ABSTRACT

Title of Document:	EVALUATION OF ENVIRONMENTAL TESTS FOR TIN WHISKER ASSESSMENT
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Tin whiskers are electrically conductive crystalline structures of tin that over time may grow outward from tin-rich surfaces and present a reliability hazard to electronic systems. While the problem has been known for decades, no satisfactory explanation of whisker growth mechanisms exists, leaving the industry to create whisker-assessment tests based on empirical data gathered under various environmental storage conditions controlled for temperature, humidity and temperature cycling. The long-term predictability of these environmental storage tests has not been addressed and the accuracy of these tests in foreseeing whisker growth is unclear.

In this thesis, different tin finishes are assessed for whisker growth in accordance with existing environmental test standards and compared to growth seen in ambient storage conditions. The results indicate that environmental tests may over-predict, under-predict, or show little distinguishable growth as compared to ambient-stored tin

finishes. In conclusion, environmental tests are not a reliable method of assessing future whisker growth.

EVALUATION OF ENVIRONMENTAL TESTS FOR TIN WHISKER ASSESSMENT

By

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Dedication

To my brother Aleksey and my sister Yulia – may you find meaning in all that you do

Acknowledgements

Foremost, I would like to acknowledge Dr. Michael Osterman for giving me the opportunity to pursue my graduate work on the topic of my choice, supporting it through the CALCE Electronic Products and Systems Center activities and the stimulating discussions, as well as keeping faith in me throughout the entire time. I am deeply grateful to Jay Brusse and Dr. Henning Leidecker of NASA, for increasing my knowledge of metal whisker and other problems in the world of electronics, as well as providing thoughtful guidance and inspiration without which the present work would be impossible.

My many thanks go to Lei Nie, Vidyu Challa, and Sungwon Han for supporting me throughout the years with their feedback and high spirits. Much of this work has relied upon the dedicated help of several visiting scholars, namely: Axel Theis, David Levi, Alexander Heronime, Choy Wai Man (Yonnis), and Dr. Tadahiro Shibutani.

I would like to thank the efforts of the Whisker Telecon Group, especially Dr. William Rollins and Dr. Gordon Davy for keeping up the discussions. I would also take this opportunity to thank and acknowledge the students and staff of the CALCE Research Center. Special thanks to Xiaofei He (CALCE, University of MD) and David Hillman (Rockwell Collins) for providing me with images of metallic formations that may be confused for whiskers. Also, I greatly appreciate the help of Dr. Andrey Kolmakov and his group at South Illinois University, for their enthusiasm in tin-oxide research, and for timely providing me with preliminary experimental measurements.

And most of all, I thank my parents and family for their endless love, understanding, and support.

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Chapter 1: Tin Whiskers – Introduction and Background

We dance around in a ring and suppose
But the Secret sits in the middle and knows
R. Frost

Metallic whiskers are conductive crystalline structures of metal that over time grow outward from the surface of the metal. This phenomenon has been noticed most commonly for Tin (Sn), Zinc (Zn), and Cadmium (Cd), while other examples, including Indium (In), Silver (Ag), Aluminum (Al), Gold (Au), Antimony (Sb), and Lead (Pb) also exist [1]. Examples of typical whiskers are given in Figure 1 and Figure 2.

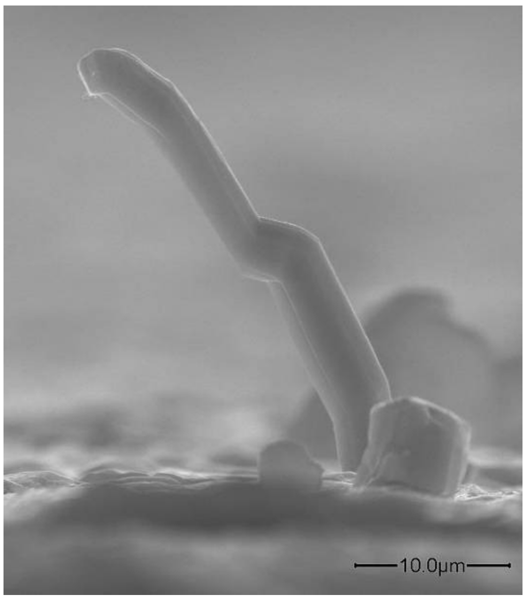


Figure 1 A typical tin whisker with two distinct kinks (bends) along its length

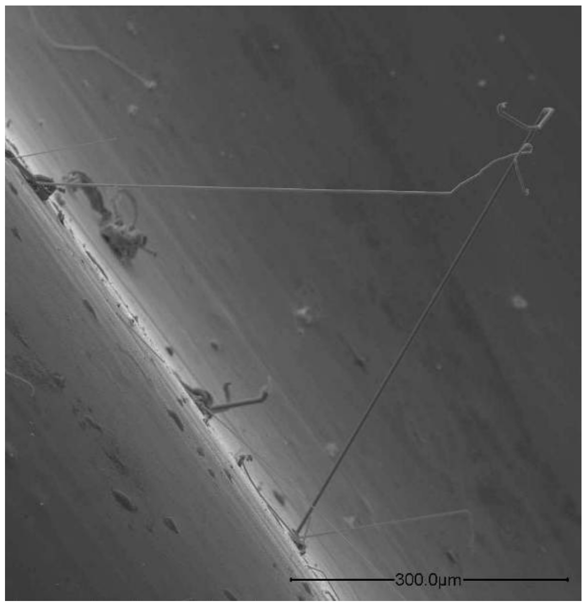


Figure 2 A pair of tin whiskers exceeding length of 300µm growing on surface of tin-plated copper-berillium (Cu-Be)

Primary attributes of metal whiskers

Morphology	Metallic	Composed usually of a single metal, with rare occasions of bi-metallic whiskers
	Shapes	Typically appear as filaments of nearly uniform cross-section along the length
		May contain kinks or bends along the length, appear as nodules or odd shaped eruptions
	Growth Mechanism	Incubation period - ranges between hours and years after metal deposition
		Growth - may last for years, with slow addition of metal to the bottom (root) of the whisker, not its tip. Although it may occur within hours of plating and progress in short time (Figure 3)
		Growth along the length only, with little to no change in thickness
	Variations in thickness	Ranging for different whiskers from sub-micron to sometimes few tens of microns
	Variations in length	Ranging for different whiskers from just a micron or two, to over 10mm in length
	Variations in density	Different surfaces may count from just a few whiskers to thousands of whiskers per mm^2
Mechanical Properties	Ductile	Can be bent over a flat surface or even in a loop without breaking
Electrical properties	Electrically conductive	Resistivity may vary depending on grain orientation
	Breakdown of oxide	Tin forms oxide films on the surface, which is insulating in nature. Dielectric breakdown strength will depend on film thickness

