, method of deposition, thickness of metal coat, character of substrate surface condition) influenced whisker growth, but only in degree. Perhaps the most intriguing observation from this 1956 paper by Arnold was a comment about neutron bombardment experiments conducted at Brookhaven National Laboratory where “tin-plated specimens” (of an unspecified nature) were exposed for 30 days at a neutron flux density of 10^{12} cm^{-2} sec^{-1}. After 12 months, these “exposed specimens” were examined and found to have a “dense growth of whiskers”, whereas the unirradiated control “specimens” had little whisker growth. Arnold mentioned similar studies underway with beta particle bombardment, but no published report of these beta particle experiments exists. Arnold also mentioned that electric and magnetic fields produced no whisker acceleration effect.

In 1959 Arnold published a second paper [19] that detailed the beneficial whisker mitigation effect observed by alloying tin (Sn) plating with lead (Pb). Arnold did note that SnPb alloys can whisker if subjected to high compressive stresses. As a result of this article the predominant mitigation strategy for Sn plating in the United States electronics industry for the next 50 years became the co deposition of Pb into the Sn electroplate in amounts ranging from 3-10% by weight. Arnold’s next publication was in 1966 [20] and it elaborated on the topic of “precautionary measures,” a topic that Arnold initially addressed in his earlier 1956 [18] paper. Specifically, fused and hot-dipped Sn coatings were recommended. In addition, Arnold commented that low relative humidity and low ambient temperatures reduced, but did not entirely prevent whisker formation.

1960s:

In 1963, a major article by Glazunova and Kudryavtsev [21] reported on Sn whisker experiments conducted on a variety of substrate materials (copper, nickel, zinc, brass, aluminum, silver, steel, and tin). The Sn coatings in this study ranged from very thin (less than 1 micron) to relatively thick (up to 50 microns). The data indicated that whiskers did not grow for very thin (~0.5 micron) Sn plating, whereas thicker plating showed a more complex behavior depending on the substrate material. For Cu substrates, whisker densities and growth rates appeared to be maximized for Sn plating 2 to 5 microns thick. When steel was the substrate material, whisker density and growth rates were maximized for Sn plating thicknesses between 5 and 10 microns. With brass substrates, Sn whisker formation remained high up to plating thicknesses of 20 microns. Glazunova and Kudryavtsev also reported on effects of electrolysis conditions during plating, effects of current density, effects of electrolyte temperature, effects of alloying the Sn plate with additions of Ni, Zn, Cu, and Pb, and the effect of post plating heat treatments. These were the first published results on the effect of heat treatment at temperatures from 100° to 180°C for times ranging from one to 24 hours. All heat treatment combinations had significant mitigating effects on tin whisker formation. Electrodeposition from solutions cooled to below zero showed enhanced whisker numbers in comparison to plating from solutions at ambient temperatures. Fusing (or reflow) was also evaluated and shown to have a retarding effect on whisker growth. Glazunova and Kudryavtsev then made a series of summary statements not previously stated in such an integrated format:

1. *The experimental data show that the growth of...crystals on electrolytic Sn coatings is a spontaneous process, independent of oxidation in a moist or dry atmosphere. The data as a whole indicate that the growth of the crystals is probably due to internal stresses of the electrolytic tin deposits. The differences observed in the...incubation period and in the rate of crystal growth...on different substrate metals is apparently due to the extent of th internal deformation of the tin lattice.*

2. *The marked acceleration of the growth of tin...crystals deposited on brass substrates is evidently due to the diffusion of zinc into the tin coating. The reduction in the rate of crystal growth with increasing thickness of the tin deposit is probably caused by the reduction of internal stresses in the coatings.*

3. *The appearance of internal stresses in the copper substrate (i.e., copper strike) when that strike is deposited in the presence of thiourea also has a marked effect on the character of growth of...tin whiskers.*

4. *The high rate of growth for tin whiskers from coatings deposited at temperatures below zero is due to formation of very fine-grained and stressed deposits under these conditions. The retardation of crystal growth after heat treatment is evidence in favor of the conclusion that internal stresses play the main role in the growth mechanism.*

5. *For these reasons, it may be assumed that the incipiency and subsequent growth of tin whiskers is a distinctive form of recrystallization of tin plating.*

Of particular note is the above comment on recrystallization, which was the second time in the published literature that recrystallization was referenced as a potential factor in the formation of Sn whiskers. The first mention of recrystallization as a factor in the formation of whiskers was in a 1958 monograph by W.C. Ellis, et al. [22], of Bell Laboratories. These recrystallization conjectures by Ellis, et al., were inferred from data and were not based on any direct metallurgical evidence of recrystallization. A little known feature of Ellis' 1958 article was his critique of the then extant dislocation theories for whisker formation and growth. By compiling a table of all known whisker growth directions, including the growth directions of kinked whiskers, Ellis was able to show that not all whisker growth directions were low-indices glide plane directions. He then stated that dislocation theory could not possibly rationalize the non-glide plane whisker growth directions and that another mechanism would be necessary…namely, recrystallization. Ellis et al., defined whisker formation and growth as a special case of recrystallization. They postulated many of the concepts that were later elaborated on by various authors. For example, Ellis states that a "*necessary condition for whisker growth…is that the grain boundary of the…nucleus be immobile save for small local fluctuations. Substantial grain boundary immobility is required to affect a decrease in free energy through the growth of a whisker, rather than by migration of a grain boundary. With a fixed grain boundary, atoms move into the boundary of the nucleating crystal and vacancies move away".* Ellis goes on to state that boundary immobility can be achieved in several ways; one way was for impurities to lock the boundary, another was for a surface tarnish film to pin the boundary at points where the boundary intersects the surface. Ellis discussed a variety of concepts without categorically rejecting any of them. However, it is clear from the discussion that the concept of recrystallization was of particular interest to Ellis, et al., because the concept was so sympathetic to the collection of data then available. The closing statement from Ellis, et al., was "*whisker growth is but a special case of recrystallization and growth involving mass transport… should promote many experiments to examine its (recrystallization concept) validity*".

S.C. Britton and M. Clarke from the Tin Research Institute published a paper in 1964 [23] that studied tin coatings electrodeposited on brass substrates. They found that undercoats of copper or nickel were effective, long lasting barriers to zinc diffusion into the tin coating. The authors commented that copper undercoats had some whisker mitigation effects for bright tin coatings deposited onto brass substrates, but marginal effects for matte tin coatings. Nickel underlays were studied for bright tin coatings deposited onto brass substrates, and no whiskers were observed for an observational period of 28 months. Britton and Clarke used both ambient and 50°C storage conditions. They observed that after 4 months at 50°C zinc (Zn) atoms were detectable at bright tin coating surfaces. Similarly, on copper underlay specimens there were copper (Cu) atoms at the bright tin coating surfaces after 8 months storage at 50°C. In general, Zn and Cu intermetallics reached tin coating surfaces after a period of time that depended on storage conditions, the type of tin film, and the film thickness. These intermetallics did not reach the surface as a uniform layer but as "islands" of copper / zinc intermetallics embedded in a matrix of pure tin. Decreased solderability and increased corrosivity were associated with the presence of these Zn and Cu intermetallics at the tin coating surface.

In 1966, W.C. Ellis published a study on the morphology of whiskers grown on Sn, Zn, and Cd plating [24]. Ellis showed that the growth directions for spontaneously grown whiskers were small crystallographic indices that were also glide plane indices. These results have been a supporting argument for the various dislocation models that utilize the concept of glide formation as an integral part of the whisker growth mechanism. Strangely enough, Ellis made no mention in this 1966 paper of his earlier 1958 findings [22] to the effect that not all whisker growth directions were low-indices glide plane directions.

Another paper that dealt with the recrystallization concept for whisker formation was published in 1969 by Furuta and Hamamura [25]. They utilized specimens of 50%Al-50%Sn that were melted and then rapidly cooled to make thin plates 0.3-0.5mm thick. Whiskers were observed growing from the Sn phase at rates between 0.5 and 5.0 Å/sec. Many of the whiskers were kinked. Furuta and Hamamura also observed that the recrystallization concepts put forward by Ellis, et al. [22], required some modification. By considering the formation of vacancies in the film that resulted from the rapid cooling, Furuta and Hamamura concluded that the growth rate (G) of a whisker was a function of the vacancy formation energy and was independent of the film thickness. Equation 1 (below) expresses the above statement in mathematical format:

$$G = \frac{2Eb^3}{RkT} D \text{ cm/sec} \qquad \text{equation (1)}$$

Where E = vacancy energy of formation
b= atomic spacing in tin
D= self diffusion coefficient of tin
R= average distance between the whisker "boundary" and the inside of the parent material
k= Boltzman's constant
T= temperature

Equation 1 indicates that whisker growth rates are independent of film thickness.

This article produces some very interesting data, but the reader is cautioned that the sample preparation technique and the alloy utilized are both very unusual. No other known published work has used similar sample preparation techniques. Equation 1 does not have any stress variable and can only be considered to be relevant for that particular situation as described by Furuta and Hamamura. Furuta and Hamamura also reported on the growth directions of the whiskers in their study. The results also showed that the growth and kink directions were very high indice planes. These results stand as unique data never before or after duplicated.

The next ten years (1966-76) produced a number of articles that were essentially review articles with an emphasis on whisker prevention practices. Much of this work came from Northern Electric Corporation. In 1968, M. Rozen of Northern Electric published an article titled "Practical Whisker Growth Control Methods" [26]. Rozen's results were for Sn electroplated from stannate baths. Northern Electric had experienced problems with Sn-coated wires plated using the stannate process. Rozen concluded that the mitigation procedures for this type of plating were as follows:

1. *All parts are plated to a 5-micron minimum thickness.*
2. *All Sn plated parts are post baked in nitrogen gas for four hours minimum between 191° and 218° C to relieve stress.*
3. *An HCL etching test was developed to differentiate between baked and non-baked parts for the purposes of quality control.*

Rozen stated that the above procedures had substantially improved the field situation and that no whisker problems had been reported for a three-year period. Rozen also noted that these procedures might not work for the new bright acid sulfate processes because heat treatments tended to blister and/or crack the bright platings.

1970s:

In 1970 Rozen and Renaud [27] followed up on the bright tin statements from Rozen's 1968 publication. Their bright tin films were deposited in both barrel and rack-plating processes. The barrel-plated bright Sn was found to be especially prone to blistering and cracking after heat treatment. Rack plating was deemed "better" and a manufacturing process was established for bright-tin rack plated parts post-baked for four hours at 205°C in a nitrogen atmosphere. Rozen and Renaud also published the first metallographic cross-sections of Sn-plated parts. These bright Sn cross-sections showed a mottled structure with no clearly defined grains, and the focus and clarity of the micrographs were not particularly good.

A third Northern Electric article was published by A. Jafri [28] in 1973, which followed up on the progress reported in the prior two Northern Electric publications from Rozen, et al. [26-27]. Jafri reported that ultrasonic agitation of the electrolyte plating bath was effective in minimizing or eliminating matte tin whisker formation. In 1975, N. Sabbagh of Northern Electric, in collaboration with E. McQueen from Sir George Williams University, published an article [29] which updated the observations and experiments conducted at Northern Electric and previously reported on by Rozen, Jafri, et al.

Sabbagh and McQueen reported that production experience with heat treatment of rack-plated bright Sn plating did not work out well even though Rozen, et al. [27], had reported promising early data.

P.L. Key of Bell Laboratories published a paper on tin, zinc, and cadmium whisker morphology in 1970[30]. Key's observations led him to comment that the absence of local depressions around whiskers, and the lack of growth interference between whiskers suggested that whiskers were able to effectively drain large regions of the plating rather than only local, neighboring regions. Key noted that the total volume of whiskers on a sample could represent as much as 15-20 percent of the total volume of the plated finish. Additionally, Key noted that tin, zinc, and cadmium finishes were usually deposited with high intrinsic compressive stresses. Key concluded that the morphology of tin, zinc, and cadmium whiskers were morphologically similar and that the surface morphology did not seem to depend upon plating conditions or substrate material. Furthermore, the longitudinal striations on whiskers crystals did not appear to have any crystallographic significance. The lack of thinning in and around the whisker base indicated to Key that the atomic transport mechanism involved in whisker growth was long range.

A relatively little known work was published in 1970 by Kehrer and Kadereit [31] of Siemens Corp. Kehrer and Kadereit used Sn film samples that were sputter deposited onto quartz substrates. Oxygen had to be incorporated in the sputtering process to obtain films that would grow whiskers. Radioactive tin was initially deposited onto the quartz substrate and selectively etched into a pattern of discrete squares. Then inactive tin was deposited over the active tin areas. The whiskers grown directly over the active tin areas were radioactive, and those grown over the inactive tin areas were not radioactive. The same result was obtained if the sequence of deposition was reversed. The principal conclusion was that material transport normal to the substrate took place during whisker formation, and that there was no large scale diffusion parallel to the substrate. This publication is one of very few that showed where the whisker material came from within the film itself.

An entire book chapter by Henry Leidheiser Jr. [32] in 1971 was dedicated to the topic of Sn whiskers. Leidheiser reviewed and reported on whisker research done up to about 1970. In 1974, a landmark review article [33] was published by S.C. Britton of the Tin Research Institute reviewing 20 years of tin whisker research. The Tin Research Institute (now known as ITRI Ltd. — International Tin Research Institute) had been collaborating with Bell Labs on whisker research since the early 1950s. A selection of recommendations made in the S.C. Britton article is listed below.

1. *Electrodeposited tin coatings on brass should be applied over an undercoat of nickel or copper. Tin coatings on steel may be better without an undercoat.*

2. *Bright tin directly on brass must not be used and the use of all bright tin coatings should be accompanied by every possible safeguard when whisker growth could be damaging.*

3. *Coating thicknesses of (Sn) electrodeposits not flow melted should be at least 8 microns.*

4. *Heat treat tin coatings after plating (e.g., 180° to 200° C for one hour). Care is needed in applying this treatment to bright tin coatings. If heat-treating interferes with subsequent soldering, a nitrogen atmosphere should be considered. A copper undercoat may help to obtain better results from heat treatment.*

5. *Storage conditions and, when possible, service environments should be controlled to avoid corrosion of the base metal at pores since this may introduce harmful stresses to the coating.*

6. *A hot-dipped (or flow-melted) tin coating is at far less risk than an unheated electrodeposited coating.*

7. *Tin-lead deposits, at least 8 microns thick, matte or bright, are probably safe and are suitable for most purposes where whisker growth is a hazard. The use of a nickel or copper undercoat on brass is a useful additional precaution. Heat treatment is not necessary and can lead to undesired fusion of the coating (tin-lead) if not well controlled. A lead content of 1% has been claimed as sufficiently effective but it seems better to select a tin-lead process giving larger and better-developed lead (Pb) content.*

8. *All tin coatings, and tin-lead coatings, may develop whiskers rapidly where they are subject to local pressures.*

9. *When the diminished solderability and ductility of tin-nickel alloy (65% tin) is not a bar to use, this coating will provide immunity from whisker growth.*

10. *Although organic coatings of the thickness commonly used for protection cannot be relied upon to prevent emergence of whiskers, the use of thick layers of resin, or the introduction of a solid insulating barrier between points in danger of short-circuiting is effective.*

11 *If in spite of all precautions, whiskers growth occurs, it may be possible to rehabilitate equipment by the physical removal of whiskers....a useful means of removal is a small searching head attached to a vacuum system. (Ed. note — this idea was initially proposed by M. Rozen of Northern Electric).*

In 1973, K.N. Tu published an article [34] on Cu-Sn bi-metallic (tin over copper) films vacuum deposited onto fused quartz substrates. The Sn was deposited onto the Cu film in varying thicknesses. Whiskers were observed to grow on Sn only when there was a Cu underlayer. Tu attributed the whisker growth to internal stresses associated with the formation of Cu_6Sn_5 intermetallics. Annealing experiments established that Cu_6Sn_5

formed at temperatures below 60^{o}C and Cu_3Sn formed at temperatures over 60^{o}C. Tu produced a considerable body of published tin whisker research over the next 30 years, either as a single author or in collaboration with others. No other author has contributed more whisker related publications over such a long span of time. These publications will be referenced below in chronological order.

