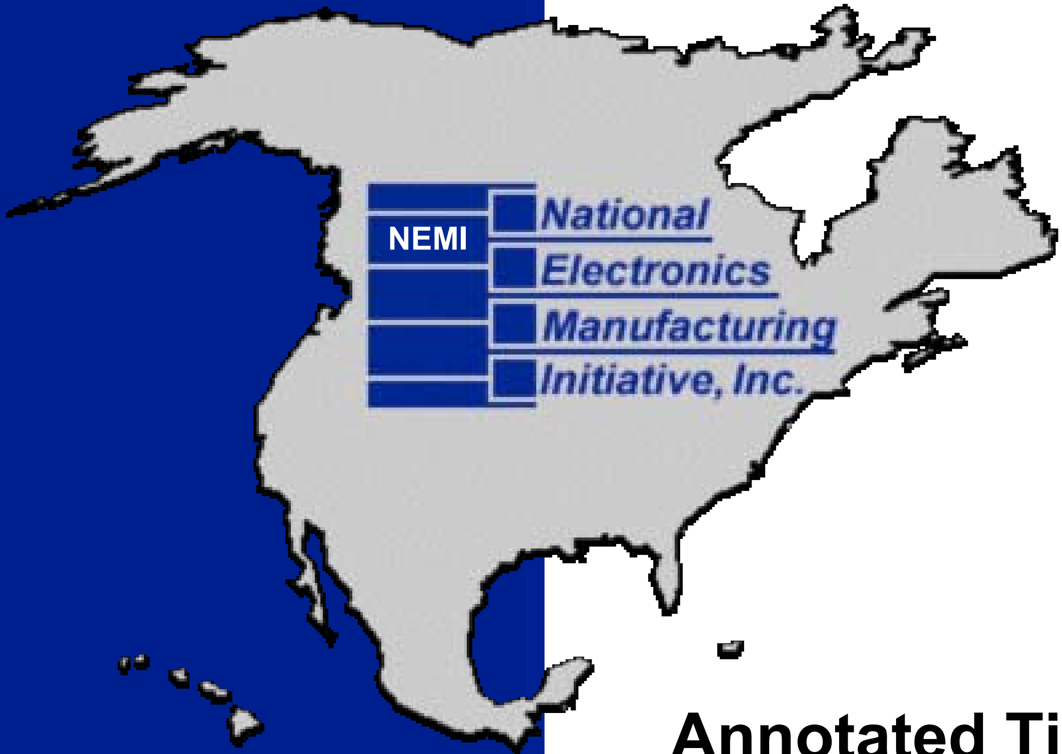

Annotated Tin Whisker Bibliography

a monograph by

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Connect with and Strengthen your Supply Chain

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A metallic whisker is a single crystalline eruption from the surface of a metal film deposited on a substrate surface. A whisker is typically 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 interest as the much-longer whisker eruptions.

Metallic whisker formation first came to the attention of the scientific community 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, the leaves of condensers were electroplated with Cd and, over time, the Cd plating grew whiskers long enough to short out the condenser plates. These observations were first reported in 1946 by H.L. Cobb [1].

In 1948, the Bell Telephone Corporation started to experience 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 Cd electroplating, but also electroplating of zinc (Zn) and tin (Sn). It was also found that whiskers occurred on aluminum (Al) casting alloy (Alcoa 750) and 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:

> *"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 in which there are, at most, only traces of organic material.*
>
> *The whiskers are not compounds but are metallic filaments in the form of single or twinned crystals".*

Most of the research since the Compton 1951 paper was focused on Sn electroplating on 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 that 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 base and not the tip, thereby voiding the Peach hypothesis. All subsequent investigations have been in agreement with the observations of Koonce and Arnold 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, and then glided to the surface depositing 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. The 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 driving force for the Frank and Eshelby mechanisms was a surface oxidation process 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.

In 1954, Koonce and Arnold [8] published additional electron microscope micrographs showing that the Sn whiskers could be kinked and/or coiled. Also in 1954, Fisher, Darken, and Carroll of U.S. Steel published the first full-fledged journal article [9] on whisker formation and growth in *Acta Metallurgica* titled "Accelerated Growth of Tin Whiskers." This article emanated from the 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 rates, reported at clamping pressures of 7500 psi, were about 10,000 Angstroms/sec. Fisher, et al., pointed out that the growth rate 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. 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 the 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.