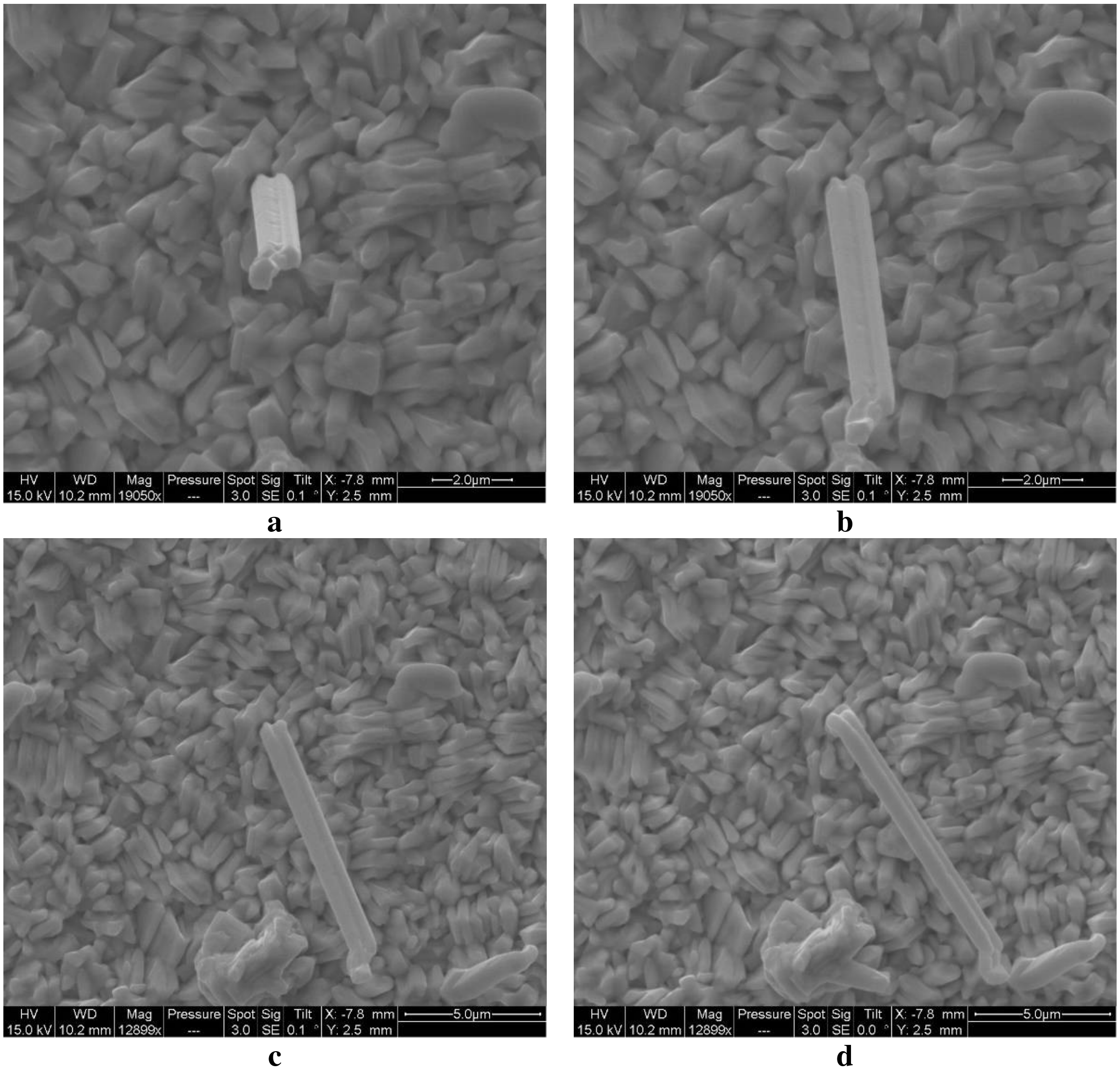


Figure 3 Progression of whisker growth (a-d) over a period of 19 minutes on Sn-Cu plating over Zn substrate, captures 5 hours after the deposition process. Note the continuously changing whisker orientation

The documented history of metallic whiskers begins in 1946, when Howard Cobb of Aircraft Radio Corporation published an article about “needle-like crystals” of cadmium (Cd) growing on Cd-plated capacitor plates in the radios [3]. At the time, Cobb summarized most of the observations that the industrial and academic worlds would come to acknowledge as the key properties of whiskers: growth over time, thickness of whiskers varying from micron to somewhat above one micron, extremely tough and electrically conductive. Bell laboratories would pick up the topic in the following years and initiate a series of long-term studies [2][15][20][41]. From them, it would become apparent that one of the few tin whisker mitigation techniques is use of Sn-Pb finishes, with at least 1% Pb by weight. The industry has successfully utilized Sn-Pb finishes for over half a century since then, before different legislations started restricting the use of Pb in electronic products. Closer to the 21st century, the topic of whisker has received much more attention due to two reasons: (1) the Pb was labeled environmentally un-friendly and its use in electronics became severely limited, and (2) the spacing in electronic systems have severely reduced, commonly less than 1mm between two conductive paths.

Metallic whiskers can create electrical shorts between two conductive surfaces, which can be permanent, if the current running through the whisker does not melt it, or intermittent, if the current is high-enough to melt the whisker (i.e. fuse it open). Intermittent shorts may arise if the whisker is moved to and from the second conductor by means of vibration or air currents. In situations of high currents and voltages, a whisker may vaporize to form a vapor arc of metallic ions that can sustain hundreds of amperes at a time, and create most impressive damages (Figure 4, [4]). When the current flow through the whisker is high enough to heat the whisker above not only the melting temperature, but above the boiling temperature for the metal (for Sn, $T_{melt} \approx 232°C$), the once solid metal whisker converts into a column of plume of metallic gas molecules which are not particularly good electrical conductors. However, if the voltage impressed across this metal plume is high enough to ionize the gas molecules (i.e., remove electrons), then plasma can form that is an excellent electrical conductor thus forming an electric arc. The voltage and current required to ignite and sustain such an arc are dependant upon a number of variables including the arc gap length between which the metal ions exist. When the arc gap is very small (~microns) it is possible to sustain metal vapor arcs for voltages as low as ~12V at current levels of a few hundred mA. As the arc gap widens, it is necessary to have higher voltages for ionization of the gas molecules and higher current available in order to boil off new metal from the surfaces to keep the plasma cloud dense enough to sustain the arc. The surrounding atmosphere can act as an arc suppressant or quencher. Reducing the atmospheric pressure can reduce the voltage and current necessary to ignite and sustain metal vapor arcs.

Figure 4 Relay failed due to tin whisker initiating metal vapor arc [4]
(Image courtesy of Gordon Davy)

<u>*Things that are not whiskers*</u>

There are a handful of metallic formations that can be confused for whiskers, but are in fact formed by other methods. Among these are: electrochemical migration dendrites, solder icicles, plating dendrites, and Sn-Cu intermetallic needles.