U. Lindborg of the L.M. Ericsson Telephone Company in Sweden published a 1975 monograph [35] on Zinc (Zn) whisker formation and growth. This is one of very few published articles on Zn whiskers. It is included here because of the great similarity between Sn and Zn films relative to the formation and growth of whiskers. Zinc plating is not used on component lead-frames as is Sn. Rather, Zn is commonly used as a finish on structural steel parts. Electroplated Zn is very susceptible to whisker formation and growth. Lindborg's paper studied specimens made of barrel-plated and electroplated Zn films on steel substrates. The internal stresses built into the deposited films was determined from the length changes of thin ribbons (i.e. cantilever beams) plated under the same conditions as the test specimens. This is the first reported whisker paper where internal stresses were measured. Lindborg reported that whisker formation was correlatable to the magnitude of the built in internal stresses (i.e. macrostresses). As the built in internal stress approached 45 N/mm^2 there was a sharp transition from zero to 1 Å/sec in the rate of whisker growth. Above 55 N/mm^2 the rate of whisker growth was consistent at about 1 Å/sec. Another key observation was that whisker growth rates did not appear to correlate with micro strain within the samples. Samples with numerous dislocations had the same whisker growth rates as specimens with fewer dislocations. In this article Lindborg never mentioned whether the measured internal stresses were tensile or compressive. However, in a future article Lindborg commented that the stresses measured on the above referenced Zn films were compressive. Lindborg clearly differentiated between macro stresses" (stress states imposed by an external factor and measurable by cantilever beam deflection or by XRD determination of crystalline lattice spacing) and micro stresses (stress states imposed by internal factors, or defects, and measurable by XRD line broadening), and he found that there was a whisker correlation with macro stresses but not with micro stresses. This conclusion by Lindborg substantiates a commonly held position that compressive stresses are the main driving force for whisker formation and growth, and not internal energy levels which consists of both macro and micro stresses.

A 1975-76 set of publications by B.D. Dunn [36][37] of the European Space Agency showed some of the first (if not the very first) high quality SEM micrographs of whiskers. Dunn also reported on the current carrying capacity of Sn whiskers. Dunn's recommendations are particularly ironic because they were not universally adopted by all satellite manufacturers with the unfortunate results that several commercial spacecraft failed operationally in the 1990s due to tin whisker problems. Dunn's recommendations were:

1. *It is strongly recommended that surfaces that may support stress-induced whisker growth, such as tin, cadmium, and zinc, be excluded from spacecraft design.*

2. *An alternative finish, which has not been seen to support whisker growth, is 60/40 tin-lead.*

Dunn's comments were the first statements in which Sn plating was proscribed for mission critical applications, such as spacecraft.

In 1976, U. Lindborg [38] proposed a two-stage dislocation model for the growth of whiskers in Zn, Cd, and Sn. The first stage was a dislocation loop-expansion stage based on dislocation climb and vacancy diffusion, somewhat like the prior theories of Frank[6], Eshelby[7], Franks[12], and Amelinckx[14]. However, Lindborg added concepts of grain-boundary and dislocation-pipe diffusion to account for the very high whisker growth rates reported in some prior literature. Lindborg also generalized the vacancy source at grain boundaries rather than inside the grains, as was the case with the earlier models. Lindborg pointed out that the claim by earlier authors on agreements between growth models based on lattice diffusion and experimentally observed whisker growth rates were "fortuitous" because the analyses were based on old diffusion data for Sn that were in error (on the high side) by about 10^6. Lindborg's second stage postulated that dislocations created by a source would glide toward the surface of the whisker and deposit a layer of Sn atoms at the whisker grain surface. Resistance to the gliding dislocation came from a network of forest dislocations inside the whisker grains. Either stage one or stage two could be the rate-determining factor in whisker growth. Stage one resulted in a non-linear whisker growth rate versus pressure dependency, and stage two resulted in a linear whisker growth rate versus pressure relationship. Lindborg speculated that the very high stress-accelerated growth of whiskers in Sn electroplate would be an example of the first stage (diffusion- limited growth) determining the growth rate. Lindborg's paper is considered a landmark article on the subject of Sn whisker mechanisms. However, Lindborg's model clearly stated that the gliding-prismatic dislocation loops deposited their extra half plane of atoms at the top surface of the growing whisker, which is in direct contradiction to the Koonce-Arnold observation that whiskers grow from the base and not from the tip. .

L. Zakraysek from General Electric published an article in 1977 [39] on whisker growth for bright Sn on lead frames (lead frames are the metallic connections used to connect encapsulated electronic chips to printed circuit boards). Zakraysek's paper had some interesting removal and regrowth experimental results. Whiskers were physically removed and regrown on the same sites. Growth-rate data was shown ranging from 1 to 20 microns/hour.

Y. Hada, O. Morkawa, and H. Togami of Hitachi, Ltd. published a 1978 study of tin whisker failures on electromagnetic relays in [40]. They reported that nickel underlays of 2 microns or more were effective in mitigating whisker formation. A detailed set of observations was made on the relationship between whisker lengths and the resultant short circuits between adjacent lead-frame terminals. Annealing experiments were performed at 140°C which showed the effects of annealing times ranging from 0.5 to 3.0 hours. The effectiveness of annealing was markedly better for thicker (10 micron) tin films than for thinner (2 micron) tin films. Hada, et al., reported whisker lengths up to 4500 microns (presumably, but not definitely stated, bright tin) which would be the longest reported whisker in any experimental paper known to this author.

1980s:

In 1980 Fujiwara, et al. [41], used Auger depth profiling and X-ray diffraction (XRD) measurements to study interfacial reactions in electroplated Sn/Cu (Sn deposited over Cu) films deposited on Kovar (Fe/Ni/Co) substrates. They found direct experimental evidence for the formation of intermetallic compounds at the Sn-Cu interface, i.e. Cu_6Sn_5 at room temperature and both Cu_6Sn_5 and Cu_3Sn at 150°C. The Cu_3Sn layer formed between the copper substrate and the Cu_6Sn_5 intermetallic layer. These results corroborated results presented by K.N. Tu in his 1973 paper [34].

Tu and Thompson published the kinetics of Cu-Sn thin film interfacial reactions in a 1982 publication [42]. The growth of Cu_6Sn_5 was linear over time and the reduction of Cu_6Sn_5 to Cu_3Sn was parabolic over time with an activation energy of 0.99eV. The Cu_3Sn formed a lamellar structure between the Cu substrate and the Cu_6Sn_5 intermetallic layer. Tu and Thompson also observed that the Cu_6Sn_5 grew at a slower rate for thicker Sn films. No explanation was given for the slow growth rate of Cu_6Sn_5 for thicker films and this anomalous observation remains unexplained in any known future publication.

A series of three Sn whisker papers from Mitsubishi Electric Corporation were published between 1980 and 1983. The first paper, by K. Fujiwara and Ryusuke Kawanaka [43] was the first published Auger data on Sn whiskers. This was a reportorial paper and no new growth mechanism proposals were made. A second paper by T. Kakeshita and co-authors [44] reported on grain size effects. Kakeshita et al. showed HVEM (High Voltage Electron Microscope) photographs of dislocation rings that were much more prevalent on fine-grained Sn plating than on larger-grained Sn plates. Kakeshita, et al., surmised that *whiskers are considered to grow on recrystallized grains.* Kakeshita's comments on recrystallization would be the third published reference to recrystallization in reference to tin whisker growth (Ellis [22] was the first and Glazunova and Kudryavtsev [21] were the second). The third Mitsubishi paper by R. Kawanaka and co-authors [45] essentially coalesced and amplified the data and conjectures presented in the first two Mitsubishi papers.

A very comprehensive tin whisker survey was published in 1984 by Gorbunova and Glazunova [46]. These authors reviewed (in Section 7) all the whisker growth mechanism evident in the published literature as of that date and concluded with a particularly poignant set of remarks:

> *"Ideas concerning the mechanism of the process include representations of the structure of the deposits, but in most cases, these are not confirmed by experiment. To obtain grounds for the proposed schemes of the process mechanism, it would be useful to have data on the fine structure of the tin lattice.*

> *This would give a clearer representation of the mechanism of action of the forces leading to "repulsion" of the monomer crystal from the bulk of the coating. At present (1985) the role of dislocations in this mechanism has not been generally recognized".*

The above referenced Gorbunova and Glazunova paper articulated a frustration with the lack of good microstructural studies on plated films of Sn, Zn, and Cd. All of these Sn plated films are soft and very difficult to polish and etch.

A study of the whisker growth directions in and the crystallographic textures of zinc (Zn) electroplate was published by T. Takemura, et al. [47], in 1986. The growth direction of a zinc (Zn) whisker on a zinc electroplate with a (1010) texture was <1000>.
The authors comment that the whisker growth <1000> direction lies on the slip (0002) plane and, therefore, the various dislocation models should be modified so as to explain the observed slip phenomena (i.e. striations on the whisker) without using the climb phenomena.

The first United States military awareness of tin whisker problems was described in a 1986 publication by B.D. Nordwall [48]. Whiskers were growing from the tin-plated lids of hybrid circuits and falling into active circuitry causing intermittent operation. The USAF discovered the problem while screening 12-year old radar systems. Visual inspection of the failing circuits found numerous whiskers up to 2.5mm in length. It was speculated that the problem was detected because these particular circuits drew very small currents (<20 microamps) which were too small to fuse the whiskers open. The USAF decided that they would replace the circuits as they failed. It was not clear from this article what long-term corrective action would be taken. The above referenced problem was also reported by J. Capitano, et al. [49].

A major treatise on tin whiskers was published in 1987 [50] by B.D. Dunn of the European Space Agency. The experimental variables were substrate material (60-40 brass and steel), type of tin film (normal, hi-compressive stress tin, and organically contaminated tin), copper barrier layer versus no copper barrier layer, fusing versus non-fused, and applied stress levels (3). Dunn found that mechanical stressing did not accelerate whisker formation and growth for his samples. This observation is in direct contradiction to the reported results from many other authors [9] [16] [17]. Dunn gave no explanation for the difference between his negative results for stress-acceleration and the positive stress-acceleration results from the above referenced work. Dunn further stated that the dominant whisker-growth mechanism was…*dependent on the presence of micro-stresses within the tin plating. Topographical observations, surface analyses, and detailed metallography of the…samples confirmed that metallurgical processes, including diffusion and recrystallization, do occur*. One interesting observation from Dunn's paper was that the electro-migration of aluminum…will also create single crystal whiskers and that these whiskers grow from grain boundary junctions, single grains, or hillocks. The discussion section in Dunn's report repeatedly emphasized the relevance of recrystallization to whisker growth. In summary, Dunn postulated a 5-stage mechanism for whisker nucleation and growth involving a screw dislocation that anchored a rotating edge dislocation. This dislocation mechanism was identical to the one originally proposed by Frank [6] in 1953. This paper is a major treatise on whisker formation and brings together a comprehensive set of original data along with a discussion that referred to and integrated many of concepts offered by previous authors.

In 1987 B.D. Dunn presented data [51] on mechanical and electrical characteristics of tin whiskers. The results showed that whiskers had a Young's modulus that ranged from 8 to 85 GPA and ultimate tensile strengths (UTS) of 8MPa. Whiskers with diameters of 3 microns were capable of carrying a 32 mA current without fusing.

In 1989 L. Corbid, then of Hi-Rel Laboratories, reviewed the use of tin in miniature electronic packages [52]. Corbid's article dealt with the same data presented by Nordwall [48] and Capitano, et al.[49], and presented additional whisker information from other military programs. Corbid claimed fusing (or reflow) did not prevent whisker formation and growth. This observation is singular and at odds with the rest of the published literature. Fusing (reflowing of the tin plating in an oil bath) has always been considered as an effective tin whisker mitigation practice. Corbid indicated that the hybrid circuit packages referenced by Nordwall [48] and Capitano, et al. [49] were plated with fused tin because Mil-Specs (MIL-T10727 and Mil-C-14550A) required that the finishes be fused. It is also the case the Mil-C-14550A requires a nickel underlay between 1-7 microns thick. Corbid also stated that the degree of whiskering did not differ for product taken directly out of inventory and field service. This report is so singular that it must be dealt with carefully. Prudence would require that the careful user be aware of these experiences, but it is also true that fusing and nickel underlays are two long-standing whisker mitigation practices which have been successfully utilized in the commercial world for over 50 years. Without a direct micro structural analysis it cannot be presumed that a fusing operation was implemented just because the specifications required that it be done.

1990s:

At the 1990 SAMPE Conference K. Cunningham and M. Donahue of the Raytheon Company presented a paper on tin whiskers [53]. This paper was based on experimental data on four different types of tin films; pure tin, 90/10 tin/lead solder, and 60/40 tin/lead solder plus reflow (i.e. fusing). All samples were subjected to a mechanical stress at elevated temperature. Results showed that all test samples showed some whisker growth. The optimum process was 60/40 tin/lead with reflow. It should not be surprising to the reader that mechanically stressed tin films grew whiskers. It is reassuring that the optimum film process involved the addition of lead to the tin film and the application of a fusing process.

Fully five years after the 1985 Gorbunova and Glazunova publication [46] that critiqued the lack of good microstructural analysis for whisker structures, a paper was presented by Ahmet Selcuker and Michael Johnson [54] of Vitramon Inc. outlining a microstructural characterization study of Sn films. Selcuker and Johnson used multi-layer ceramic capacitor (MLCs) samples of tin (Sn) plated over a Ni underplate on a silver (Ag) substrate frit. SEM x-sectional micrographs revealed a network of polygonized grains with distinct grain boundaries. The micrographs were not of the highest quality due to the difficulty of etching Sn electroplating. Selcuker and Johnson also showed that grain size could be significantly refined (i.e., decreased) by plating at lower-current densities. This particular observation of an inverse relationship between Sn plating grain size and deposition current densities is, to this author, counterintuitive and in contradiction to later published reports (see Lee and Lee, reference [61] below). Annealing experiments by Selcuker and Johnson showed that annealing in air at 150°C for as little as 45 minutes doubled the average grain sizes from 5 to 10 microns,. Brightener additions were also shown to reduce the plating grain size. None of the Selcuker and Johnson micrographs showed any whiskers. The reader should also note that the Sn films on the MLCs in this study were barrel plated. Lead-frame Sn finishes are typically rack plated.

In 1993, M.E. McDowell of the United States Air Force [55] outlined the method used by the USAF in dispositioning Sn plated parts in inventory. No position was taken relative to a prohibition of Sn usage (as previously recommended by Dunn of the European Space Agency). This would prove to be unfortunate, as later events were to show, because in future years there were several significant reliability failures on USAF equipments attributable to tin whiskers.

A 1993 paper [56] by R. Diehl from Burndy Connector Corporation was the first publication from a connector company that dealt with reliability problems due to tin (Sn) whisker formation. Diehl concluded that additions of lead (Pb) were necessary to ensure that tin electroplate did not grow whiskers in service and Burndy Corporation adopted the addition of Pb for all their tin plated connector products.

A new concept in whisker formation and growth theory was offered by K.N. Tu [57] in 1994. Tu proposed a "cracked oxide" concept, which enabled a localized relief of internal stresses by permitting whisker growth to emerge through a crack, or weak spot, in the oxide layer. This concept of a locally weak, or cracked, oxide layer remains a viable candidate mechanism for whisker formation even though no direct evidence has yet been offered. Tu also developed a model for whisker growth that expressed whisker growth rates as shown in equation (2) below;

$$G = \frac{2}{\mathrm{Ln}\,(b/a)} \frac{\sigma_o \Omega s D}{kTa^2} \qquad \text{equation (2)}$$

Where G = growth rate
σ_o = stress level in the film
Ω = molar volume
b = whisker spacing
a = whisker diameter
k = Boltzman's constant
T = temperature

In 1994 P. Harris of ITRI published a monograph [58] that reviewed the current state of knowledge regarding whisker growth, and recommended methods of avoiding whisker problems. The reader is cautioned that these recommendations were made in 1994. One recommendation, adding 1-2% Cu to a Sn film, is not a recommended mitigation practice by most current practitioners.