The next commentary published after Hasiguti's article was a 1956 letter to the editor by J. Franks [11] 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 [12] based on Sn electroplated onto a steel substrate. Franks proposed a dislocation mechanism whereby whisker-generating dislocations are pinned due to lattice faults, which 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. [13], published an article on a helical dislocation model for whisker formation and growth. Helical dislocations are spiral prismatic dislocations that 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.

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 [14] reported on clamp pressure experiments 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) communication [15], 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. Furthermore, Pitt and Henning 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. 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 on hot-dipped tin and 50%Sn-50%Pb (lead) plating on substrates of both steel and Cu. While whisker densities decreased with additions of Pb, 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 than was the case for 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.

Starting in 1956, S.M. Arnold of Bell Laboratories published three monographs on whisker topics over a ten-year period. The first article in 1956 [16] was a review article compiling all the observations made in the Bell Laboratories whisker program to that date. Whisker mitigation strategies were discussed for the first time in the published literature. Arnold commented that the 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 the comment about a neutron bombardment experiment conducted at Brookhaven National Laboratory where “tin-plated specimens” (of an unspecified nature) were bombarded for 30 days at a neutron flux density of 10^{12} cm^{-2} sec^{-1}. After 12 months, these “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.

Again in 1956, Arnold published a paper [17] that detailed the beneficial effects of alloying Sn plating with Pb to mitigate the formation of whiskers. Arnold did note that even SnPb alloys can whisker if subjected to high compressive stresses. For example, SnPb plated washers subjected to high bolt-head pressures produced whiskers regardless of the Pb concentration. As a result of this article, the predominant mitigation strategy for Sn plating in the United States electronics industry became the addition of Pb to the Sn electroplate. Arnold's next publication was in 1959 [18] and it elaborated on the topic of "precautionary measures," a topic he initially touched on in his earlier (1956) 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, the growth of whiskers.

In 1963, a major article by Glazunova and Kudryavtsev [19] reported on Sn whisker experiments conducted on a variety of substrate materials (copper, nickel, zinc, brass, aluminum, silver, steel, and tin itself). 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. 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 nickel (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 a significant mitigating effect 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 of the plating was also evaluated and shown to have a retarding effect on Sn whisker growth. Glazunova and Kudryavtsev then made a series of summary statements not previously stated in such an integrated format.

> *"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 the internal deformation of the tin lattice.*
>
> *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.*
>
> *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.*

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.

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

Of particular note is the comment on recrystallization (above), which is the second time that the concept of recrystallization in Sn 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 [20] 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 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. Whisker formation and growth was defined as a "special case of recrystallization".

In 1966, W.C. Ellis published a study on the morphology of whiskers grown on Sn, Zn, and Cd plating [21]. Ellis showed that the growth directions for spontaneously grown whiskers were of small crystallographic indices that are also the indices for the glide planes. 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 the 1966 paper of his earlier findings [20] to the effect that not all whisker growth directions were low-indices glide plane directions.

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" [22]. 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 "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 these "bright" platings.

In 1970 Rozen and Renaud [23] followed up on the bright tin statements from Rozen's 1968 publication. Their bright Sn –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 [24] in 1973, which followed up on the progress reported in the prior two Northern Electric publications from Rozen, et al. Jafri reported that ultrasonic agitation of the electrolyte-plating bath was effective in minimizing or eliminating whisker formation in matte tin. In 1975, N. Sabbagh of Northern Electric, in collaboration with E. McQueen from Sir George Williams University, published an article [25] 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., had reported promising early data.

An entire chapter of a book written by Henry Leidheiser Jr. [26] 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 [27] 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 the 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 [28] on Cu-Sn bi-metallic films vacuum deposited on quartz substrates. The Sn was deposited on top of the Cu film in varying thicknesses. Whiskers were observed to grow on Sn only when there was a Cu underlayer. Tu attributed the growth of the whiskers to internal stresses associated with the formation of the Cu_6Sn_5 intermetallic. Tu would develop a considerable body of published research on tin whiskers over the next 30 years either as a single author or in collaboration with others. No other author has contributed so much to whisker related published literature over such a long span of time. These publications will be referenced below in chronological order.