Electrochemical Migration

Metal migration in the presence of moisture and bias (also known as electrochemical migration or ECM) can produce surface dendritic growth. Such growth is two-dimensional and stays completely on the surface, unlike metal whiskers that will protrude outward from the surface. The ECM dendrites are typically multi-branched and form by migration of ions from the anodic side to the cathodic side where they are deposited [5][6]. Figure 5 presents an example of an ECM dendrite. Such dendrites are conductive, and can cause shorts within electronic systems, if proper precautions are not taken to limit presence of moisture in-between two conductors.

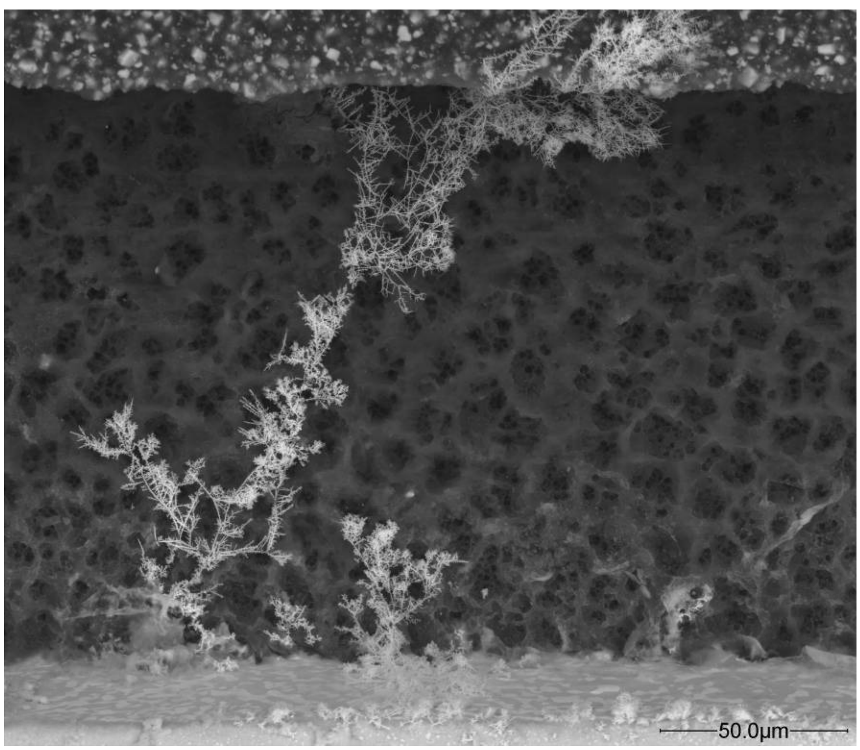


Figure 5 Example of a metallic dendrite growth induced by presence of moisture and electrical bias (Image courtesy of Xiaofei He, University of MD)

Solder Icicles

Another set of formations that may be mistaken for whiskers are solder icicles. If the soldering iron is removed too slowly, a drop of liquid solder may follow the tip of the iron, solidifying in air [7]. This occurs most commonly in manual soldering (although it can be an issue on automated soldering lines as well), with the size and frequency of icicles is dependent both on solder type and temperature of the soldering iron. Examples of shorter icicles can be seen in Figure 6 and Figure 7. Such solder icicles will not grow over time; they appear smooth along their length, not displaying any striations, and commonly have a gradually increasing diameter towards the surface as well as a sharp tip.

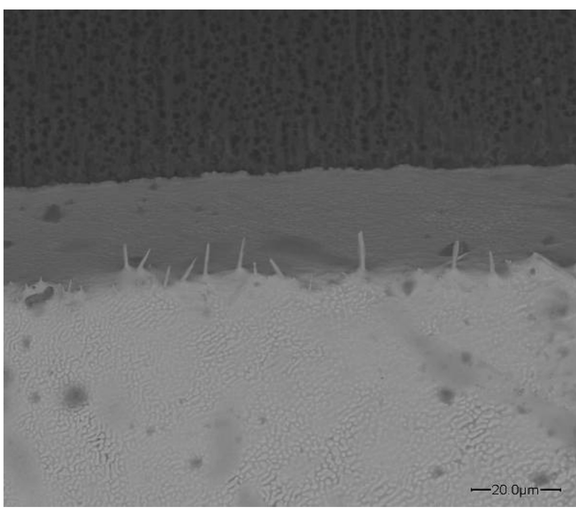


Figure 6 Example of soldering icicles produced during hand soldering of Sn-3.0Ag-0.5Cu solder, when iron was removed too slowly

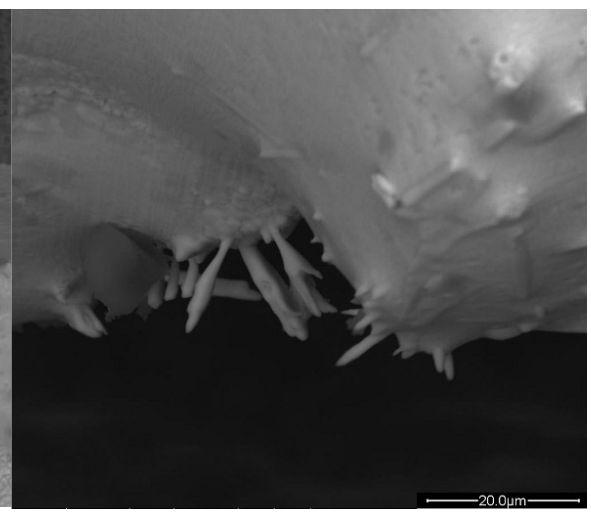


Figure 7 Examples of soldering icicles produced during automated soldering of Sn-3.0Ag-0.5Cu solder

Plating Dendrites

A problem more exclusive to electroplating and known as "plating dendrites" can also be mistaken for whiskers. Here, a protrusion from the Sn-plated surface will form when little or no additives are activated in the plating process. As a result, points of high potential on the surface (commonly high-sitting surface features) will attract more Sn ions and grow higher above the surface during the plating process. Properly chosen additives in plating solutions act as blockers to the Sn ions, and prevent metal deposition at such elevated surfaces, promoting more even deposition throughout (Figure 8). The phenomenon was referred to as “dendritic whiskers” by one researcher [8].