J.R. Downs published a 1994 article [59] about a Zn whisker related lawsuit that was financially damaging to the company involved. This particular lawsuit was about a Zn whisker problem, but the same difficulties could easily arise for Sn whiskers. Downs reiterated the case study of a rotary switch utilized in critical medical equipment, which developed shorting due to Zn whiskers. This particular switch manufacturer knew that Sn and Cd had whisker growth capability, yet had no idea that Zn had similar problems. The company had no intent to harm and was without knowledge of the problems associated with low voltage circuitry and Zn plated parts. Unfortunately, for the manufacturer, the liability law in most states holds the manufacturer responsible, even if the manufacturer is unaware of the problem that caused the product failure.

K.N. Tu continued his research on Cu/Sn interfacial reactions in a 1996 paper [60] that studied interfacial reactions between eutectic SnPb solder and Cu substrates. Tu found that the morphology of solder/substrate interfacial reaction products was different for tin-lead (SnPb) in comparison to pure tin on copper. The eutectic SnPb solder formed a scalloped (i.e. separate and distinct) series of intermetallic formations, whereas pure tin solder formed a continuous layer intermetallic at the substrate interface. Similar scalloped type intermetallic formations were referenced for reactions between eutectic SnAg and Cu as well as for eutectic SnBi and Cu. The kinetics of scallop formation were discussed and a model was developed.

A major paper on Sn whisker growth mechanisms was published in 1998 by B.Z. Lee and D.N. Lee [61] of Seoul University who presented one of the first direct measurements of residual stresses in Sn electroplate. A cantilever beam method was used to determine internal stress levels. The stress measurement results showed that the initial as-deposited stress was tensile, and that the stress quickly relaxed to a zero value and, thereafter, increased to a compressive stead-state value. Samples that were annealed immediately after deposition had zero stress states which remained stable over time. The observational period for the above stress measurements was 30 days. Lee and Lee also determined the preferred orientation indices of the deposited films using X-ray diffractometry and compared the orientations of whisker grains to the preferred orientations. They discovered that whisker grains were always oriented differently in comparison to the immediately surrounding as-plated tin (Sn) grains. Their Sn was plated onto phosphor-bronze substrates from a stannous acid bath at room temperature. Tin whiskers grew spontaneously in a few days. Lee and Lee did not state whether the Sn was matte or bright, but the polygonized nature of the grain structure would indicate that there were no brighteners added to the Sn plating solution. The average grain-size of the electrodeposits was 1.0 microns, which is a relatively small grain size for matte tin plating. Unlike some previously published data (Selcuker, et al.[54]), heat treatment of the Lee and Lee Sn-plated samples at 150°C did not result in any significant grain size increase. Moreover, contrary to the published results of Selcuker, et al., the Sn plate for Lee and Lee's samples showed larger grain sizes with decreasing electrodeposition current densities. Lee and Lee determined the growth direction of their whiskers with electron beam diffraction. By comparing the angle of growth for the whiskers against the preferred orientation results, Lee and Lee deduced the orientation of the grain from which the whiskers grew. A summary of the key Lee and Lee conclusions follows:

1. C*ompressive stresses in the film built up over time due to the diffusion of copper atoms from the substrate into the tin film and the subsequent formation of the intermetallic* Cu_6Sn_5. *The as-deposited stress state for the tin film was net tensile (+11MPa) and changed to a compressive stress (-8MPa) after a few days. After whisker formation and after about 50 days the stress level was decreased (-5MPa).*

2. *Tin whiskers grow from grains whose orientation is different from the major orientation of the tin film. ...the tin surface oxide film can be sheared along the boundaries of the grains.*

3. *To release the compressive stress in the film, tin whiskers grow from the grain whose surface oxide is sheared.*

4. *The whisker growth is controlled by the expansion of the prismatic dislocation loop on the slip plane by climb...i.e., by the operation of a Bardeen-Herring dislocation source. The dislocation loop expansion is restricted by the grain boundary. The loop then glides along its Burgers vector direction. As a result, the tin whisker grows by one atomic step. The continuous operation of the Bardeen-Herring dislocation source gives rise to whisker growth until the stress is relieved.*

Items 1 and 2 (above) were new contributions to the Sn whisker database. Item 3 was a restatement of prior ideas (Tu [57]) substantiated, in this case, by actual residual stress measurements. Item 4 was essentially a restatement of the Lindborg [38] thesis with essentially no new supporting data presented. Lee and Lee's model also showed dislocations moving to the surface of the whisker and depositing atoms at that surface in a manner similar to that described by Lindborg, Franks, and Eshelby. There was no mathematical model for whisker growth rate in the Lee and Lee paper. Lee and Lee's publication has been a significant reference for all subsequent whisker research. The stress measurements made in conjunction with a comprehensive set of crystallographic orientation information are recognized as a unique contribution to the whisker data history. It is unfortunate that the authors never followed up on this unique and important set of observations with any future work.

The Lee and Lee paper ended the 20th century set of published whisker formation theories. While considerable insights had been made into the factors involved in formation and growth of metallic whiskers, there was no consensus on the growth mechanism/s, and there was no general agreement on an acceleration test so vitally needed by electroplaters to assure customers on the reliability of electroplated tin as regards whisker formation.

A review paper about tin whisker concerns on passive components was published in 1998 [62] by G.J. Ewell from the Aerospace Corporation and F. Moore, from the Boeing Corporation. This paper stated some experiences with capacitors that are useful anecdotes for the researcher and potential users of Sn plated electrical components. For example, Beyschlag GmbH has stated (private communication with the authors) that their lead-frame packaged resistors have been using pure tin plating for 35 years (i.e. since 1953) and there have been over 60 billion components manufactured without any complaints concerning whiskers. Ewell and Moore surveyed the USA GIDEP (Government Industry Data Exchange Program) database and found 7 whisker alerts posted with none concerning capacitors and only 1 concerning a resistor. A similar survey of the NASA and Aerospace Corporation Alerts and Reports database showed no whisker problem reports for capacitors and resistors. Ewell and Moore indicated that the reason for the lack of whisker related problems on capacitors and resistors appeared to be related to regular usage of one or more of the whisker mitigation practices detailed in the early reports from both Bell Laboratories and the International Tin Research Institute (ITRI). Nickel underlays, heat treatments, and additions of alloying elements such as Bismuth appeared to have been effective mitigators for these component types. This paper would be one of the few known publications providing feedback that generally accepted mitigation practices for whisker formation have been effective.

I. Yanada of Uyemura International Corporation published a paper on Sn-Bi and Sn-Ag electroplated films in 1998 [63]. Yanada tested his specimens at 50^{o}C for three months and determined that Sn-10%Bi and Sn-5%Ag had no visible changes in surface morphology, whereas the pure tin specimens had numerous small (~ 10 microns) tin whiskers.

In 1999 M. Ishii, et al. [64], published an article on whisker problems in ultra-fine pitch circuits. Their ultra-fine circuits referred to lead-frame spacing (or pitch) of 50 microns. A lead-frame spacing of 50 microns would correspond to a gap of 20 microns or less between adjacent leads. They reported that pure tin lead-frames on ultra-fine circuits were experiencing a high incidence of shorting due to whiskers. Annealing treatment at 150^{o}C for 2 hours mitigated the problem.

The anticipated lead (Pb) elimination directives of the European Union (scheduled to be enacted in Y2006) have highlighted a need to generate more confidence in high tin content plating, given the need to phase out the generally accepted whisker preventive qualities of Pb in Sn plating. Various consortia were established to initiate research into whisker physics and whisker mitigation practices. In the first two years of the 21st century, there were more presentations/papers on Sn whisker matters than in the prior 15 years. Websites abounded with Sn whisker papers and background information. New analytical tools were brought to bear in hopes that new information would further clarify the mechanism/s of whisker growth. New authors entered the field and old ones reentered. A new set of claims were put forward by various companies stating that they had proprietary tin plating processes that were whisker-free. Details of the test results behind these proprietary processes have not been generally available. It does appear that these so-called proprietary processes all attempt to produce Sn plating with polygonized grains of a fairly large (about 1-5 micron) grain size. Additionally, the test methodology behind the claims of whisker-free appears to be natural aging (i.e., storage at ambient condition). Such results are confused with respect to what is meant by a “no whisker” statement. Are all “whiskers” counted as such, or are there arbitrary length limits (such as 10 microns) before a whisker is “counted”? Some of the user communities have become increasingly concerned about the risks inherent in accepting claims of proprietary whisker-free Sn plating processes and are banding together to develop so-called user perspectives.

2000 through 2003:

In March of 2000 General Electric issued a Service Bulletin [65] stating that whisker problems had been found on certain GE relays that had been in field service for more than 10 years. The recommended corrective action was to brush off and vacuum up the removed whiskers. This would be similar to the actions taken by Northern Electric Corporation back in the 1960s.

Probably the first paper published in the 21st century on Sn whiskers was by Schetty [66] in 2000 (and republished in 2001[67]). Schetty (then from Shipley Company) examined Sn, SnBi, SnCu, and SnPb plating on brass and lead-frame alloy 194 substrates, with and without Ni underplate. All test samples were heat aged at 50^{o}C for a minimum of 3 months. In all cases some whisker growth was noted, although often of extremely short (10 microns or less) lengths. However, it was noted that a 10 micron thick Sn-10%Bi plating on a substrate of alloy 194 (A Cu lead-frame alloy) had whisker growth in excess of 25 microns after heat aging at 50^{o}C for 3 months. This is an alarming observation since bismuth (Bi) is considered to be a whisker mitigating alloying element for tin, and 10 micron thick Sn based platings are thought to be relatively immune to early whisker formation. In this author’s opinion, it is frequently observed that aging tests (such as the 50^{o}C test used by Schetty) often result in the formation and growth of tin whiskers, but these whiskers are relatively few in number and are relatively short (generally less than 100 microns). Schetty also stated that a proprietary Shipley Sn plating solution was evaluated that showed no whiskers after natural aging for eight months on a plated lead-frame alloy 194. Additionally, Schetty showed data for Ni underlays which demonstrated effective whisker mitigation for all tin coatings tested under all the storage conditions utilized. It was particularly noted that Ni underlays mitigated whisker formation for Sn-Cu alloys which are noted for their tendency to form extremely long whiskers in relatively short periods of time.

In 2000Yun Zhang, Chen Xu, et al. [68], studied 5 tin plating chemistries with copper substrates. The specimens included bright, satin bright, and matte tin films along with a Sn/10Pb plated piece part acquired from a job shop. All samples were plated to a 3 micron thickness and aged at both ambient and 50^oC. Specimens from all categories were bent over a mandrel to 45, 90, and 180^o. Some of the satin bright and matte tin specimens were reflowed at 260^oC before the mandrel bending operation. The results showed that higher carbon content (0.2 wgt. %) bright tin specimens grew long (>200 micron) whiskers in the region subjected to mechanical bending. Lower carbon content bright tin (0.2 wgt. %) and all the satin bright and matte tin specimens grew relatively short (< 30 microns) after aging. The reflowed specimens did not show any observable whisker growth after bending and heat aging. Zhang, et al., observed that bright tin specimens were difficult to reflow because they would discolor and dewet.

R. Schetty, et al. [69], showed data in a 2001 publication that confirmed the often-quoted whisker mitigation effect of thicker tin coatings. The data also showed that as little as 0.1 microns of Ni underlay was an effective mitigation practice for C194 and C151 substrates. However, Schetty also showed data which indicated that increasing Cu content in the plating bath from zero to 6.4% by weight had a "beneficial" effect on whisker formation (i.e. the higher Cu concentrations were mitigating).

R. Schetty, now of Technic Inc., published a 2001 paper [70] which reported data from a proprietary non-MSA tin plating. This proprietary tin coating did not evidence whiskers when tested under a variety of storage conditions ranging from ambient to thermal cycling. Schetty showed data that indicated the preferred orientation for tin coatings deposited from "standard" MSA electrolytes was (211), whereas the preferred orientations for the proprietary tin process was (220). Furthermore, the stress state of the proprietary tin films was near zero and did not change over time (as determined by the $\sin^2\Psi$ XRD technique). MSA deposited tin coatings were initially compressively stressed and the stress became more compressive over time. It should be noted that stress measurements were made using XRD on tin coatings deposited onto brass substrates. Schetty also noted that other authors had presented data showing that (220) orientations were whisker resistant. However, Schetty's paper is the first (known to this author) to categorically state, and demonstrate, a relationship between whisker formation resistance and preferred orientation.

Yun Zhang, Chen Xu, et al. [71], published a 2001 paper that focused on whisker growth and index (i.e. density and ultimate length) data for matte, satin bright, and bright tin coatings. The internal stresses of the films were determined by XRD and results indicated that internal stresses were a key factor in promoting whisker growth.

In a second 2001 paper [72], Chen Xu, Yun Zhang, and co-workers reviewed the dynamics of whisker growth and assessed various whisker growth mechanisms as proposed by a variety of researchers. The compressive stress build up over time for electroplated tin on copper substrates was attributed to copper diffusion from the substrate into the tin film. The tin film tensile stress state for tin over nickel on copper substrates was attributed to nickel's ability to block copper diffusion from the substrate into the tin. Auger and SEM/EDS mapping were done to determine the elemental composition in and around the whiskers. The mapping showed that whiskers were mostly tin but with some evidence of copper. XRD stress measurements over a 15 month observation period showed that as plated compressive stresses increased over time and it was speculated that the increase in compressive stress over time was due to the build up of copper-tin intermetallic at the substrate-coating interface. This paper was the first published account of FIB (Focused Ion Beam) analysis on tin coatings. The FIB technique does not require mechanical polishing and chemical etching to reveal the cross-sectional microstructure. A milling action is effected by impinging gallium ions onto the plating surface. Successive cross-sections can be exposed through continuous milling in the FIB tool and the resulting images can be continuously monitored and photographed. What would take months of tedious mechanical polishing and etching can be done in a matter of hours with significantly better results than are normally obtainable with mechanical polishing and etchings. A set of FIB X-sections were shown for matte, satin bright, and bright tin coatings with whiskers. Each X-section showed that the root of the whisker grain was in contact with copper-tin intermetallic emanating from the tin-copper substrate interface. It was not noted whether the FIB X-sections as shown were for samples that were aged at ambient conditions or from samples aged at 50^{o}C.

In a later 2001 publication there was an account of Focused Ion Beam (FIB) microscopy on Sn whiskers by Isabelle Baudry and Gregory Kerros [73] of ST Microelectronics. Kerros and Baudry showed a FIB cross-section for a whisker growing from a deposited Sn film. It is apparent that the whisker in the Kerros and Baudry FIB was in contact with the copper-tin intermetallic emanating from the coating-substrate interface, as was the case in the Chen Xu, et al. [72], publication. Kerros and Baudry drew no conclusions or inferences in their report.

In 2001 and 2002, Motorola researchers presented two papers on Pb-free plating for lead frame packages. The first Motorola publication by N. Vo, et al. [74], was about whisker formation as a function of plating bath performance for a variety of compositions, including SnBi and SnCu, with and without Ni underplating. Some whiskering was observed on all the Sn-based plating, including SnPb, and Ni underplating did not absolutely prevent whisker growth. Temperature cycling from -55° to +85°C accelerated whisker growth, even for those samples with a Ni underplate. In the second Motorola paper [75] from Wulfert and Vo, the same experimental samples used in the first Motorola paper were reported on again but after more time had elapsed. It was noted that the SnCu (Sn0.7Cu) samples had developed, over time, longer and more numerous whiskers in comparison to the pure Sn plating.