A 1975-76 set of publications by B.D. Dunn [29] [30] 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 in that they were obviously 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 of the L.M. Ericcson Telephone Company in Sweden [31] 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, Eshelby, Amelinckx, and Franks. 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 theory based on lattice diffusion and the experimentally observed growth rates of Sn whiskers was "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 the source would glide toward the surface of the whisker and deposit a "layer" of Sn at the surface of the whisker. Resistance to the gliding dislocation came from a network of "forest dislocations" inside the 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 states that the gliding-prismatic dislocation loops deposit their extra half plane of atoms at the surface of the 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 [32] 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.

From 1980 to 1983, a series of three papers from Mitsubishi Electric Corporation were published on Sn whiskers. The first paper, by K. Fujiwara and Ryusuke Kawanaka [33], 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 [34] 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 [20] was the first and Glazunova and Kudryavtsev [19] were the second). The third Mitsubishi paper by R. Kawanaka and co-authors [35] 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 [36]. 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 plated films are soft and very difficult to polish and etch.

Fully five years after the 1985 Gorbunova and Glazunova publication, a paper was presented by Ahmet Selcuker and Michael Johnson [37]of Vitramon Inc. outlining a microstructural characterization study of electrodeposited Sn in relation to whisker growth. Selcuker and Johnson used samples of Sn plated over a Ni underplate with a substrate of Ag frit on multi-layer ceramic capacitors (MLCs). The SEM micrographs of the polished and etched MLC cross-sections revealed a network of polygonized grains with distinct grain boundaries. The cross-sectional 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 on the 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 below). Annealing experiments by Selcuker and Johnson showed that average grain sizes were doubled, from 5 microns to 10 microns, by annealing at 150°C for as little as 45 minutes in air. Brightener additions were also shown to reduce the plating grain size. None of the Selcuker and Johnson micrographs showed any whiskers.

In 1993, M.E. McDowell of the United States Air Force [38] outlined the method used by the USAF in dispositioning Sn plated parts in inventory. No position was taken relative to the prohibition of Sn usage (as previously recommended by Dunn of the European Space Agency). This would prove to be an unfortunate situation, as later events were to show, relative to reliability failures on USAF equipments.

A 1993 paper [39] by R. Diehl of the Burndy Connector Corporation was the first publication by a connector company that dealt with the reliability exposures from Sn whisker formation. Diehl concluded that additions of Pb were necessary to ensure that the Sn plate did not grow whiskers in service and Burndy Corporation adopted the addition of Pb recommendation for all of their tin plated connector products.

A new concept in whisker formation and growth theory was offered by K.N. Tu [40] in 1994 where he put forward the concept of a “cracked oxide” that enabled the localized relief of internal stresses by permitting a whisker growth to emerge through the crack in the oxide layer. This concept of a locally weak, or cracked, oxide layer remains a viable candidate mechanism for whisker formation and growth even though no direct evidence has yet been offered.

A major paper on Sn whisker growth mechanisms was published in 1998 by B.Z. Lee and D.N. Lee [41] 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 for a Sn film plated on one side of a cantilever beam, thereby causing the beam to deflect. Lee and Lee also determined the preferred orientation indices of the deposited films using X-ray diffractometry and compared the orientations of the whisker grains to the preferred orientations. They discovered that the whisker grains were always different in orientation in comparison to the majority of the individual 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.), 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. 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 [40]) substantiated, in this case, by actual residual stress measurements. Item 4 was essentially a restatement of the Lindborg [31] thesis with essentially no new data presented in support. The Lee and Lee 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.

The Lee and Lee paper ended the 20th century set of published whisker formation papers. 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 no general agreement on an acceleration test so vitally needed by electroplaters to assure customers on the reliability of the plating/s as regards whisker formation.

The anticipated lead(Pb)-elimination directives of the European Union (scheduled to be enacted in Y2006) highlighted the 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 re-entered. 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 5 microns) 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.

Probably the first paper published in the 21st century on Sn whiskers was by Schetty [42] in 2000. Schetty (then from Shipley Company) examined Sn, SnBi (bismuth), SnCu, and SnPb plating on brass and lead frame alloy 194 with, and without, Ni underplate. In all cases, some whisker growth was noted although often of extremely short (10 microns or less) lengths. A proprietary Sn plating solution was evaluated that showed no whiskers on plated lead frame alloy 104 after natural aging for eight months.

The first published account of Focused Ion Beam (FIB) microscopy on Sn whiskers was made by Isabelle Baudry and Gregory Kerros [43] of ST Microelectronics in 2001. Kerros and Baudry showed the first FIB cross-section ever published of a Sn whisker growing from a deposited Sn film. Kerros and Baudry drew no conclusions or inferences in their report.