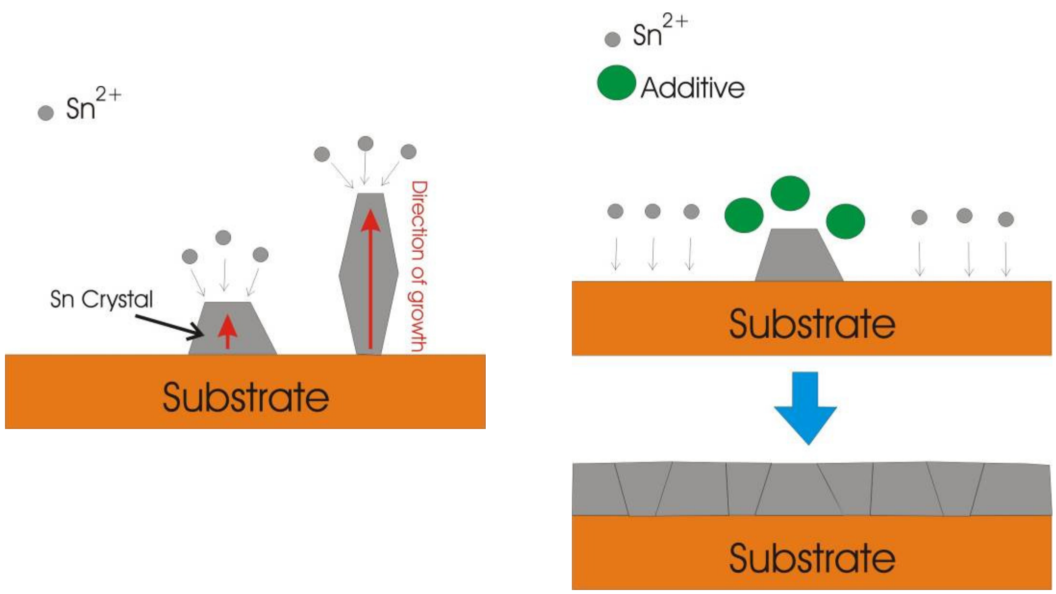


Figure 8 Process of Sn plating dendrite formation when organic additives are missing (left), as compared to plating with additives, where additives block high-point formations are promote even plating (right)

The plating dendrites have a variety of appearances: very smooth and regular crystals (Figure 9), or plate-like protrusions (Figure 10), or irregular crystal pile-up (Figure 12). There may be a single such formation on the entire plated surface, or in extreme cases – they may cover up the surface (Figure 11). Their main differentiations from whiskers are absence of further growth and lack of regular striations along and/or perpendicular their growth.

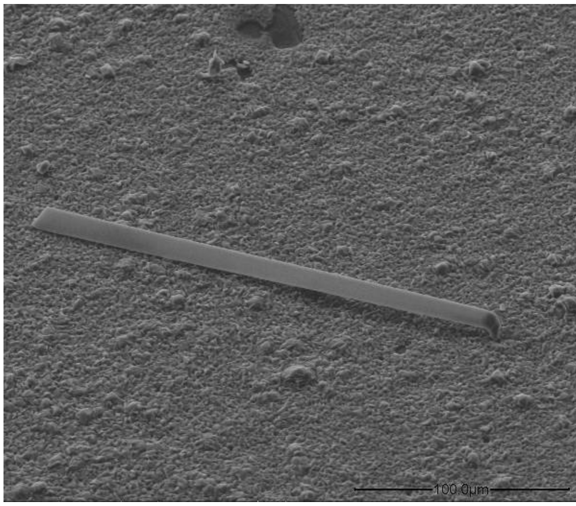


Figure 9 Plating dendrite as a smooth and regular crystal

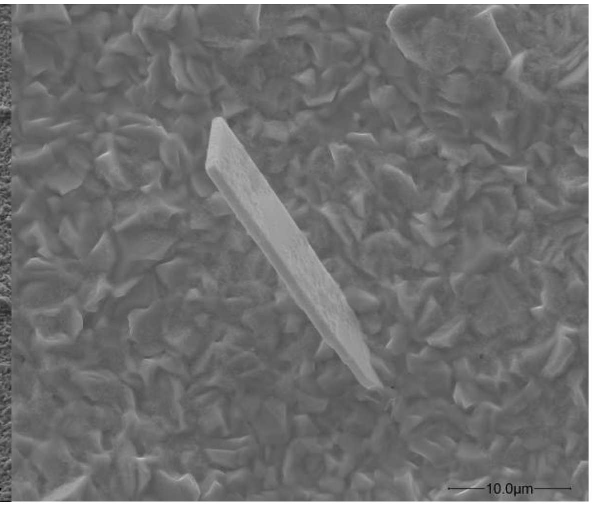


Figure 10 A plate-shaped plating dendrite

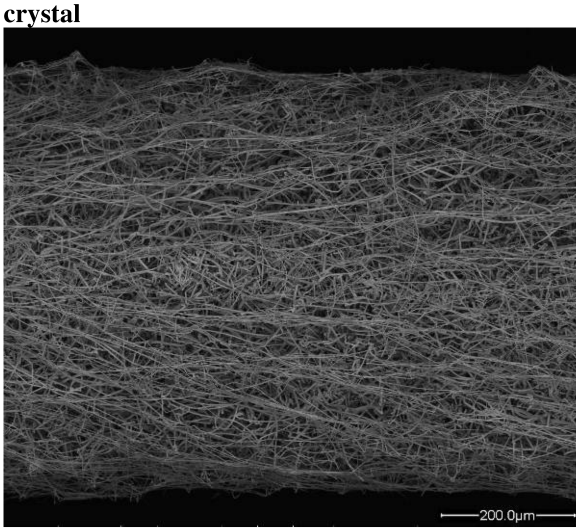


Figure 11 Multitude of Sn plating dendrites appeared during Sn-plating of a W probe

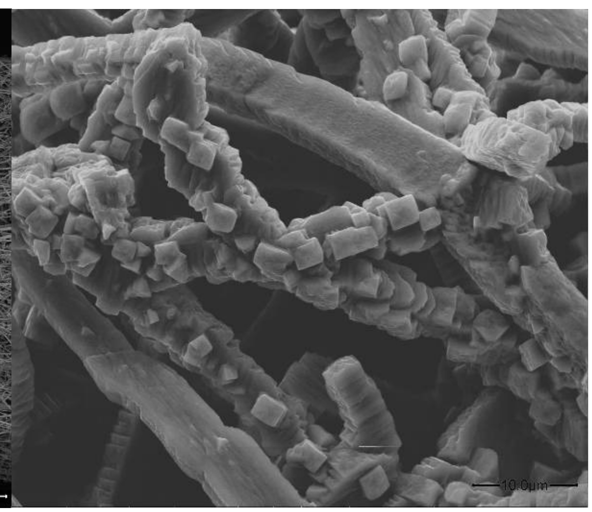


Figure 12 Extremely irregular plating dendrite formations

Sn-Cu Intermetallics

During high-temperature soldering of Sn-rich solders to Cu substrates, long hexagonal intermetallic Cu_6Sn_5 compounds may be formed [9][10]. They are hollow on the inside, and most of the time will remain in the bulk of the solder, invisible, until revealed (can be done so through intentional etching away of the surrounding solder material). On occasion, however, they may protrude out of the bulk solder, and may be mistaken for whiskers [11]. These Cu_6Sn_5 intermetallics are unlikely to grow further under ambient conditions, and the distinct hexagonal shape differentiates them from whiskers Figure 13. The hollow opening at the end may also appear on occasion to serve as another indicator that this is an intermetallic compound and not a whisker Figure 14.