A case history of whisker induced relay failures was reported by Craig Stevens of the Foxboro Company [76] in 2001. The relays failed in service after 8 years due to tin whiskers. This particular case study is easily found on the web by simply typing “tin whiskers” into most search engines. The relay finishes had been switched over from leaded tin to pure tin in 1983 as a cost savings. Since the failed devices were utilized in nuclear facilities a total field replacement action was initiated

Because of U.S. industry interest in the European Union Pb-free initiatives, the U.S. government’s National Institute of Standards and Technology (NIST — formerly the National Bureau of Standards) became active in Sn whisker research. The first NIST publication was by K.W. Moon, et al. [77], in 2001. A key tenet of this NIST paper was that Sn whisker formation is highly dependent upon plating bath impurities incorporated into the plating as precipitates. Moon, et al., used very pure plating solutions and added varying amounts of Cu^{+2} to the plating bath. This report showed some very high quality mechanically polished cross-sections of the Sn platings. Cross-sectional micrographs clearly showed that very pure Sn plating had no discernible grain boundary precipitates of Cu_6Sn_5, whereas the Cu^{+2} doped Sn plating had clear evidence of Cu_6Sn_5 precipitates arranged along the columnar grain boundaries. The columnar grain diameter was approximately 1.0 micron. The report stated that the tin plating was a commercial MSA electrolyte. A private communication [78] indicated that the 250 micron copper substrates did show some flexure after tin deposition. A subsequent NIST presentation [79] in 2002 extended the discussion from the 2001 paper. The key points of the NIST publications were summarized as follows:

1. *...no whiskers were observed in pure Sn electrodeposits. This appears to be in conflict with many commercial observations. The electrolyte used in the NIST experiments contained < 0.8 ppm (mass) of Cu. In commercial practice, electrolytes can contain up to 300 ppm Cu.*

2. *The second major observation is the dramatic differences in whisker growth with Cu addition when two different substrates were used. Substrate 1 had 40 nm of vapor deposited cu on a Si substrate without a bond layer. Substrate 2 was essentially a pure Cu substrate. No whiskers formed on the Cu-coated Si substrate. Because the 40 nm of cu was completely reacted to form Cu_6Sn_5 IMC at the Sn/Cu interface debonding may have occurred that led to relaxation of the residual stresses in the film. .*

The NIST research opened an entirely new concept of whisker prevention or mitigation practices...namely, the reduction of internal compressive stresses by eliminating the possibility of intermetallic compound formation from co depositions in the plating structure itself. This effect is distinct from the formation of Cu_6Sn_5 between the Cu substrate and the electrodeposit. These results were obtained from laboratory plating apparatus and have not been duplicated in any prototype commercial facility as of the date of this treatise.

A 2002 publication [80] by W.J. Choi, T.Y. Lee, and K.N. Tu from the UCLA Department of Materials Science and Engineering was the first published Sn whisker report on the use of micro-diffractometry using synchrotron radiation. Choi, Lee, and Tu used a focused 1.5 micron square synchrotron X-ray beam and characterized the orientation and stress state of the region in and around a whisker root. Some key observations were:

1. *....the stress is not biaxial… is highly inhomogeneous...with variations from grain to grain. Stress is biaxial only when averaged over several grains.*

2. *....no long-range stress gradient was observed around the root of the whisker...indicating that the growth of the whisker has released most of the local compressive stress.*

3. *....the compressive stress (levels) is quite a low value...but we can see a slight stress gradient from the whisker root area to the surroundings. This means the stress level just below the root is slightly less compressive than the other area.*

A second paper [81] from the UCLA Department of Materials Science and Engineering was published in 2002 by K.N. Tu and K. Zeng. Tu and Zeng evaluated eutectic SnCu plating on lead frame materials and showed FIB images of eutectic SnCu cross-sections. A lift-out FIB cross-section was examined in a TEM. The FIB images show many *"bright images of grain boundary precipitates of Cu_6Sn_5 in cross-sections of the eutectic SnCu, whereas similar FIB cross-sections showed no grain boundary precipitates in the pure Sn deposit."* Tu and Zeng concluded that the "*pre-existence of these (Cu_6Sn_5) precipitates in SnCu enhances whisker growth*." Tu and Zeng then proposed a model in which whisker growth occurred only in those regions where the surface oxide layer was *"not too thick so that it can be broken at certain weak spots on the surface, from where the whiskers grow to relieve the stress."* The following equation was proposed to determine the diameter of a whisker:

$$\text{R (radius of whisker)} = \Gamma \div E \qquad \text{equation 3}$$

Γ = surface oxide energy per atom

E = strain energy per atom in the finish

G.T.T. Sheng, and co-authors (including W.J. Choi and K.N. Tu), published a 2002 article [82] on whiskers studied by utilizing FIB (focused ion beam) microscopy and TEM (transmission electron microscopy). The specimens were lead-frames plated with either 15 microns of eutectic Sn-Cu or pure tin, and subsequently aged at room temperature. There were many more whiskers observed on eutectic Sn-Cu specimens in comparison to pure tin samples. Fib examination showed that the eutectic Sn-Cu (>1% Cu) had significant amounts of Cu_6Sn_5 precipitates in the cross-sectional microstructures. Sheng, et al., surmised that the driving force for the formation of whiskers, in the system studied, was the compressive stress induced by the diffusion of copper into the tin film and the subsequent formation of Cu_6Sn_5 precipitates in the film grain boundaries. The internal stress levels were maintained by the continuing diffusion of copper from the substrate into the film. The TEM samples taken from the whiskers showed numerous dislocations in the vicinity of whisker kinks (i.e. bends), but the authors discounted this observation because they felt the dislocations were induced by the sample preparation process.

A 2002 paper by J. Chang-Bing Lee [83] and co-authors from Advanced Semiconductor Engineering studied the whisker-forming properties of 2 different SnCu plating solutions on lead frame base metals. In this study HAST (High Acceleration Stress Test) thermal cycling at 130°C was used to age test samples. After 300 hours of HAST there was no observed whiskering on samples from solution #1 with Sn -2% (or less) Cu plating. Solution #1 tin plating with copper concentrations above 2% always grew whiskers. Solution #2 was designed to give a more randomized grain structure in the SnCu film. HAST tests on solution #2 films showed no whiskering on any of the samples. An extensive amount of analysis was done on all the samples. Preferred orientations were determined, solderability evaluations were conducted, and various base metals were evaluated. The critical reader will note that HAST testing was done at a temperature high enough (130°C) to effectively anneal the tin films and preclude the formation and growth of whiskers. In fact, SnCu films are prone to whisker formation and growth to a greater degree than pure Sn. The Cu atoms appear to increase the internal stress gradients in the film by forming intermetallic precipitates in the grain boundaries that then cause the formation of whiskers. The importance of the Chang-Bing Lee, et al., paper is that it indicated that Sn-2% Cu films can be suitable whisker-free finishes for lead-frames if the plating solution is appropriately selected.

Chen Xu and co-workers from Lucent Technologies published a 2002 paper [84] in which XRD, FIB, SAM, and SEM/EDS tools were used to analyze Sn plating and Sn whisker growth. The FIB cross-sections were the most comprehensive yet published. Plating stresses were evaluated using both the bent strip method and XRD. The XRD tool used by Xu, et al., had a spot size of 50 microns square so it was not capable of resolving stresses within individual grains. Xu, et al., added a mechanical deformation set to the samples in both the tensile and the compressive mode. Some of the observations and findings from Xu, et al.., were:

1. *The whisker only grows externally and there is no visible whisker growth within the coating.*

2. *For bright tin, whiskers grew from nodules such that the filament (i.e., whisker) was not in direct contact with the original Sn coating....the nodule apparently acts as a precursor state for the formation of the filament whisker...the nodule is seen before the filament during aging experiments at room temperature as well as aging temperatures of 50°C.*

3. *…the Ni underlayer imposes a tensile stress on a Sn coating and, therefore, stops the whisker growth....this difference (from pure Sn coatings) is ultimately responsible for the spontaneous whisker growth from Sn plated over Cu and no observed whisker growth from Sn plated over a Ni underlayer.*

Xu, et al., speculated that the compressive stresses built up over time in Sn films plated on Cu substrates were due to the diffusion of Cu from the substrate into the Sn plating. Xu also observed that compressively bent samples whiskered more than the non-bent samples, and both the compressively bent and non-bent samples whiskered more than the tensile-bent samples.

Yun Zhang, Chen Xu, C. Fan, J. Abys, and A. Vysotskaya of Lucent published a 2002 paper [85] on whisker growth for tin coatings on copper substrates with and without a nickel underlay. In an attempt to validate the "cracked oxide" hypothesis Zhang, et al., prepared samples with a "flash" of precious metals (Au, Pd, and Ag) on top of the tin coating. Additionally, some of the samples were subjected to a 90^o bend and others were reflowed at 260^{o}C. All substrates were oxygen-free copper sheet 50 microns thick. Aging was done at 50^{o}C. The tin coatings were proprietary chemistries of bright, satin bright, and matte tin. In the authors own words, the most significant finding in this study was that tensile stress significantly hindered whisker formation. I.e. Tensile stress retarded whisker formation, while compressive stresses accelerated whisker formation. Reflow and nickel underlays significantly mitigated whisker formation. The precious metal overlays effected a slight reduction in whisker formation. To this author, the most unique observation in this paper was the observation of the interface between the nickel underlay and the tin coating. Zhang, et al., observed that after annealing at 175^{o}C the boundary between the nickel and tin moved into the nickel, rather than into the tin as is the case for the copper-tin interface. What this observation means is that more tin diffuses into nickel than nickel into tin. And that means that nickel underlays will result in tensile stress buildup in tin films rather than compressive stress build up due solely to the relative amounts of nickel/tin interdiffusion. Copper, on the other hand, diffused very rapidly into the tin coatings while tin did not appear to diffuse into the copper. This means that copper substrates/underlays will build up compressive stresses in the tin coatings. The same authors published [86] a 2002 document that summarized their findings to date. A unique reference was quoted [87] from a Master's Degree thesis by a C.M. Liu under the direction of Professor C. Kao of the National Central University-Chungli City, Taiwan, which showed a diffusion couple experiment between tin and nickel. The results, obtained by measuring the movement of titanium markers placed at the interface between the tin and nickel, showed that the tin diffused into the nickel in greater quantity than did the nickel into the tin. This observation corroborates the observations made by C. Xu, Y. Zhang, C. Fan, and J. Abys as referenced above [86]. Based on their work the above authors concluded that whisker formation was driven by compressive stresses and that tensile stresses mitigated whisker formation. They recommended that either zero or tensile stresses be maintained in the tin coatings through the life of the application. To achieve a tensile stress state over long periods of time the authors recommended large grained tin coatings and the use of nickel underlays with copper substrates. Reflow and thicker (>10 microns) tin coatings were also recommended.

G.T. Sheng, et al. [88], utilized FIB (Focused Ion Beam) and TEM (Transmission Electron Microscopy) in a 2002 study of tin whiskers on 15 micron SnCu and pure Sn electroplated films. K.N. Tu was one of the co-authors. The cross-sectional micrographs of the SnCu films showed many Cu_6Sn_5 precipitates in the film grain boundaries. The authors postulated that the driving force for the enhanced whisker formation in SnCu films (enhanced in comparison to whisker formation in pure tin films) was due to internal stresses generated by Cu_6Sn_5 precipitates. The grain boundaries of pure tin films were "clear". The TEM micrographs of whiskers did show evidence of high dislocation density at whisker kinks, but the authors surmised that the defects were most probably introduced during sample preparation.

Andre Egli, and co-workers of Shipley Company, published a paper [89] in 2002 that correlated observed XRD patterns with whisker growth in Sn electrodeposits, and proposed a model to predict the risk of whisker growth in Sn deposits. The whisker growth risk factor was correlated to differences in the crystallographic orientation of adjacent grains. Egli's thesis was that there were discrete low-angle ranges for grain-boundaries that permitted enhanced whisker growth. His idea was that low-angle grain boundaries inhibited the relaxation of stress by creep mechanisms, which then favored the relaxation of stress by the formation and growth of whiskers.

The first published 3D non-linear stress analysis of Sn whisker formation was done in 2002 by John Lau of Agilent Technologies and Stephen Pan of Optimal Corporation [90]. Their model implicitly assumed that Sn whisker formation was an extrusion process where compressed tin plating was literally forced through a "weak spot" in the oxide layer. The analysis did show that some extrusion could occur from stress levels equivalent to those actually observed in tin films, but the amount of material required to grow an actual whisker was much more than the model showed possible through an "extrusion" process. This work should be considered as an initial attempt and work is continuing to refine the model.

A number of website postings and presentations were made on whisker observations by the NASA Goddard Space Flight Center in 2002. Possibly the most comprehensive paper of the NASA publications was authored by Jay Brusse, et al. [91], in which an extensive set of observations on multi-layer ceramic capacitors was described. These devices (known as MLCs or MLCCs) have a particular importance to the subject of Sn whiskers. Since 1992, virtually all MLCs have been using a barrel-plated Sn deposit over a Ni underlay on a substrate of Ag. To the best of anyone's knowledge, including this author, there has never been a field service incident where Sn whiskers were observed on MLC end-cap metallurgy. Nevertheless, Brusse was able to grow whiskers from MLC end-cap Sn plating after the MLCs were subjected to thermal cycling between -55°C and +100°C. As of June 2002 the whiskers were about 50 microns in length. Subsequent monitoring was planned to see if the whiskers would continue to grow.

P. Elmgren, of Molex Corporation, published a report in 2002 [92] on tin whisker formation on a variety of tin based finishes with and without underlays of copper and nickel. Copper underlay is an old mitigation practice recommended in some published reports for tin platings for brass substrates. Elmgren's specimens were mechanically bent, so as to induce compressive stress in the films, and then aged at 50°C. Bright, satin bright, and matte tin specimens were utilized. Elmgren observed that tin finishes with copper underlay had significant whisker growth, whereas those tin finishes with nickel underlay showed no whisker growth. Elmgren also studied bright and matte SnCu

(99Sn/1Cu and 96Sn/4Cu) films with Ni underlay and observed spontaneous whisker growth after aging.

The Government-Industry Data Exchange Program (GIDEP) issued an Agency Action Notice on Tin Whiskers in 2002 authored by J. Khuri [93]. This notice was an action by the Department of the Navy to remind the electronics industry of the potential risks associated with the use of pure tin-plated finishes on electronic components and assemblies. The notice also recommended that pure tin finishes be avoided if at all possible. Some of the recommended actions included the use of Sn-Pb solders, which is an option available to the military but not to the commercial world intending to market in the European Union.

In May of 2002 R. Schetty presented a paper at the 2002 IPC/JEDEC Conf. [94] that showed data whisker data for a proprietary tin coating(see Schetty-2001; ref. [69]). This proprietary coating did not form whiskers when tested under a variety of conditions. Furthermore, this coating had a tensile stress state at deposition which remained tensile under a variety of storage conditions. XRD analysis showed that the preferred orientation of this proprietary film was consistently (220), whereas standard MSA tin had a (211) preferred orientation. Schetty also analyzed the preferred orientation of three different lead-frame copper alloys (Olin's 7025, 194, and 151) and determined that all three materials had (220) preferred orientations. Schetty then published a paper at the 2002 AESF SUR/FIN Conference [95] that compared whisker formation on Sn films deposited from 3 different MSA (methane sulfonic acid) electrolyte to films made from a proprietary non-MSA electrolyte. All the Sn films were 10 microns in thickness and samples were stored under three different storage conditions; 55^{o}C (dry bake), 20^{o}C and 50% RH, and temperature cycling from -65^{o}C to +150^{o}C. For each test condition the non-MSA Sn films did not have any whiskers, whereas the MSA Sn films had whiskers. Schetty observed that the non-MSA Sn films had a preferred orientation of (220) and that the MSA films had (211) preferred orientations. Schetty also observed that the non-MSA Sn films did not build up compressive stresses over time as has been reported for MSA films. However, it must be pointed out that the specimens used in this study were 10 microns thick and the XRD method of determining stresses would only involve the top 1-3 microns of Sn film. The stress state of the Sn film at the substrate-film interface would not be determinable by XRD for 10 micron films.