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.

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., [44] was on 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, Wulfert and Vo [45] 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.

Because of the impending 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. [46], in 2001. A key tenet of this NIST paper was that Sn whisker formation is highly dependent upon impurities in the plating bath, which are 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 copper precipitates of Cu_6Sn_5, whereas the Cu^{+2} doped Sn plating had clear evidence of Cu_6Sn_5 precipitates arranged in columnar patterns parallel to the growth direction of the plating. Grain boundaries were not evident in the as-polished cross-sections, but etching did bring out a grain structure in the plating with a grain size of approximately 1.0 micron. This report did not state whether the plating was matte Sn, satin bright Sn, or bright tin, but a private communication [47] determined that the plating solutions were bright Sn. A subsequent NIST presentation [48] 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 present 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 results between the two (i.e., Substrate 1 was a Cu-coated silicon (Si) substrate; Substrate 2 was essentially a pure Cu substrate) substrate materials. No whiskers formed on the Cu-coated Si substrate...Thus, debonding may have occurred that led to relaxation of the residual stresses in the film and the suppression of whisker formation.*

The NIST research has opened an entirely new concept in whisker prevention or mitigation practices...namely, the prevention of internal compressive stresses by eliminating the possibility of intermetallic compound formation in the plating structure. 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 [49] by W.J. Choi and K.N. Tu from the UCLA Department of Materials Science and Engineering, et al., was the first published report on the use of micro-diffractometry using synchrotron radiation. Choi and Tu, et al., were able to focus the XRD beam down to a 1.5 micron square, and characterize the orientation and stress states of the region in and around the whisker root. Some key observations were:

1. *....the stress is not biaxial… is highly inhomogeneous...with variations from grain to grain.*

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 [50] 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 some 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 conclude that the "*pre-existence of these (Cu_6Sn_5) precipitates in SnCu enhances whisker growth*." Tu and Zeng go on to propose a model in which whisker growth occurs only in regions where the surface oxide layer is *"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 is proposed to determine the diameter of a whisker:

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

$$\Gamma = \text{surface oxide energy per atom}$$

$$E = \text{strain energy per atom in the finish}$$

A 2002 paper by J. Chang-Bing Lee [51] and co-authors from Advanced Semiconductor Engineering studied the whisker-forming properties of SnCu plating on lead frame base metals (e.g. Olin 151). In this study HAST (High Acceleration Stress Test) thermal cycling at 130°C was used to age all the samples. After 300 hours of HAST there was no observed whiskering on the samples with Sn -2% (or less) Cu plating. Tin plating with copper concentrations above 2% always grew whiskers, even after 300 hours of HAST. An extensive amount of analysis was done on all the samples. Preferred orientations were determined, solderability evaluations were conducted, various base metals were evaluated, and various types of SnCu plating baths were studied. The critical reader will note that the HAST test 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 and Bing Lee paper is that it indicates that annealing may be an effective whisker mitigation practice for SnCu films as well as for pure Sn films.

Chen Xu and co-workers from Lucent Technologies published in 2002 a paper [52] 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 compressive stresses that built up over time in Sn plating on Cu 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.

Andre Egli, and co-workers of Shipley Company, published a paper [53] 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 the magnitude of the difference in crystallographic orientation of adjacent grains. Egli's analysis 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 3D non-linear stress analysis of Sn whisker formations was done in 2002 by John Lau of Agilent Technologies and Stephen Pan of Optimal Corporation [54].

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 as of the date of this treatise.

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 [55] 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 the end-cap Sn plating after the MLCs were subjected to thermal cycling between -55°C and +100°C. The whiskers, as of the time the report was made (June 2002) were about 50 microns in length. Subsequent monitoring was planned to see if the whiskers would continue to grow.

A subsequent NASA Goddard Space Flight Center publication [56] showed that the SnNiAg-frit end-cap metallurgy of MLCs was capable of growing whiskers up to 200 microns after thermal cycling between -40°C and + 90° C. These NASA reports evidence 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.

The National Electronics Manufacturing Initiative (NEMI) has initiated a number of Sn whisker and Pb-free initiatives. There are two 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; the other is a modeling effort chartered with exploring and evaluating whisker growth models. A set of experiments was initiated by the two NEMI projects that evaluated matte Sn from several different suppliers and sources 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. 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.

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