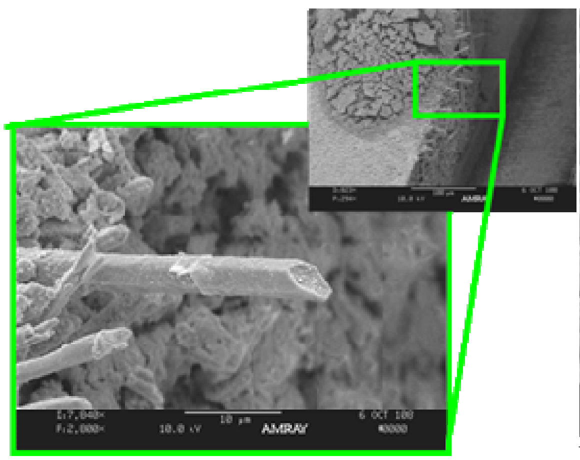


Figure 13 A tube-like Cu_6Sn_5 intermetallic protruding outward from soldered surface (Image courtesy of Dave Hillman, Rockwell Collins)

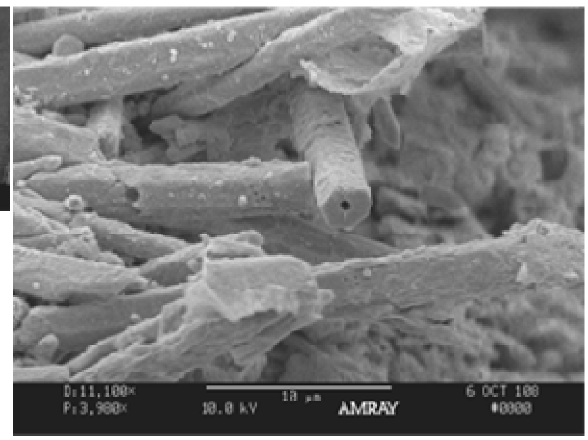


Figure 14 Examples of Cu_6Sn_5 hollow tube-like intermetallics (Image courtesy of Dave Hillman, Rockwell Collins)

Factors Contributing to Whisker Growth

The summary of literature on the factors contributing to whisker growth on thin (not bulk) deposits of tin is presented in Figure 15. All of these are macro-scale factors tat can be controlled and measured before, during, or after the metal deposition. Note that it is still unclear how any or all of these relate to the necessary two processes in whisker formation: stable supply of tin atoms to the root of the whisker, and a single initiation (or catalyst) to induce whisker growth.

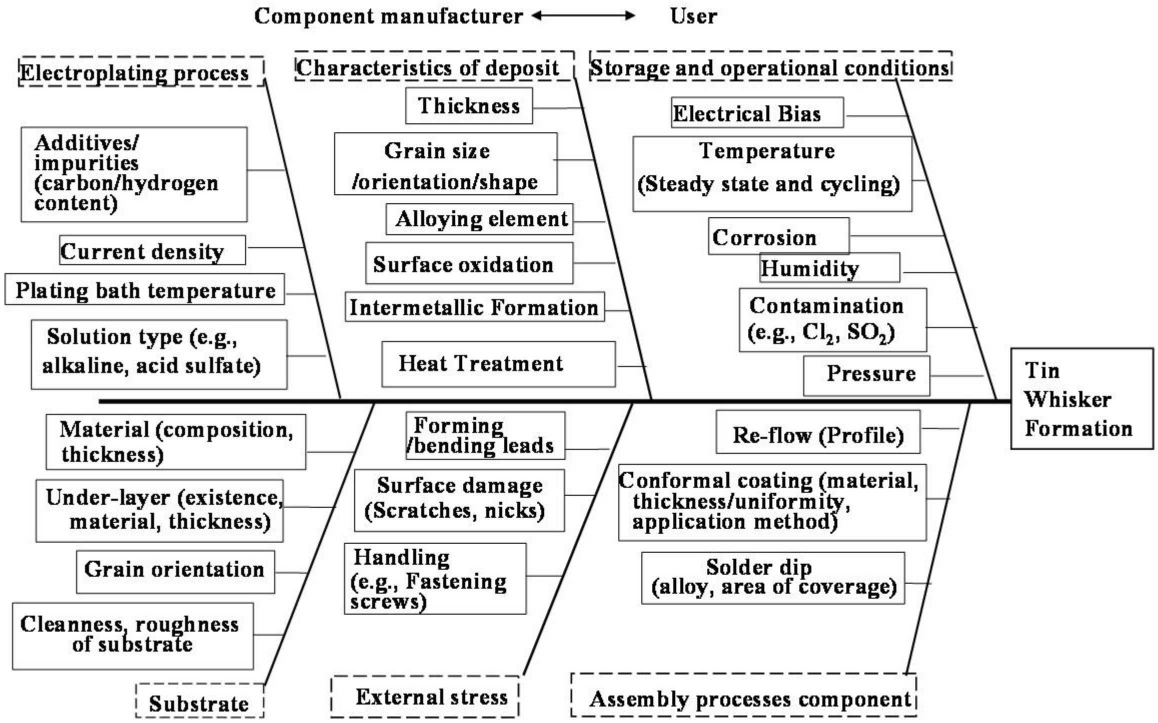


Figure 15 Factors contributing to whisker growth in thin deposits of tin (adapted from Y. Fukuda)

Electroplating Process

Additives of organic compounds (commonly referred to simply as organics) are used during electroplating for leveling-out of the Sn. There effect can be seen in Figure 8 (right), but their excess has sometimes been shown to greatly increase whisker propensity [12], while the use of low-organics (electroplating baths with relatively few additives) Sn deposition process did not yield any whisker growth even after long-term high temperature and high humidity storage of 95°C/95%RH [13]. Use of higher current densities promotes a lower cathode efficiency of Sn deposits, resulting in high hydrogen evolution, which in turn has been correlated to higher whisker propensity [14].

Substrate

Although tin has been shown to grow whiskers even when vapor deposited on mica or paper [15], majority of tin use in electronics has tin electroplated on a metallic surface. Brass (Cu-Zn alloy) has been cited as the most whisker-prone substrate for tin [16], while tin-coated Alloy42 (Fe-42Ni) tends to procude whiskers under temperature cycling tests [17]. Smoother substrates showed to be more prone to whisker formation [18].

Characteristics of Deposit

Most typically, 3-8µm of Sn is cited as the whisker-promoting plating thickness [43], although tin deposits with thicknesses of up to 20µm have produced whiskers on brass substrates [44]. Further, immersion Sn finishes of sub-micron thicknesses have on occasion produced whisker growth [45][49]. Grain sizes and orientations were studied to determine whisker-prone grains [50][51][52][56]. No definite conclusions have been agreed upon to date. On occasions, bulk tin has also been cited to grow whiskers.