Another 2002 SURFIN paper was presented by K. Whitlaw and J. Crosby [96] of Shipley Inc. Whitlaw and Crosby studied 22 different Sn finishes on substrates of brass, Olin 194, and alloy 42 lead-frames. In general, the results confirmed the benefits of nickel barrier layers, thicker deposits, and post-plate annealing as whisker mitigation practices. An unexpected result was the total freedom from whiskering seen with some bright Sn and Sn-Cu films with high carbon content and fine (<1 micron) grain structures. Whitlaw and Crosby state that the bright Sn results were due to the use of "modern" additives that affected the crystal orientation and structure of the films. In addition, a significant amount of data was presented for a variety of tin plating and substrate types. Some of Whitlaw and Crosby's summary statements are listed below:

1. *Alloy 42, with a few notable exceptions, gave generally good results.*
2. *Copper plated substrates gave very poor results.*
3. *3 micron tin coatings on either brass or Olin 194 substrates gave generally poor results.*
4. *A nickel undercoat was very effective in minimizing whiskers on brass substrates.*
5. *The only matte tin processes that came close to the whisker performance of matte 90/10 SnPb were the 95/5 and 90/10 SnBi processes.*

6. *Thicker (~10 microns) tin coatings were helpful in reducing whisker formations.*

A 2002 NASA Goddard Space Flight Center publication [97] showed that MLC SnNiAg-frit end-cap metallurgy was capable of growing whiskers up to 200 microns in length after thermal cycling between -40 °C and + 90 °C. These NASA reports evidenced the longest Sn whiskers ever grown on Sn plating with a Ni underplate. It was noted by this author that these MLC parts were barrel-plated, which is fundamentally different from rack-mounted Sn plating with respect to the residual strain energies. Secondly, this author noted that over a ten-year period there were never any reported Sn whiskers on field service MLCs from an installed base of about 50 million MLCs. Nevertheless, the intrinsic potential of the MLC end-cap metallurgy to grow whiskers under the right conditions should be noted and considered when any MLC application is under review.

A 2002 internet publication by M. Osterman [98] reviewed the standard set of mitigation practices and then presented some data on the effect of conformal coating on whisker mitigation. Osterman stated that conformal coatings should be regarded as an additional mitigation practice over and above some other strategy. However, data on uralane coatings did show that the risk of whisker formation and growth can be diminished, but not eliminated, by the use of conformal coatings.

The first comprehensive bibliography on Sn whiskers was published in 2002 by the NASA Goddard Space Flight Center [99]. There were 15 NASA Goddard publications, 3 military specifications reviews, and 126 industrial and academic publications listed. The listings were presented in chronological order. J. Brusse (of NASA), et al.[91], summarized the information contained on the NASA web site in a paper presented at the 2002 Capacitor and Technology Symposium.

A paper on substrate effects on whisker formation was presented in 2002 [100], and re-published in early 2003 [101], by R. Schetty, Y. Zhang, and K. Hwang. They evaluated 3 commercial lead-frame alloys (C7025, C194, and C151) as well as steel, phos-bronze, and brass. The authors concluded that substrate stress was an important factor that influenced the stress state of the tin coating, and that substrate stress could be affected by different pre-treatment methods. They additionally concluded that preferred orientations and stress states depended in large measure on substrate pre-treatment, and that that any tin chemistry can result in tensile or compressively stressed coatings depending on the pre-treatment process. The bright and matte tin produced from sulfamate chemistries had very different preferred orientations, which indicated that the organic additives had a controlling effect on the preferred orientation for any given combination of substrate and base chemistry of the tin coating bath.

In December of 2002, N. Vo and M. Tsuriya of Motorola published [102] on various acceleration test methods used on pure tin, tin-bismuth, tin-copper, and tin over nickel specimens all on copper substrates. Some platings were also done on alloy 42 substrates. Various plating chemistries were evaluated for their whisker mitigation properties. Temperature cycling (-55 ^{o}C to +85 ^{o}C) and isothermal storage with high humidity (55 ^{o}C at 95% RH) were used as acceleration tests. Some specimens were subjected to a simulated soldering operation which melted the finishes. Results showed that nickel underlays did not eliminate whisker growth at the above test conditions. It was also observed that whiskering tendencies were unaffected by the different plating chemistries utilized to prepare the specimens. The whiskers were observed to grow from surface grains and appeared to be induced by intermetallic formation in the immediately adjacent grain boundaries.

The National Electronics Manufacturing Initiative (NEMI) has initiated a number of Sn whisker and Pb-free initiatives. There are three Sn whisker projects: one is chartered to investigate acceleration tests, with the objective of recommending a test methodology as a standard for evaluating whisker growth risk factors; another is a modeling effort chartered with exploring and evaluating whisker growth models; and a third is a USER group chartered with developing an industrial consensus on the use of tin and tin alloy films . A set of experiments was initiated by the NEMI modeling and acceleration test committees that evaluated matte Sn films from several different suppliers relative to whisker growth. Preliminary results have been reported at several symposia in Y2002, namely at a September Y2002 joint NEMI/IPC symposium in Montreal and at a workshop held during the November Y2002 IPC annual meeting in New Orleans. At the March TMS meeting in San Diego a whisker workshop was hosted by NEMI. All of these workshop presentations are posted on the public NEMI website (www.nemi.org). Most of the references noted in this treatise are posted on the NEMI members-only FTP site, along with some interim reports from NEMI project members. An outline of the 2002 NEMI experimental work was presented at the JEITA meeting in April of 2002 by I. Boguslavsky, et al. [103]. Commercial plating solutions were used to deposit pure matte-Sn films on lead-frame substrates. The results indicated significant differences between the solutions. All of the specimens have been kept on test for longer durations with the results to be presented at future conferences. In July of 2003 the NEMI modeling committee issued an interim status report [104] that stated general support for the possible role of recrystallization in whisker formation. The NEMI committee felt that the role of stress in whisker formation was controversial. Some of the members felt that a positive stress gradient across the boundary of the whisker grain was critical for whisker formation and growth, others felt that the driving force for whisker growth was related to the differences in free energy between the whisker grain and the immediately adjacent grains. The committee also felt that the data for dislocation based theories was lacking.

J. LeBret and M. Norton from Washington State University reported on electron microscope studies on Sn whiskers in a 2003 publication [105]. The tin films were sputter deposited on to brass substrates. Some of the specimens were aged at room temperature and others were aged at 50^{o}C and 150^{o}C. No whiskers were observed on the specimens aged (annealed) at 150^{o}C. Transmission electron microscopy showed that the whiskers in this study were dislocation free and that they had no extended defects. Lebret, et al., noted that the presence of whisker axes that were not expected (in slip directions) also suggests that dislocation growth mechanisms were not applicable in this study. In other TEM samples, it was possible to find whiskers that had nucleated in thin areas enabling examination of those areas. Again, no evidence of dislocations in the whiskers or the underlying grains was found. Lebret, et al., surmised that evidence of intermetallic formation and the temperature dependence of whisker growth pointed to a recrystallization process as a fundamental aspect of whisker formation.

I. Boguslavsky and P. Bush discussed recrystallization principles as applied to whisker growth in a 2003 paper [106] presented at the APEX 2003 meeting in Anaheim, CA. In this paper, whisker growth was extensively discussed in relation to classical recrystallization process theory. The driving forces for recrystallization were stated to be stress fields due to dislocations (i.e. micro stresses) and the driving force for secondary grain growth was stated to be grain boundary network stresses. Some x-sectional FIB micrographs showed aspects of classical recrystallization and grain growth associated with whisker nucleation.

In 2003 Whitlaw, Egli, and Tobin [107] presented data on a "new" pure tin process designed to produce a tin deposit with crystal orientation combinations that minimized whisker growth, particularly when used with a specific substrate preparation process. They recommended that the substrate materials be etched to a minimum depth of 2.5 microns prior to plating. Recommended mitigation practices were annealing (one hour at 150^{o}C) or the use of undercoats such as nickel or copper. When using copper undercoats, crystal orientation of the copper deposit was of critical importance. Almost identical data was presented by Whitlaw and Tobin [108] at the 2003 AESF SUR/FIN Conference.

A number of company internal reports have been made available to customers regarding tin whiskers. One such report by M. Dittes, P. Oberndorff, and L. Petit [109] from Infineon Technologies, ST Microelectronics, and Philips respectively, presented results for pure Sn films on typical lead-frame materials. The thickness of the Sn deposits ranged from 1.5 to 15 microns. One observation was that a 150^{o}C post bake for one hour was an effective whisker countermeasure. This annealing result has been the focus of a great deal of user interest relative to the use of pure Sn films on lead-frames. The authors of the above internal report presented the above, and other findings, at the 2003 IEEE Electrical Components Conference [110]. In this IEEE report the authors reported on whisker mitigation effects for nickel (Ni) and silver (Ag) underlays. For ambient storage conditions it was observed that no whiskers formed on any of the tin samples with either Ni or Ag underlay. The reader is cautioned that "no whiskers" in this case meant that there were no whiskers greater than 50 microns in length. However, the data also showed that all whisker growth ceased after about 150 days. A subset of the above information was compiled by M. Dittes and R. Schwarz in an Infineon technical note document [111].

A 2003 Texas Instruments internal report by D. Romm, et al. [112], studied whisker growth on a variety of commercial matte Sn plated on a variety of lead-frame substrates. All the specimens were subjected to some kind of acceleration test. In addition, some of the test samples were subjected to the acceleration test with adjacent leads at a 5V electrical bias The results showed that some matte tin films did not grow whiskers and some did. Whiskers were found on some large-grained Sn deposits and no whiskers were found on some finer grained films. Whiskers were found quite consistently on the electrically biased samples.

Alcatel Corporation has drafted a document [113] which outlines acceptance testing criteria for Sn finishes. One Alcatel test requires a 5V bias between adjacent leads on component packages. The Alcatel bias test requirement was based on the Texas Instruments report referenced above [113].

HP has issued a position statement [114] similar to that of Alcatel. In 2003 IBM's eSystems Development Lab issued a specification [115] that listed acceptable finishes for electrical components. Pure Sn finishes were not permitted without the addition of one of several mitigation practices. NiPdAu was the preferred IBM lead-frame finish.

Whitlaw, Egli, and Tobin of Shipley Corporation in 2003 published [116] data on copper underlays which showed that the as-plated orientation of the copper underlay was critical in mitigating the formation of whiskers on tin coated copper based alloy substrates. The copper underlay had to have a preferred orientation of (220). When the underlay had a (111) orientation the propensity for whisker formation was increased. These observations could possibly explain the variety of results reported in the historical literature regarding the effectiveness of copper underlays for whisker mitigation. The authors offered no explanation for the apparent orientation dependence of the mitigating effect for copper underlays.

Chen Xu, et al. [117], of Cookson Electronics showed data in 2003 on the whisker mitigation effects for a variety of nickel underlays and reflow. For the various nickel underlay types (bright nickel, matte nickel, etc.) the measured tin coating stress was tensile and became more tensile over time. All the nickel underlays were bright nickel coatings made with various amounts/types of organic additives. The resultant tin coatings had as-deposited stresses ranging from -69 MPas to +140 MPas. For both room temperature and 50^oC storage conditions tin whiskers were not observed on any of the nickel underlay types for a 6 month observational period. For reflowed tin coatings the stresses for room temperature aging after 12 months of observation ranged from zero to +/- 2MPa. After 18 months the reflowed tin had residual stresses ranging from -3 to 0 MPas for room temperature aging, and -4 to +2 MPas for aging at 50^oC. Temperature cycling did produce whiskers (relatively short whiskers at <50 microns) on tin coatings with nickel underlays for all varieties of nickel utilized in this experiment. All stress measurements reported in this paper were determined by the XRD $\sin^2\Psi$ technique.

K. Tsuji of Ishihara Chemical Co. published a paper at the IPC-Jedec conference in October of 2003 [118], which discussed the role of grain boundary and surface free energies on whisker growth. Tsuji suggested that the nodule growths observed immediately before whisker formation could be explained by recrystallization and that the whisker growth could be understood as a natural result of surface free energy minimization. Tsuji went to state that the minimization of surface free energies can be achieved by growing in specific directions and growing facets on the lateral surfaces. From this statement, Tsuji felt that some important characteristics of whiskers, e.g. the growth directions, the stability of the cross-sectional shapes, and the temperature dependence of whisker growth could be rationalized. The Tsuji paper published the first ever electron beam back scattered photographs (EBSB) of tin whiskers. Tsuji was able to focus the electron beam onto individual grains and generate pole figures from which orientation and lattice strain determinations were made.

A paper on X-ray diffraction measurement techniques as applied to the characterization of tin plated lead-frame packages was presented at the 2003 IPC-Jedec conference by S. Madra [119]. A detailed tensor analysis technique was presented which purported to show that stresses were lowest for the (110), (210), (220), (320), and (420) planes of the body-centered tetragonal tin structure, and that these low-stress orientations "*should be favorable against whisker formation*". Madra then modeled the effects of molding on the stress state of tin coated lead-frames and showed that the molding operation could induce compressive stresses in the tin coating. Madras then claimed that compressive stresses caused grain realignment in the tin coatings, thereby establishing large stress gradients between adjacent grains that resulted in atom transport across grain boundaries and subsequent texture transformation and whisker formation. Tensile stresses were claimed to have no effect on "grain orientations" and, therefore, effectively inhibited texture transformations and whisker formation.

M. Dittes, et al. [120], presented a study at the 2003 IPC-Jedec Conference on temperature cycling effects for tin coatings deposited on alloy 42 (Fe-42%Ni) substrates. As a control, SnPb parts were plated and exposed to the same storage and test conditions as the pure tin coatings. The conclusions from this report were that whisker growth on tin plated alloy 42 substrates had a strong dependence on the number of applied thermal cycles, whereas the formation of whiskers on tin plated copper substrates did not have such a strong dependence on thermal cycling. The maximum length of the pure tin whiskers was significantly longer than the maximum length of the tin-lead whiskers. Dittes, et al., theorized that differences in CTE (coefficient of thermal expansion) between alloy 42 and the tin coatings resulted in higher compressive stresses in the tin film when exposed to temperature cycling. The whisker lengths for pure tin coatings on alloy 42 substrates ranged up to 150 microns for samples with tin film thicknesses of about 8.0 microns.

W. Choi, et al., continued to study tin whiskers using synchrotron X-ray micro-diffraction techniques [121] on eutectic tin-copper (SnCu) films. Their data showed that tin whiskers grew in the <001> direction, which is the z-direction for tin's body-centered tetragonal crystal structure. The whisker grain itself had a (210) orientation, which was a different orientation than the surrounding (321) grains. Strain measurements were made using white synchrotron radiation to create Lauë diffraction patterns. Analysis showed that stresses at the whisker root were near zero, and that the surrounding regions were more compressively stressed than the whisker root region, although non-uniformly so. i.e. The stress gradients around the whisker root were not radially symmetric. The authors went on to observe that whiskers were observed on both sides of the formed lead-frames used in this study, which implied that the compressive stresses necessary to form and grow whiskers resulted from internal (internal to the film) generation of intermetallic compounds, both at the film-substrate interface and within the grain boundaries of the film material.

Anthology of Mitigation Practices

Introduction

Mitigation refers to processes that greatly enhance resistance to whisker formation for tin-based films. Underlays, alloying, plating chemistry, and heat treatment encompass the variety of accepted mitigation practices. This anthology summarizes the historical commentary for the most commonly accepted mitigation practices. The information is essentially a reordering of the chronological bibliography presented in the preceding section.