Co-deposition of Sn with Pb has been shown early on to be a mitigator to whisker growth [15], although other researchers have shown that Sn-Pb finishes can grow whiskers under high mechanical stress [21][22], current bias of 10^4 A/cm^2 or more [23], and under temperature cycling and temperature humidity conditions [24], on occasion producing whiskers of bi-metallic composition, where both Sn and Pb are visible in the bulk of the whisker. Whiskers on Sn-Bi [25][26][27], Sn-Cu [26][28], Sn-Ag [26], Sn-Mn [30][31][32], and Sn-Ag-Cu [29] compounds have also been reported. As a recent addition to the field, whisker growth on Sn-rich solders with small additions of Rare Earth Metals (REM) has been shown to consistently grow whiskers within hours of sample preparation. Among REM studied were cerium, lanthanum, neodymium, lutetium, and erbium [33][34][35][36][37][39][40]. Recently, researchers demonstrated that presence of tin oxide is not an absolute necessity in whisker growth by growing whiskers in vacuum on surfaces that had oxides etched [52][54]. These findings contradict the assumptions that whisker growth requires a layer of oxide on the surface [55][56].

In Sn-Cu systems, the formation of Sn-Cu intermetallic has been suggested as a driving force for whisker formation [55], although other research has shown that whisker growth also exists when deposited on substrates that do not form an intermetallic with Sn [57] (or refer to Figure 3, where Sn-Cu plating does not form intermetallics with the Zn substrate).

External Stress

Extremely high rates of whisker growth have been observed in presence of external pressure applied to tin-finished surface [58][59]. Nicks and scratches have also been observed to promote whisker growth [42], although not quite as fast as growth cited in high-pressure load applications.

Use of Environmental Testing in Whisker research

Some of the earlier works on metal whiskers have shown that in addition to ambient whisker growth, it can occur in vacuum conditions as well as when submerged into oils, as determined by Arnold in his 1956 publication [2]. At the same time, he observed that while whiskers could grow at temperatures as low as -40F (-40°C), the optimum temperature is perhaps 125F (~52°C). In his earlier paper [20], Arnold makes mention that the environment is not the decisive factor in whisker growth, since whiskers have been observed to appear in "various" conditions of temperature, relative humidity and pressure. But according to that paper, the optimal condition for whisker density has been observed to be 125F (~52°C). Since then, a myriad of literature has claimed that whisker growth is maximized by the 50°C storage conditions; all of these publications in one way or another looping back to these two publications by Arnold. Harris[19] speculated that the 50°C temperature may be contributing to faster grain growth due to more rapid diffusion of Sn atom, but possibly also changing the nature of growth, and perhaps inducing some abnormal grains to grow. Nevertheless, at least two sources [42][43] have experimentally found whisker growth to be higher at 20-25°C storage conditions as compared to dry 50°C. A more clear demonstration was given by Woodrow [60], where Sn-plated brass specimens have produced minimal growth while in ambient conditions, but later on placement of specimens in 50°C/50%RH environment greatly increased the rate of whisker formation. In conjunction with work that showed less whisker growth at 50°C as compared to room temperature, this shows the importance of humidity as a factor in whisker growth.

Glazunova and Kudryavtsev [44] have demonstrated an equal amount of tin whisker under room conditions, in 98% relative humidity (RH), in dry oxygen, and in a vacuum of 10^{-5} mm Hg (10^{-2} Pa). Again, growth occurred also on tin finishes submerged into Vaseline oil.

In 2001, the National Electronics Manufacturing Initiative (NEMI, which later went international and became iNEMI) initialized a group responsible for producing a set of environmental test conditions that could be used for predicting the propensity of tin whisker formation. The group conducted five phases of testing to try to identify the testing conditions to accelerate whisker formation. This work resulted in JESD22-A121A [45]. The test standard identifies a temperature cycling condition, an elevated temperature humidity condition, and a control ambient storage condition. More details on the test standard will follow in Chapter 3.

Elevated temperature humidity conditions (ETH, also sometimes called damp heat or high temperature high humidity storage), have been called out as possible whisker growth contributors back in the 1956 by Arnold, and since then received great attention throughout the years. Perhaps the most comprehensive study of various ETH conditions was conducted in Phase V of the iNEMI testing [46]. It detailed work on Sn-plated surfaces from three industrial suppliers for two plating thicknesses (3µm and 10µm), use of reflow as preconditioning, and ten ETH storage conditions as listed in Table 1.

Table 1 Evaluation Test Matrix for iNEMI Phase V project, detailing Elevated Temperature Humidity studies and their durations

Temperature [°C]	**% Relative Humidity**			
	10	**40**	**60**	**85**
30	625 days	--	333 days	435 days
45	--	--	420 days	--
60	462 days	422 days	412 days	273 days
85	--	--	--	167 days
100	--	--	333 days	--

As a result of the test, an important issue with corrosion and whisker growth has been identified, where whisker growth in corroded areas was identified as different from that in areas, where corrosion was not observed. Typically, whiskers were found in or near the corroded areas, with low density and shorter whiskers away from areas of corrosion. As a result, iNEMI group has outlined steps within JESD22-A121A standard to minimize corrosion during ETH storage, and allows disregarding test specimens from the evaluation, if corrosion has been observed on them [47]. The experiments described in Chapter 3 and Chapter 4 had special precautions taken to not allow corrosion to initiate on the surface, thus eliminating that concern.

The first citation of the use of temperature cycling (or temperature shock) is in a 2001 paper by Nakadaira [61], where different Pb-free finishes (namely Sn, Sn/2Bi, Sn/0.7Cu) were studied as possible finishing materials for interconnect lead-frames. The study was meant to evaluate manufacturability, whisker growth, solderability, and solder joint reliability of these finishes in combination with Pb-free solders. It is thus unknown where the selected test conditions of -35°C/+125°C and -55°C /+85°C for temperature shock came from, although one may assume that these conditions were used for reliability testing of finished parts. But the results suggested that the latter condition was a far more aggressive whisker promoter. Continuation of this paper published a year later [62], detailed results of 39 weeks of ambient storage, and stated that although whisker growth has occurred, it was still far behind the growth seen in -55°C /+85°C conditions. This condition was later on incorporated into JESD22-A121A test standard.

Within Phase II evaluation [26], iNEMI group has also conducted sequential testing, using a sequence of temperature cycling conditions (-55°C / +85°C), followed by 30°C/90%RH storage. Their results indicated that the addition of humidity exposure did not significantly add to whisker growth, if the temperature cycling was conducted first.

Chapter 2: Measurements of Whisker Growth

We measure shadows, and we search
among ghostly errors of measurement
for landmarks that are scarcely more substantial
E.P. Hubble

Quantification of whisker growth may include various parameters, depending on the particular needs of the documentation. For example, in the case of collecting data for the melting current of a metal whisker, the radius of the whisker is most important [63]. But to assess possibility of whiskers bridging between fixed spaced isolated conductors requires collecting data for the number of possible whiskers or surface density, their lengths, and their direction of growth. The following section describes a methodology for collecting data on all three parameters and the ambiguities existing in their current definitions.

Density

Whisker density is defined as the number of whiskers per unit area. Ideally, measurement of whisker density would be done by counting all whiskers on a given surface and dividing by total surface area. However, it is generally impractical to measure density in this manner. Therefore, the density is measured by random selection of smaller-size regions, counting whisker in selected regions, dividing by that area, and then evaluating the distribution of collected whisker densities. Unlike the total number of whiskers over total area, sampling allows for examination of density variation. .

The following are guidelines used for whisker density reported throughout this work:

- Density measurements done under Scanning Electron Microscope, where high depth of field gave accurate identification of surface features. Additionally, Secondary Electron and Backscattering Electron detectors allowed differentiating between metallic whiskers and debris present on the surface.
- Minimum of 30 areas per experimental condition for density measurements
- Use of consistent area dimensions for density counts (e.g. $0.62mm^2$) for all individual measurements of density within the same experimental condition. Note that while the area was kept same for all density measurements within one experiment, it might have differed from experiment to experiment.
- Counting only whiskers that have their base located in the field of view of the area. Meaning that whiskers that have their roots located out of field of view, while visible whiskers originating outside of selected area, would not be counted. An example of this counting scheme is demonstrated in Figure 16. The importance of using both Secondary and Backscattering electron detectors is also illustrated in Figure 16, since any one image may provide incomplete information: Secondary Electron (SE) image gives only surface topography differentiation, while Backscattering Electron (BSE) image provides a difference in materials, with darker shades representing lower atomic number elements, but loses in topography. Thus surface debris can be clearly identified as a feature with the SE detector, but as a non-metallic particle with the BSE detector.

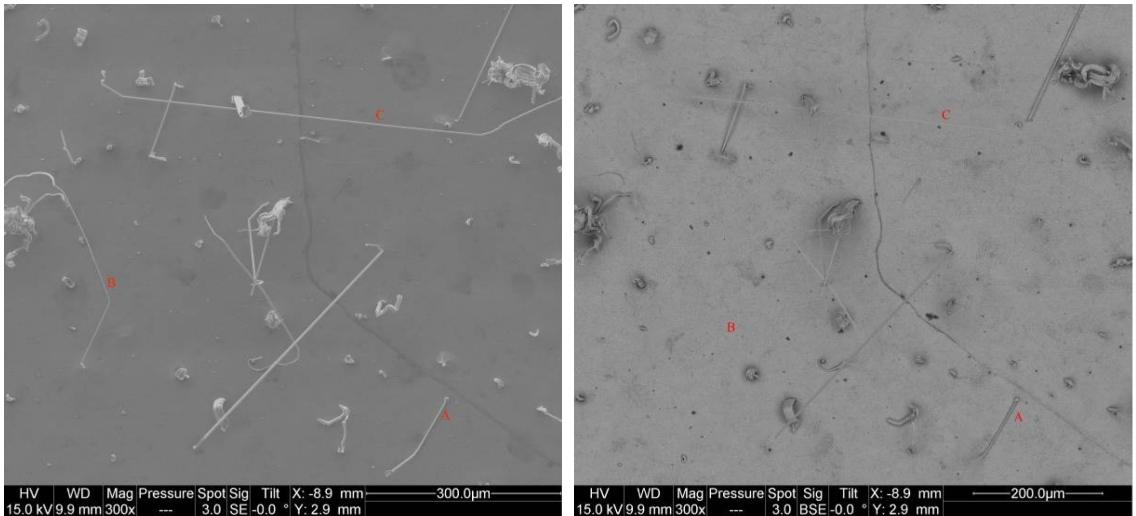


Figure 16 Example of whisker count on a 0.62mm^2 area displayed both as a Secondary Electron image (left) and Backscattering Electron image (right). Whisker A lies entirely within the picture, and is counted. Whisker B has its root visible in the picture, while part of whisker comes out of the view, yet it still is counted. Whisker C originates outside of the view and a part of it is visible in the image – it will not be included in the count.

<u>*Length*</u>

A whisker length historically has been defined in one of two ways: (1) the segmented length, or (2) the effective shorting length. The two definitions are described below:

(1) The segmented length is defined as the summation of lengths for all individual segments of the whisker. This definition has been used in the original version of JEDEC “Measuring Whisker Growth on Tin and Tin Alloy Surface Finishes” standard JESD22-A121 (published May 2005) and is illustrated in Figure 17. Summation of the individual length segments can be correlated to total volume of metal inside the whisker (volume = length * cross-sectional area). To do so, the cross-sectional area of the whisker must also be measured. Due to the complex polygonal shape of most whisker cross sections, it is common to assume a circular cross section and measure the thickness of the

whisker thus having area = $\pi * \text{thickness}^2/4$. This measurement method is useful if one needs to consider the amount of material that is making up the whisker.

(2) The effective shorting length is defined as the distance from root of the whisker to the point furthest away on the whisker. This can be visualized by placing a sphere encompassing the whisker with its center at the whisker root. The radius of the sphere would thus be equal to the effective shorting distance (Figure 18). This definition has been utilized in more recent standards: JESD22-A121A (published July 2008) and IEC 60068-2-82 (published May 2007). The justification for a switch from sum of lengths method to the shorting distance method is primarily the ease of measurement – a single line length defining all whiskers, no matter how complicated the shape. It may be considered useful when assessing whiskers growing in electrical systems, with the major problem resulting only if a whisker is capable of spanning certain distances.

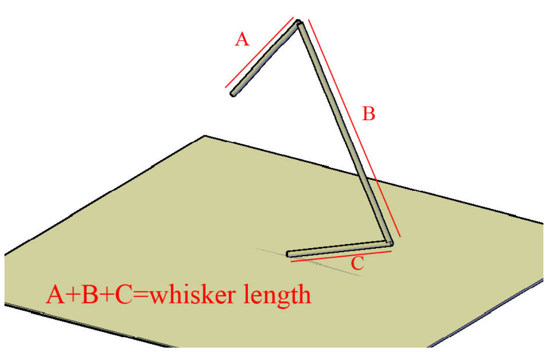


Figure 17 Whisker length as a sum of individual segments - JESD22-A121

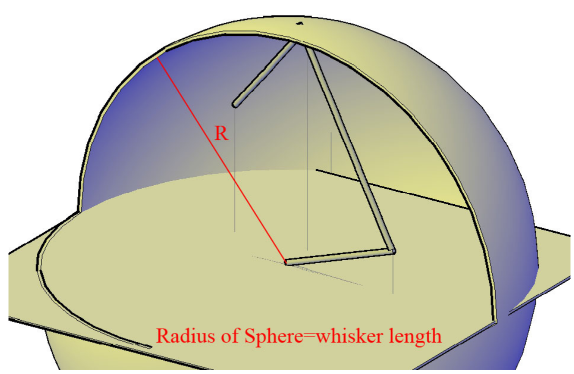


Figure 18 Whisker length as an effective shorting distance - JESD22-A121A and IEC 60068-2-82

One major drawback of the shorting distance measurement in predicting the possibility of the short is ignoring the fact that whisker are very capable of bending in the presence of an electrical bias [63] or under external forces such as air currents. Thus a whisker that contains a curve along its length may straighten out during such bending, thus exceeding the originally measured shorting distance.