Heat Treatments:

Heat treatments may be subcategorized as annealing, fusing, and reflow. Annealing is a heating and cooling process typically intended to soften metals and make them less brittle. Fusing and reflow are similar in that both melt and resolidify tin plating under relatively slow cooling conditions. Fusing is done by submergence in oil at temperatures slightly above the melting point, whereas reflow is usually done with a conveyor belt furnace where the temperature at some point on the conveyor belt exceeds the melting point of tin for a relatively brief period of time (e.g. 1-5 minutes).

The first definitive statement about annealing in tin whisker literature was by V.K. Glazunova [16] in 1962. Glazunova noted that annealing at 100 ^{o}C, for not less than 6 hours, or at 150 ^{o}C, for not less than 2 hours, significantly increased incubation periods and decreased whisker growth rates for tin coatings on steel substrates with a brass underlay. In some cases whiskers were completely eliminated over a 3 year observation period. The same basic assertions were restated by Glazunova and Kudryavtsev [21] in 1963.

In 1968 M. Rozen of Northern Electric published [26] the first article in a series of tin whisker papers by Northern Electric personnel. Rozen based his annealing studies on the work published by Glazunova, et al., referenced above. Rozen's test specimens were tin plated steel, where the tin was deposited from a stannate bath, and tin plated brass with a 2.5 micron underlay of copper, again deposited from a tin stannate bath. Stannate baths produce what is commonly called matte tin. Rozen annealed his samples at temperatures between 191-218 ^{o}C for a minimum of 4 hours in a nitrogen atmosphere and found that whisker formation was essentially eliminated. Rozen noted, for the first time, that annealing modified the intermetallic compound formed at the tin-copper interface so as to make that intermetallic more resistant to hydrochloric acid attack. In addition, annealing was noted to increase the grain size of the tin film. Two years later (1970) Rozen and Renaud published [27] annealing data for bright tin-plated deposits. All the samples in this work were tin on brass with a 2.5 micron copper underlay. The results showed that bright tin deposits tended to blister and crack when annealed.

In 1975, Sabbagh and McQueen of Northern Electric published an update [29] on the Northern Electric experience with tin whiskers. After a 6 year observational period, no whiskers were observed on tin plated brass annealed at 191 ^{o}C for 3 hours. However, whiskers were reported after 6 years for tin plated steel annealed at 165 ^{o}C and after 4 years for tin coatings applied to copper coated steel annealed at 194 ^{o}C for 4 hours. In summary, Sabbagh and McQueen concluded that annealing is a method for retarding, but not eliminating, the formation and growth of whiskers.

K.N. Tu in 1973 [31] studied annealing effect on intermetallic formation between Sn and Cu. Tu determined that at temperatures above 60 ^{o}C the Cu_6Sn_5 intermetallic started a conversion to Cu_3Sn at the Cu-intermetallic boundary.

In 1974 S.C. Britton of the Tin Research Institute (now ITRI) published [33] a review of the known data on tin whisker growth based on over 20 years of observations. Britton's own data indicated that annealing tin deposited on brass substrates merely delayed the onset of whisker formation. Annealing at 200 ^{o}C for tin on copper substrates appeared to eliminate whisker formation for an observation period of 5 years. However, Britton stated that he saw no beneficial effect for tin over copper annealed at 150 ^{o}C for one hour. But a review of the data presented in [33] indicates that annealing at 150 ^{o}C did delay the onset of whisker formation for tin deposited onto a copper substrate. Furthermore, at no point in his treatise did Britton comment on the length or growth rates of the observed whiskers.

Glazunova, in collaboration with K.M. Gorbunova, published [46] a whisker review paper in 1983 some 20 years after her last publications [16][21]on the subject. Glazunova and Gorbunova made some very significant statements relative to the effect of annealing on tin whisker formation.

1. *Heating of steel components with tin coatings on copper substrates at 180 ^{o}C for 1 hour…eliminated the possibility of whisker formation even after 25 years of storage.*

2. *For tin coatings on steel without a substrate (i.e. underlay) heating at 100 to 180^{o}C for 9 hours and 1 hour respectively, leads to complete elimination of whisker growth.*

3. *Twenty years of observations for specimens with tin coated on brass substrates with a nickel substrate (i.e. underlay) heated to 180^{o}C for 1 hour showed no whisker formation.*

4. *For tin coatings on a brass substrate, heating even at 180^{o}C for 9 hours did not lead to complete whisker suppression, but did greatly reduce it…the whiskers were only 30 microns long instead of being 3mm long.*

Glazunova and Gorbunova stated that annealing reduced the residual stresses of the tin films and quoted a Russian source [122] for the corroborating X-ray data. This is the first known statement (to this author) in the scientific literature about X-ray stress measurements relative to whisker formation and growth.

In 1994 K.N. Tu [57] studied the effect of annealing at 150 ^{o}C for tin evaporated onto copper films which had been evaporated onto a quartz substrate. Tu concluded that annealing prevented whiskers from forming on the Sn-Cu films. Hillocks (surface protrusion on the order of 1-5 microns) were observed.

Lee and Lee published a 1998 paper [61] that studied stress in deposited tin coatings using a cantilever beam method. The Lee and Lee measurements showed that for tin over copper stresses were near zero at deposition (i.e. time zero) and became more compressive with time. However, when the specimens were annealed at 150 ^{o}C for 2 hours immediately after deposition, the cantilever beam results showed that stresses stayed at near zero for an observational period of 30 days. Unfortunately, Lee and Lee never published any updates to the above stress data.

The next published commentary on annealing effects on tin films was in 2002 from Whitlaw and Crosby of Shipley, Inc. [96]. Various tin and tin alloy films were deposited on Olin 194 and Alloy 42 substrates. Olin 194 is a copper based lead-frame alloy with about 2.0% Fe and .1-.2% Zn. Alloy 42 is 58Fe-42Ni. Some of the experimental cells were annealed at 150 ^{o}C for 1 hour. The observational periods for the data presented in this paper ranged up to 3 months. In all cases, the annealed cells had very little whisker formation in comparison to the non-annealed cells. However, there was some observed whisker formation in the third month for some of the cells. In all cases the cells were stored at 52 ^{o}C and 98% RH.

Annealing has been recommended by Infineon / ST Microelectronics / Philips (i.e. E3) as a mitigation practice for tin coatings over copper based substrates. The E3 recommendation was based on an observational period of about 400 days. Annealing does have a long history of positive reports with respect to being a significant mitigation practice for tin films. However, the E3 results were not totally consistent. In some cases the authors pointed out that annealing merely delayed the onset of whisker formation. But it must be pointed out that historical reports rarely mentioned whisker lengths achieved after annealing. When there was mention of whisker lengths, it was generally reported that annealing significantly reduced the ultimate length of the whiskers and significantly delayed the onset of whisker formation.

Underlays:

An underlay is a coating applied onto a substrate material, which is followed by a second coating of a different material. Underlays used with tin coatings are typically nickel, copper, and silver. Nickel is the most commonly utilized underlay for tin coatings. Copper has been utilized for brass and iron based substrates. Silver is less commonly utilized. Underlays are used to enhance the corrosion resistance of the surface coating, to act as diffusion barriers between the substrate material and the surface coating, and to change the basic state of stress in the surface film.

The first positive statement on underlays as a whisker mitigation practice came in 1974 [33] from S.C. Britton of the Tin Research Institute (now ITRI-International Tin Research Institute). Britton reported that observations over 12 years had determined that copper underlays were useful on brass substrates, but deleterious on steel. Britton also studied over a 6 year period nickel underlays for 9 micron thick bright tin deposited onto brass substrates and reported no whisker growth. The nickel underlay results were also positive for 5 micron thick bright tin films on brass substrates (although not as good as for the 9 micron thick tin films). The opinion at this time was that nickel acted as a diffusion barrier between the substrate and the tin coating. Britton's storage condition was 20 ^{o}C in a dry environment. Britton also commented on favorable results from the use of lead (Pb) underlays. However, further research into the use of lead underlays was terminated due to the more practical mitigation practice of using lead as an alloying element in the tin plating electroplating solution.

In 1987 B.D. Dunn of the European Spacing Research and Technology Center published an internal report [50] that evaluated copper underlays for tin coatings on brass substrates. Unlike the favorable 1974 report from S.C. Britton [33], Dunn reported prolific whisker growth for tin coatings on brass substrates with a copper underlay. Dunn's storage conditions were 20 ^{o}C and 40-80% RH.

In a 1997 review article Ewell and Moore [62] reported on service experiences from several manufacturers of passive components relative to tin whisker formation. Several manufacturers reported utilizing nickel underlays with no reported tin whisker problems for observational periods ranging up to 5 years and more. All MLC (multi-layer capacitors) have been manufactured with barrel plated tin over a nickel underlay since about 1992 with no reported incidents of whisker formation in field service conditions.

This author can report that there have been no reported incidents of tin whisker formation in field service for bright tin on copper with nickel underlays, both with electroless nickel and electrolytic nickel, for over twenty years of observation. Under conditions of temperature and humidity cycling the electroless nickel underlay performed better than the electrolytic nickel with respect to whisker formation.

In 2002, Chen Xu, et al. [84], from Cookson Electronics Corporation, published stress measurements for tin coatings on copper substrates with a nickel underlay. Xu, et al., found that nickel underlays resulted in tin coatings with tensile residual stresses, whereas the tin films without a nickel underlay usually had residual compressive stresses. Furthermore, Xu reported that whiskers did not form on tin coatings with nickel underlays after 4 months of observation at storage conditions of 25 and 50 ^{o}C. These results would be the first known evidence in the known scientific literature that nickel underlays changed the tin coating stress state from compressive to tensile. Yun Zhang, Chen Xu, et al.[85] showed data indicating that tin diffused into the nickel underlay in greater quantities than did the nickel into the tin. This was the first such statement in the published technical literature.

Whitlaw and Crosby [96] from Shipley Corp. reported in 2002 that nickel underlays on tin coated copper based C194 substrates effectively eliminated all evidences of whisker formation for observation periods of 4 months at storage conditions of 52 ^{o}C at 98% RH.

Vo and Tsuriya's 2002 paper [102] showed that nickel underlays did not completely mitigate whisker formation when storage conditions of 60 ^{o}C/95% RH or temperature cycling of -45 ^{o}C to +85 ^{o}C were utilized. The observed whiskers averaged < 50 microns in length, but a few individual whiskers were observed with lengths of 70 microns.

A joint Infineon Technologies/Philips/ST Microelectronics paper [110] was presented at the 2003 IEEE EC&TC which stated that both silver (Ag) and nickel (Ni) underlays had prevented whisker formation on tin coated copper substrates after an observation period of 14 months at ambient storage conditions. The same report indicated that temperature cycling between -55^{o}C and 85/125^{o}C had little effect on whisker formation for tin coatings on copper substrates (with or without underlays), but that temperature cycling did accelerate whisker formation for tin films on alloy 42 (Fe-42Ni) substrates.

Based on the above [110] results, M. Dittes from Infineon Technologies authored a 2003 technical note [111] which stated that Infineon would use one of three mitigation practices (listed below) on all matte tin plated copper based alloy lead frame products:

1. *Silver underlay (Ag> 2 microns)*
2. *Ni underlay (Ni > 0.5 microns)*
3. *Annealing (150 ^{o}C for 2 hours)*

Chen Xu, et al. [117] published data in 2003 that extended the observational period of his earlier works [68][71][72][84-86] to 18 months. Xu also showed results for 3 varieties of bright nickel and one of matte nickel. In all cases, the nickel underlays resulted in no observable whiskers after storage at ambient conditions. The residual stresses in tin coatings with nickel underlays were always tensile and became more tensile over time.

Alloy Tin Plating:

Tin coatings are typically alloyed by co-depositing elements such as lead (Pb), silver (Ag), bismuth (Bi), copper (Cu), nickel (Ni), iron (Fe), zinc (etc.), Historically the emphasis has been on alloying tin coatings with about 10% by weight of lead for whisker mitigation purposes. Currently, there are a significant number of supplier proposals to alloy tin coatings with silver, bismuth, and relatively small amounts of copper, either individually or in combination. Silver and bismuth are considered by most to be whisker mitigators, while copper is generally considered, with very little dissent, to be a significant accelerator of whisker formation and growth.

The first published account on alloying effects relative to whisker formation was by Glazunova and Kudryavtsev in 1963 [21]. A wide range of alloys were studied including 60-40 SnPb, 45-55 SnCu, 65-35 SnNi, and 80-20 SnZn. All the alloys, except the 90-20 SnZn, were found to markedly reduce the propensity to form and grow whiskers. In addition, Glazunova and Kudryavtsev studied tin alloys with 2-3 % of bismuth (Bi) and antimony (Sb). Both the bismuth and antimony alloys increased the incubation time for whisker formation by 3-4 months. No mention was made in this work on the growth rates and ultimate lengths of the whiskers that eventually did form.

In 1966 S.M. Arnold from Bell Laboratories published an article [20] on tin whisker mitigation practices. Arnold stated that tin alloys with antimony (Sb), cobalt (Co), copper (Cu), germanium (Ge), gold (Au), lead (Pb), and nickel (Ni) appeared to be the "most promising" with respect to whisker mitigation. Arnold then went on to say that tin-lead alloys were the most practical tin alloys because of ease of plating, cost, process control, appearance, solderability, and whisker mitigation. Bell Labs had observed numerous tin-lead coatings over a 12 year observational period under conditions of both ambient storage and high humidity storage. For all these tests, only a very few short (<500 microns) whiskers had ever been observed. Based largely on these Bell Laboratory results, the predominant whisker mitigation practice for electroplated tin over the next 4 decades was tin-lead alloy with the lead content averaging about 10% by weight. However, immediate implementation of PbSn alloys was delayed until the late 1960s because lead (Pb) was not a practical addition to the tin plating baths in common usage at the time (1964). By the end of the 1960s plating baths based on fluoroborate solutions became available which permitted the introduction of lead as an alloying material for tin coatings.

Glazunova and Kudryavtsev in 1963 [21] studied the effects of relatively small amounts of alloying in tin films and found that for tin-nickel it was necessary to have nickel concentrations greater than 12% by weight before whisker mitigation was observed. Bismuth and antimony additions of 2-3% by weight were found to slightly delay the onset of whisker formation.

S.C. Britton and M. Clarke studied the effects of Zn diffusion from brass substrates on tin whisker formation in a 1964 publication [23]. They concluded that whiskers grew much more profusely on brass substrates than on copper or steel substrates, and that the effect of brass substrates on whisker formation was more pronounced for the “bright” tin coatings than for “non-bright” coatings. The authors indicate that their findings were consistent with the observations of “others” almost without exception. Britton and Clarke also demonstrated that Zn atoms got to the surface of tin coatings after several months of storage, and that the amount of Zn at the surface continually increased over time. Cu atoms also got to the surface. The authors concluded that over time tin coatings were transformed into coatings that consisted of islands of copper and zinc regions surrounded by a continuous matrix of tin.

S.C. Britton, in 1974 [33], stated that alloy deposits of tin-nickel (65% tin-35% nickel) never evidenced any whisker growth. However, the solderability of tin-nickel alloys was deemed inferior to tin-lead and no commercial usage of tin-nickel was ever made. Britton also stated that bright tin must never be used directly on a brass substrate, but that some underlay of nickel or copper should be used between the bright tin coating and the brass substrate.

R. Kawanaka, et al. [45], studied the influence of co-deposited impurities on the formation of tin whiskers in a 1983 publication. Kawanaka observed that the technical community generally recognized that whiskers would easily grow on tin films deposited on substrates of copper or copper alloys, most especially on brass, and that the presence of either copper or zinc atoms in the tin films would significantly enhance whisker formation. Kawanaka used Auger microscopy to detect the presence of copper and zinc atoms at the surface of the tin film and within the whisker structure.

In 1984 Gorbunova and Glazunova [46] reviewed alloying effects on tin whisker formation and growth. They concluded that additions of 1-15% of alloying material do not appreciably retard the formation and growth of whiskers. Gorbunova and Glazunova particularly commented on the widely used coatings of tin-bismuth alloy (0.3 to 3.0 % Bi) as having “liability to whisker growth, although…less marked than on pure tin”. Gorbunova and Glazunova also commented on the common practice of depositing a chemically reduced (i.e. immersion) pure tin coating onto a prior coating of tin-lead. They stated such coatings are extremely prone to whisker formation with the whiskers reaching maximum lengths “not observed ever on galvanic deposits”.

Yanada in 1998 [63] presented both bismuth (Bi) and silver (Ag), in amounts ranging from 5-15% by weight, were useful for preventing changes in surface morphology and the formation of whiskers. Yanada’s observational periods ranged up to 3 months and the sample storage condition was isothermal at 50 ^{o}C. Pure tin coatings were observed to develop changes in surface morphology (i.e. nodules) as well as whiskers.

Schetty in 2000 [66] published data for tin alloy coatings stored at 55 ^{o}C for three months. Substrates of both brass (Cu-Zn) and alloy 194 (Cu-2%Fe-.12%Zn) were used. The results indicated that alloys of Sn-1Cu, Sn-2Cu, Sn-3Cu, Sn-5Bi, Sn-10Bi, and Sn-10Pb all evidenced whisker formation and growth.

N. Vo, et al., of Motorola published [74] data in 2001 on a variety of tin alloy coatings and concluded that "Sn-Bi out-performed the Sn-based finishes in terms of whisker-free life, needle length, and quantity". However, solderability of all Pb-free finishes was deemed to be poor relative to the eutectic tin-lead alloy.

K.W. Moon, et al., from NIST (National Institute of Standards and Technology) published a paper in 2001 [77] on the effect of copper concentrations in tin films relative to whisker formation. Moon concluded that copper alloying reduced the grain size of the deposited tin coating and produced intermetallic compound (specifically Cu_6Sn_5 intermetallic) precipitates in the tin coating grain boundaries. Moon, et al., did not observe whiskers on any pure tin coatings for observational periods up to 60 days at ambient storage conditions. However, whiskers were observed within two days on the Sn-Cu alloy coatings.

In 2002 J. Chang-Bing Lee, et al. [83] reported on whisker formation in Sn-Cu alloy coatings. Lee concluded that Sn-Cu films could be made whisker free by using plating additives to significantly modulate the tin coating microstructure. Lee recommended that this "proprietary" version of Sn-2%Cu would deliver excellent solderability, freedom from whiskering, and compatibility with SnAgCu and SnPb paste in board level assembly operations.

Sheng, et al. [88], in 2002 studied whisker formation in Sn-Cu alloy coatings and concluded that Cu alloying in amounts of about 1% significantly increased the number of whiskers formed and the whisker growth rates relative to pure tin. Focused Ion Beam (FIB) microscopy was used to study the microstructure of the SnCu alloy films. The results showed that the SnCu coatings had significant amounts of Sn_6Cu_5 intermetallic precipitates in the grain boundaries. These results duplicate the findings reported in the paper by K.W. Moon, et al. [70], as referenced above.

K. Whitlaw and J. Crosby of Shipley Corporation presented a large data set at the 2002 AESF SUR/FIN Conference in 2002 [96] which summarized whisker mitigation findings on tin-alloy coatings as follows:

"A*ll the pure tin processes were significantly worse than the tin-lead base case…*
The three tin-bismuth coatings, the bright 90Sn-Pb, two of the three bright pure tin coatings, and the bright tin-copper alloys were not statistically different than the matte 90Sn-10Pb alloy. All three tin-silver alloys and one of the three bright tin coatings had statistically significantly worse whiskering than the standard 90-10 tin lead".

Storage conditions for the Whitlaw and Crosby test matrix tests were 52 ^{o}C and 98% RH.

The reader will no doubt be confused by the many seemingly contradictory statements made in the above references with respect to various mitigation practices. In many of the published reports there was little or no effort to characterize tin coatings in any systematic way. Several published reports refer to different "types" of bright tin or to several different types of SnCu coatings. For example, internal stress levels and degrees of preferred orientation can vary significantly for what are ostensibly one "type" of tin coating. It would seem reasonable that the data conflicts are in large part due to subtle, but important, differences between the experimental tin coatings. Any mitigation practice may be successful only when the tin coating has certain built in characteristics.

Fused or Reflowed Tin Plating :

S.M. Arnold [20] published the first comments regarding fusing and hot dipping whisker mitigation effectiveness. However, in the same reference Arnold showed a photograph of a fused (in hot oil) tin plated steel bracket with a significant number of long whiskers evident. So it was not evident that fusing was uniformly effective as a whisker mitigator based on this particular paper.

S.C. Britton in 1974 [33] stated that hot dipped or flow melted tin coatings were at "far less risk (for whisker growth) than an electrodeposited film". No specific data was quoted by Britton. This particular paper was a review and compilation of experiences collected over a twenty year period.

B.D. Dunn, of the European Space Agency, published an internal report in 1987 [50] that showed a positive whisker mitigation effect for the fusing of tin plated steel after mechanical stressing in a c-clamp fixture.

Cunningham and Donohue in 1990 [53] studied the whisker mitigation effects of hot dipping and reflow processes. They concluded that the mitigation results were mixed with whiskers easily growing in mechanically stressed areas even though the tin had been reflowed or hot dipped. McDowell in 1950 [55] also stated that fusing had positive whisker mitigation effects.

In 1994 Harris of ITRI [58] restated the opinion that fusing is an effective whisker mitigation practice. No new data was presented in support of this observation.

Zhang, et al.[68], in 2000 published data on fused matte, and satin bright tin coatings. After 7 months of aging at 50 ^{o}C no whiskers were observed on any of the samples. However, the bright tin coatings were not reflowed as they were subject to dewetting and surface discoloration effects when reflowed.

In summary, fusing and/or reflow do have a mitigating effect on whisker formation, but they are techniques sensitive to subsequent handling damage. Scratches and / or mechanical stressing can initiate whisker formation on fused or reflowed coatings. However, it may be that the ultimate length of these whiskers formed by mechanical damage on fused coatings is relatively short in comparison to whiskers formed from electroplated coatings.

Physical Properties of Sn, Ni, Cu, and Their Intermetallics:

The physical properties of Sn, Ni, and Cu are generally known and are found in many handbooks. The physical properties for the intermetallics of Sn, Ni, and Cu are not generally known and cannot be found in the typical handbook reference. R.J. Fields and S.R. Low of the NIST (National Institute of Standards and Technology-formerly the National Bureau of Standards) Metallurgy Division have a research publication [123] that documents the physical properties for Cu_6Sn_5, Cu_3Sn, and Ni_3Sn_4, which are three of the most common intermetallic compounds found at interfaces between tin coatings and copper or nickel substrates. The samples used by the NIST researchers were prepared by very rapid solidification from supersonic, inert gas, metal atomization. This technique produced a very fine powder which was compressed under high pressure at elevated temperatures until the material was fully compacted. This technique produced a very fine grain sized material that was more than 99% single phase intermetallic. All the intermetallics were extremely hard and brittle and were chemically, physically, and mechanically similar to the actual intermetallic layers that form in solder joints. Table I (below) summarizes the results of the Fields and Low data and adds similar information for Sn, Ni, and Cu taken from reference handbooks. The reader is cautioned that the data in Table I is based on measurements from fine-grained, randomly oriented, poly-crystalline material and does not reflect the inherent anisotropy found for single crystalline or bulk material with significant preferred orientation indices. Young's moduli, coefficients of expansion, and Poisson's ratios are all parameters that have considerable anisotropy for tin.

Parameter	Cu	Ni	Sn	Cu_6Sn_5	Cu_3Sn	Ni_3Sn_4
Young's Modulus GPa	124	214	42	85.56	108.3	133.3
Poisson's Ratio	.33-.36	.31	.36	.309	.299	.330
Thermal Expansion Coefficient ppm/oC	16.6-17.6	13.0	23.0	16.3	19.0	13.7
Density gms/cc	8.90	8.90	7.28	8.27	8.90	8.65
Molar Vol. cc/gm-mole	7.11	6.59	16.00	118.50	35.16	33.98
Atomic or Molecular Weight gm-atoms	65	58.7	118.00	980.00	313.00	294.00

Table I-Selected Mechanical Properties for Cu, Ni, Sn; and their Intermetallics

Stress Measurements in Tin Films:

Stress (or strain) measurements form the basis for almost all theories regarding the formation and growth of whiskers. There have been two principal methods utilized for the determination of macro-stresses in thin coatings; one method utilizes flexure of thin cantilever beams, and the second method utilizes diffraction techniques (usually X-ray diffraction) that directly measure the lattice strains of the crystalline structure and then utilize algorithms to transform the measured strain into stresses. A third technique, X-Ray line broadening, has been utilized to study micro-stresses in tin films. Macro-stresses are considered to be those tin coating stresses caused by misfit strain at the substrate/coating interface, direct loading stresses, and other long-range residual stresses built into tin coatings during the deposition process. Macro-stresses result in flexure beam curvature and the shifting of XRD peaks. Micro-stresses are short range stress fields caused by the presence of internal defects, such as dislocations, and this type of stress field can be detected by the broadening of XRD diffraction peaks relative to the width of the diffraction peaks for well annealed specimens. Micro-stresses will not result in flexure beam curvature or XRD line displacement. Much of the argument between whisker theorists revolves around the relative role of macro and micro-stresses in whisker formation and growth.

Flexure beam methods utilize curvature induced by the deposition of a coating material onto one side of an initially flat substrate configured as a thin, relatively narrow, cantilever beam structure. Misfit strain established at the coating-substrate interface induces a state of stress into both substrate and coating. The direction and magnitude of the induced curvature establish the nature of (i.e. compressive or tensile) and the magnitude of the induced stresses throughout the flexure beam structure. For a relatively simple two part structure (i.e. coating and substrate) the coating stress is usually determined by utilizing Stoney's equation [124], which was initially developed in 1909. The equation in its simplest form is shown below.

$$\sigma = \frac{E\,h^2}{(1-\nu)\,6Rt} \qquad \text{equation (3)}$$

where

σ = stress
E = Young's modulus
h = coating thickness
ν = Poisson's ratio
R = the radius of curvature
t = substrate thickness

The application of Stoney's equation presumes a number of assumptions, one of which is the assumption that all the stresses in the substrate and coating material are elastic and there is no plastic deformation, creep, or any other form of relaxation. Stoney's equation, as shown in equation (1), presumes no significant stress gradients in either the substrate or the coating, and the σ value represents an average stress value for the coating in "the plane of the coating". i.e. The coating stresses are presumed to be biaxial in the plane of the film and σ_{zz} (i.e. stresses normal to the plane of the coating) are zero.

The version of Stoney's equation shown above (equation 1) does not take into account the intermetallic compound layer that is always formed between any tin coating and the commonly used copper and iron based substrate materials. With the presence of an interfacial compound the structure is a three film composite. For this situation it is not possible to apply equation (1) to determine the nature of the stress in the tin coating. To determine the stress in a tin coating it is necessary to measure the flexure, then etch off the tin coating, and remeasure the flexure. Equation (2) below shows the version of Stoney's equation used to determine the stress in a tin coating based on the radii of curvature as measured before and after the tin coating is stripped.

$$\sigma = \frac{E \quad h^2}{6\,(1-\nu)\quad t} \; \frac{Ro - R}{RRo} \qquad \text{equation (4)}$$

where Ro = flexure curvature before tin coating is stripped
R = flexure curvature after tin coating is stripped.

There are only two known (to this author) whisker publications that report stress data as measured by the above described flexure beam technique. The first such paper was published in 1998 by Lee and Lee [61]. Lee and Lee used equation (2) to determine the stress in both annealed (at 150 ^{o}C) and as deposited tin films. The as deposited films had initial stresses of +11 MPa (tensile), which changed to a compressive stress state after a "few" days, and reached -8 MPa (compressive) after 8 days. Thereafter, the compressive stresses were gradually relieved by whisker formation, reaching 5 MPas after 50 days. The annealed samples developed an initial stress state of +14 MPas which was completely relieved in one day of storage at room temperature. Thereafter, no residual stresses developed and no spontaneous whisker growth took place. However, it must be noted that Lee and Lee's data was for an observational period of 30 days and no update for longer observational periods has been published.

The second known whisker paper which reported flexure beam stress results was a paper by Yun Zhang, et al. presented at the 2002 IPC SMEMA/APEX conference [85].
Zhang, et al., used the flexure beam to monitor stresses for bright and satin bright tin coatings *in situ* (i.e. during deposition). Their data showed that bright tin had compressive stresses ranging from -80 MPas at the onset of deposition to -4MPas at tin coating thicknesses of 3 microns or greater. The stresses for satin bright tin were tensile at the onset of deposition, but for tin thicknesses of 3 microns or more measured as deposited stresses were essentially zero and remained zero for thicknesses up to 10 microns.

X-ray diffraction (XRD) is a standard technique for measuring macro-stresses in metallic films as stated in ASTM standard E-915. It cannot be the purview of this treatise to describe the different types of XRD techniques for the reader. However, it is important for any serious student of whisker fundamentals to understand the various XRD techniques and their capabilities and limitations. Beam size, white radiation versus monochromatic radiation, beam intensity, and detector capability are just some of the elements that go into determining the applicability of any one XRD technique to stress determination. Perhaps the most fundamental aspect of XRD techniques is that XRD does NOT measure stress; XRD purports to measure the lattice strain of the crystalline material. It is then necessary to apply some algorithm (along with the assumptions implicit to that algorithm) to convert the measured strain data to a stress value. Furthermore, XRD can only measure elastic strains.

Some early papers made non referenced statements that XRD measurements showed that stresses were either compressive or tensile. The first known (to this author) definitive XRD stress measurements in the published literature were in a series of articles by Yun Zhang, Chen Xu, and co-workers [68][71-72][84-86][117]. The technique utilized involved monochromatic X-radiation with a beam size of several hundred microns square. A rotating crystal technique ($\sin^2\Psi$) was utilized to determine lattice spacings for certain selected crystallographic planes. The measured strain data was converted to stress values under the usual bi-axial stress assumption. The bi-axial stress assumption is that the stress in the z-direction (that direction normal to the plane of the tin film) is zero. Zhang, Xu, et al., presented data for bright tin, satin-bright tin, and matte tins, with and without nickel underlays, for observational periods in excess of one year (as of Y2003). Their basic conclusions are summarized as follows:

1. *Bright tin films over copper substrates are initially compressive and the compressive stress state increases over time.*

2. *Stresses in satin bright tin films over copper substrates are close to zero and are stable over time.*

3. *Stresses in matte tin films over copper substrates are initially close to zero, either tensile or compressive, and build up increasing compressive stresses over time.*

4. *Stresses in tin over nickel underlay on copper substrates are initially tensile and show increasing tensile stresses over time.*

S. Madra [119] utilized XRD to measure stresses on lead-frame platings for a Quad Flat Pack SMT (Surface Mount Technology) package that had been encapsulated at 185 ^{o}C (for an unspecified amount of time). Madra utilized monochromatic Cu radiation (CuKά) and the $\sin^2(\psi)$ method to determine lattice parameters for the tin coating immediately adjacent to the molded housing. Madra's XRD principal stress result for post molded samples was -1.2 MPas.(compressive). Apparently, Madra did not measure stress states before encapsulation, rather he assumed that the tin pre-mold stress state was zero. Based on the XRD measurements and the stated assumptions, Madra concluded that the encapsulation process induced compressive stresses in the tin film. From a modeling exercise, Madra concluded that the CTE (coefficient of thermal expansion) of the molding compound would have to be specifically selected to minimize encapsulation process effects on the tin film stress state. Madra further concluded that mold compound CTEs (coefficient of thermal expansion) should be between 25 and 28 x 10^{-6} / ^{o}C to minimize induced stresses for tin lead-frame finishes.

The availability of synchrotron X-rays has opened up new possibilities for X-ray stress measurements. There is no need for beam focusing due to the extremely high intensity of the synchrotron radiation. Measurements can be made at any arbitrary angle of incidence, which eliminates the need for detector translation. A white beam can be made monochromatic with relative ease, which enables the selection of a sufficiently high Bragg angle for any family of lattice "planes". With this kind of flexibility it is possible to make direct measurements on planes that are both parallel to and perpendicular to the film surface, which eliminates the need for the usual extrapolations. The highly parallel, highly intense, and well collimated synchrotron beam makes it possible to micro focus the beam down to beam sizes on the order of 1.0 micron square. A 1.0 micron square beam can be positioned within an individual grain for some tin coatings, thus permitting a much localized determination of strain. However, a micro focused beam makes it very difficult to do the specimen rotations necessary to satisfy the Bragg angles for a single grain without inadvertently translating the sample relative to the micro focused beam. The use of a micro focused "white" beam obviates the need for sample rotation, but white beam doesn't have the inherent precision of a monochromatic beam / sin2Ψ technique. To date (November, 2003) there have been only two publications and one internal NEMI report that utilized synchrotron radiation to characterize tin coatings.

The two publications [80][121] both utilized the Lawrence Berkeley National Laboratory synchrotron. Results showed that the basic preferred orientation of the film (a SnCu film) grains was (321) with the whisker grain itself having a (210) grain orientation. The whisker growth direction was <001>. Stress measurements showed that the region immediately around the whisker root had a near zero stress state with the surrounding regions at a "more compressive stress state". All the calculated stress levels were less than 10 MPas. Around the whisker root there were stress gradients extending out laterally only a "few" grains. The authors commented that the measured strains ranged down to 0.01%, which was only slightly larger than the "sensitivity" (0.005%) of the white beam Lauë technique utilized in these experiments. From the data the authors concluded that stresses state were not truly bi-axial for individual grains; i.e., that there was a measurable σ_{zz} stress value. This observation should not be surprising since the usual assumption of a biaxial stress state is merely a convenience that makes the stress calculations much simpler. The overall stresses measured in these studies were low but were not beyond the capability of the system to detect. The "white beam" strain sensitivity of the synchrotron was defined to be 0 .005% and the lowest measured strain values were about 0.01%. No attempt was made to assess stresses as a function of depth from the surface.

The NEMI modeling committee worked with Professor P. Stephens from the State University of New York at Stonybrook to evaluate synchrotron beam radiation for tin coating strain determinations. Professor Stephens summarized his findings in a report to the NEMI committee [125] in May of 2002. Stephens utilized the beam line facility at Brookhaven National Laboratory (NLSL) which provided a set of monochromatic synchrotron beams 2mm x 1mm (i.e. 2000 x 1000 microns) in size. The samples were pure tin coated lead-frames from a quad flatpack package that had been temperature cycled 1500 times between -40 and +125 ^{o}C. Three monochromatic wavelengths were utilized (.50, .65, and 1.15 Angstroms). By comparing diffraction patterns from the three different wavelengths, Stephens assessed the variation in lattice strain as a function of distance from the surface. He concluded that the "deeper" tin layers were compressed in the z-direction relative to the surface layers and that the compression increased with increasing distance from the surface. This feasibility work has not been followed up on as of November, 2003.

Electron Beam Back Scattering (EBSD) is a relatively new diffraction technique that has been used to determine tin film stress and crystallographic orientation. Tsuji [119] has published EBSD data for individual tin grain orientations. Tsuji's EBSD beam size was about 1 micron square which is also the grain size minimum for matte tin films. Tsuji had to polish off about 0.5 microns from the film to get a flat enough sample for the EBBS analysis. The major limitation of EBSD is the need for an extremely flat surface.

Preferred Orientation in Tin Films:

Table II (below) is a summary of tin film and whisker orientation data available in the published literature to date.

All the whisker growth direction data in Table II was obtained from transmission electron beam diffraction. The whisker grain data was obtained by calculation [61] or micro X-ray diffraction [121]. The preferred orientation determinations for tin coatings were made by either the "times random" or "pole figure" techniques.

The user must be aware that no supplier of plating chemistries will guarantee that their process will result in a specific preferred orientation for the as plated film. It may well be that there is a correlation between whisker formation propensity and film preferred orientations, but can that desirable preferred orientation characteristic be controlled in a production environment? At the present time the consensus is that preferred orientation cannot be satisfactorily controlled for commercial application. This author would also comment that the usual preferred orientation data, based on times random or pole figure assessments, does not indicate the relative number of grains with one orientation with respect to other orientations. E.g., does a times random orientation index of 2.0 mean that a certain percentage of the grains have that particular orientation? And, if so, what is that percentage? What is missing from the data set is a correlation between the X-ray stress and orientation data from macro and micro beam analyses. There is a fair amount of macro X-ray data and there is just beginning to be a fair amount of micro X-ray data. What is needed is an understanding of the correlation between the two.

Diffusion:

Diffusion is a recognized element in whisker formation. Tin atoms must diffuse to the whisker site. Nickel underlays are reputed to act as diffusion barriers to copper.

Whisker Growth Direction	**Whisker Grain Orientation**	**Film Orientation/s-XRD** **P=Primary** **S=Secondary** **T= Tertiary**	**Commentary**
<001>	(220)	(321) P	**Choi, et al. 2003 [121]** Synchrotron study –individual grain orientation
NA	NA	(220)-P	**Madra 2003 [118]**
NA	NA	Inverse pole figure maps	**Tsuji 2003 [119]** E-Beam Back Scattering on individual grain
<110>-kink to<100> <103> <321>	NA	NA	**Lebret and Norton 2003 [105]** TEM used to determine growth direction Samples prepared by sputtering
NA	NA	(220)P(200)S_ (220)P (220)P (321)S (220)P (220)P (220)P(321)S(211)T	**Schetty, Zhang, & Hwang 2003 [101]** 60/40 Tin-Lead (SnPb) - whisker resistant 97/3 Tin-Lead (SnPb) - whisker resistant Reflowed Tin - whisker resistant Tin (Sn) - whisker resistant Tin(Sn) - whisker resistant Tin(Sn) - whisker prone
NA	NA	(101)(211)(112)(312) (432)(321)(211)	**Whitlaw, Egli, & Tobin 2003 [107]** whisker resistant-8% of grain angles at critical pts. whisker prone-65% of grain angles at critical pts.
NA	NA	(103)P(101)S (321)P(211)S (420)P(220)S (220)P(211)S	**Egli, et al., 2002 [89]** Whiskers observed: inter-grain angle 13.6° Whiskers observed: inter-grain angle 13.7° Whiskers observed: inter-grain angle 18.7° No whiskers : inter-grain angle ~ 42°
<100> <100>	(220) (420) (620) (420) (501) (321)	(200) (220)	**Lee and Lee 1998 [61]** Electrodeposited at 0.5 amps/dm^2 Electrodeposited at 3.5 amps/dm^2
<100> <001> <101> <123> <111>	NA	NA	**Ellis, Gibbons, and Treuting 1958 [22]** A collection of data from various 1950s era sources. Ellis's summary was that whisker growth directions are usually, but not always, coincident with slip directions. And because there were exceptions to the slip plane direction it was, therefore, unlikely that dislocation glide mechanisms were operative.

Table II - Summary of Whisker Growth Direction and Substrate Crystal Orientation Data following topics will be presented as a guide to those interested in the subject relative to whisker formation and growth theory. Tin does not diffuse into copper, whereas copper does diffuse into tin. Pertinent reference material on relevant diffusion couples is scanty. A brief overview of the following subjects follows:

1. *Tin self diffusion.*
2. *Fast diffusers (Cu, Ni, Au) in tin.*
3. *Relative diffusion of tin with nickel and copper.*

Tin Self Diffusion:

Tin diffusion in tin (i.e. self diffusion) proceeds along grain boundaries at a much higher rate than for the regular lattice. A 1984 publication by P. Singh and M. Ohring [126] used radio isotopes and very fine grained, polycrystalline, sputtered tin thin films to study self diffusion for tin. Their basic summary was that tin diffuses through grain boundaries and, over time, diffuses from grain boundaries into the crystalline lattice structure of the enclosed grains. The Singh/Ohring data is summarized, together with other referenced sources, in Table III (below). The reader is cautioned that the Singh/Ohring self diffusion data for tin was obtained with very fine grained (130-530 nm.), randomly oriented tin films. Electroplated films have grain sizes ranging from 500 nm to 5000 nm, and they are always textured (i.e. non-randomly oriented). An earlier (1962) study by Lange and Bergner showed grain boundary diffusion data [127] which was very similar to the Singh/Ohring data.

There have been two studies [128][129] on tin self diffusion as a function of crystallographic orientation. The data are summarized in Table III (below). In summary, there does not seem to be much anisotropy for tin self diffusion in the bulk lattice. There is no data for variations in grain boundary diffusion as a function of the grain boundary angle. Activation energies for grain boundary tin self diffusion average around 10 kCal/mole, whereas activation energies for lattice self diffusion average around 25 kCal/mole. The importance of the above data set is that whisker growth rates are consistent with the measured diffusion rates for grain boundary tin self diffusion. And the relative dominance of the grain boundary diffusion mechanism for tin self diffusion has to be considered when constructing any whisker formation and growth theoretical proposal.

A key summary reference for much of the above diffusion data was a book chapter by W.K. Warburton and D. Turnbull [130] from the Engineering and Applied Physics Department at Harvard University.

Fast Diffusers in Tin (Copper, Gold, Silver, Zinc, and Nickel):

The elements copper, gold, silver, zinc, and nickel are all fast diffusers in tin when compared to tin self diffusion. These diffusers are 1 to 10 orders of magnitude faster than "ordinary" tin self diffusion and the diffusivities are highly anisotropic, being fastest in the tetragonal (or c) direction. From reference [131] the fastest diffuser in tin is nickel and the slowest of the fast diffusers in tin is copper. Most of the fast diffuser studies were based on single crystal tin specimens. As a result, the calculated diffusivities are lattice diffusion coefficients. There are essentially no grain boundary data for fast diffusers in tin. All investigators presume that fast diffusers migrate through tin via an interstitial mechanism.

Diffusion Coefficient (Sn in Sn)	Activation Energy	Reference
$D_c = 3.6 \times 10^{-13}$ cm^2/sec (@ 25 ^{o}C) $D_a = 9.2 \times 10^{-13}$ cm^2/sec (@ 25 ^{o}C)	Q_c = 9.4 kcal/mol Q_a = 6.7 kcal/mol	F.C. Frank - 1953
$D = 10^{-12}$ cm^2/sec (@ 25 ^{o}C)		Fisher, Darken,& Carroll-1954
$D = 10^{-12}$ cm^2/sec (@ 25 ^{o}C)		Hasigtui-1955
$D = 10^{-12}$ cm^2/sec (@ 25 ^{o}C)		Furuta and Hamamura-1969
$D = 10^{-16}$ cm^2/sec (@ 60 ^{o}C)		Kehrer and Kadereit - 1970
$D = 1.8 \times 10^{-18}$ cm^2/sec (@ 25 ^{o}C)		Dunn - 1987
$D = 10^{-8}$ cm^2/sec (gr. bdry @ 25 ^{o}C) $D = 10^{-6}$ cm^2/sec (gr. bdry @ 150 ^{o}C)	Q = 25 kcal/mol	K.N. Tu-1994
$D_a = 5 \times 10^{-11}$ cm^2/sec @ 80 ^{o}C (apparent D - coarse grained Sn) $D_a = 1 \times 10^{-10}$cm^2/sec @ 80 ^{o}C (apparent D - fine grained Sn) $D_b = 1 \times 10^{-8}$ cm^2/sec @ 50 ^{o}C (grain boundary D)	9-11 kcal/mol (grain bdry. diff.)	P. Singh and M. Ohring, "Tracer Study of Diffusion and Electromigration in Thin Tin Films", J. Appl. Phys., 56(4): pp. 699-674, August 1984.
$D = 5 \times 10^{-9}$ cm^2/sec @20 ^{o}C $D = 2 \times 10^{-8}$ cm2/sec @50 ^{o}C	9-10 kcal/mole (grain bdry. diff.)	W. Lange and D. Bergner, Phys. Status Solidi, 2: pp. 1410, 1962.
D= 2-14 cm^2/sec @200 ^{o}C (the [001] direction-lattice D) D=1-2 cm^2/sec @ 200 ^{o}C (the [100] direction-lattice D)	25 kcal/mole (lattice diff.) 23.2 kcal/mole (lattice diff.)	Meakin and Klokholm-1960
D=5-11 cm^2/sec @200 ^{o}C (the [001] direction-lattice D) D= 1.4 cm^2/sec @ 200 ^{o}C (the [100] direction-lattice D) $D= 10^{-18}$ cm^2/sec @20 ^{o}C $D= 10^{-17}$ cm^2/sec at 50 ^{o}C	26 kcal/mol (lattice diff.) 25 kcal/mole (lattice diff.)	Coston and Nachtrieb-1966

Table III - Diffusion Data from Published Scientific Literature for Tin Self Diffusion

Tin Diffusion in Copper and Nickel:

This author is not aware of any published data for tin diffusion into copper. However, it is widely known that tin does not measurably diffuse into copper and this knowledge is based on years of observations made on tin plated onto copper substrates. For whisker theorists, it is important to know the relative diffusion rates for the various material couples; e.g. copper/tin, nickel/tin, etc. Because copper diffuses into tin in much greater amounts than tin into nickel, a compressive stress state is created in the tin film. The copper atoms essentially force their way into the tin microstructure and cause a compressive stress to be generated as a result thereof. Observation shows that the copper appears to diffuse mostly through grain boundaries in the same manner as tin self diffusion.

Nickel is an even faster diffuser in tin than copper. However, tin diffuses into nickel in much greater amounts than does nickel into tin. Nickel has a very low solubility limit in tin (approximately 0.5 weight ppm at room temperature [131]. So nickel will diffuse into the tin at an even faster rate than does copper. However, the amount of nickel in the tin will always be extremely small. Our knowledge of tin diffusivity into nickel is limited to three references [85][86][87]. None of the three references give quantitative data for tin diffusivity in nickel. However, all three references show that the boundary between nickel and tin moves under the influence of temperature into the nickel layer. This means that tin film over nickel on copper will be put into a tensile stress state because relatively more tin is moving into the nickel layer than nickel into tin.

The diffusion data in Table III shows clearly that the relative diffusion of copper/tin and nickel/tin couples is completely different. The fact that tin diffuses readily into nickel is consistent with the observation that nickel underlays are almost always very effective tin whisker mitigation factors. The built in tensile stresses inherent in tin deposited over nickel on copper are explainable by the relative diffusion of tin / nickel couples. It is much more difficult to understand how copper underlays can sometimes mitigate whisker formation. There is no known information on relative diffusion for tin / copper couples.

Whisker Lengths:

Whisker lengths are important measurements when one is trying to assess the reliability impact for whisker growths in various kinds of electronic circuitry. This author has no doubt that many readers will challenge any statements made about "the longest whisker is…..". Length categorizations are made more difficult because many published accounts do not characterize the type of tin plating as matte, satin bright, or bright. And even such characterizations as matte, satin bright, and bright permit a variety of quite different film stress states and crystalline morphologies. At risk of contradiction it would appear from the published records that the longest bright tin whisker ever recorded was by Hada, et al.[40] at slightly over 4000 microns and that the longest definitely identified matte tin whisker (albeit on a lead-frame substrate) of record was 800 microns [91].

Conclusion and Commentary

This document will be the third issue of a tin whisker annotated bibliography and the first issue of a tin whisker bibliography and anthology. Some effort has been made to solicit reviews of the commentary by the authors referenced, and especially so for the later papers. However, it has not been possible to solicit extensive reviews of the commentary prior to finalizing this particular document. Commentary is invited and every effort will be made to release future versions of this document which will include any responses received from quoted authors.

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