Length Formula

In order to measure the length using either an optical or a scanning electron microscope (SEM), the standards suggest that the whisker needs to be rotated and tilted such that its length is perpendicular to the viewing direction and can be measured from a single view. If the observer, however, would not tilt the whisker and align it with the view, only a two-dimensional projection pf the whisker is visible. The error in measuring only a projection of the whisker instead of its actual length is:

$$\% \text{ Error} = (1-\cos\alpha)*100\%$$

Where α is the angle between the whisker and the plane perpendicular to the view (Figure 19). In case we are looking perpendicularly down on the sample – α would be the angle between the whisker and its plane of origin. This angle, or its complimentary angle, is commonly defined as the whisker growth angle. As demonstrated by [65][66][67], tin whiskers do not tend to have a preferential angle of growth, however, they rarely grow parallel to the surface. Therefore, α can be any angle except close to 0°, making % error only larger.

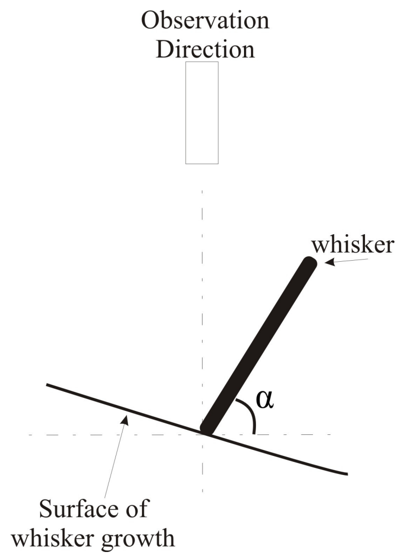


Figure 19 Depiction of angle α that is responsible for errors in whisker length measurement, if only a single measurement is taken from one observation direction. Obviously, if α=0 and whisker is perpendicular to the field of view, true length of whisker would be measured

Given that JESD201 and IEC 60068-2-82 both state that passing a whisker test requires maximum observed whisker length to be less than a stated critical length, proper identification of the whisker length is crucial. For example, a whisker that is 70µm long that was growing at 60° angle from the surface, and observed perpendicular to the surface would appear to be only 35µm long, and therefore pass a threshold set by IEC 60068-2-82 of 50µm.

Clearly, the acceptance standards (JESD201 and IEC 60068-2-82) and estimates of whisker failure risk require accurate measurements of whisker length. This has been reflected in the standards with precise instructions for tilting and rotating the whisker under microscope to see its actual length. To test how long it would take SEM operators to position whiskers perpendicular to the view, three individuals were asked to conduct a single length measurement under SEM, an experienced user may take up to 10 minutes to position the whisker perpendicular to the view. The time spent on measurement only increases for less experienced operators or ones that are not familiar with whiskers. If time limits are imposed on inspection, it is likely that long whiskers can be missed or whisker lengths may be inaccurately measured.

A training session conducted by HP [68] suggested that the ability to detect the longest whisker on a sample is highly variable from an observer to observer. This problem is two-fold: the observers either have not found the same whiskers or, once found, the whisker's length was measured inconsistently. While the method presented below does not guarantee finding the longest whisker, it does give an easy and reliable way of correctly measuring whisker length – independent of measurement approach; shorting distance method or whisker segment method. It also avoids the problem of shadowing whisker by geometries of a sample, once the sample has to be tilted significantly. For example, a leaded component with a whisker growing on one lead may need to have a significant degree of tilting to align the whisker perpendicular to the line of view. Component body or other leads, however, may prevent viewing of the whisker from a desired angle.

The method for measuring length is a fairly straight-forward geometrical derivation, that calculates the length of a line in three-dimensional space by using two views of that line (in our case – whisker, or its segment) that are off-set by a known angle.

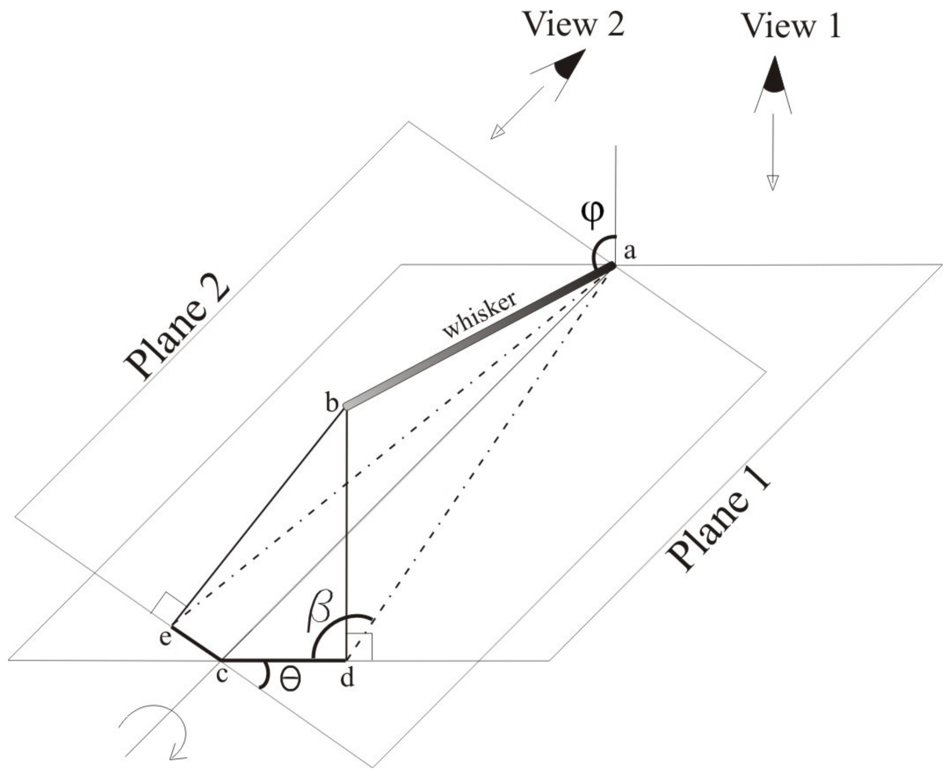


Figure 20: Schematic of measuring a line in 3-d space via two views offset by a known angle θ

The formula is:

$$L_{ab} = \sqrt{\frac{L_{cd}^2 + L_{ce}^2 - 2L_{cd}L_{ce}\cos\theta}{\sin^2\theta} + \left(L_{cd}\tan\beta\right)^2}$$

Variables are identified below, and represented in Figure 20:

Axis along L_{ac} is the tilt axis

L_{cd} = projection of whisker length on axis perpendicular to tilt axis in Plane 1

L_{ce} = projection of whisker length on axis perpendicular to tilt axis in Plane 2

θ = tilt angle between Plane 1 and Plane 2

β = angle between L_{cd} and L_{ad} in Plane 1

φ = growth angle of whisker. (Will be provided later in the chapter)

Note: Angle α defined for %Error equation above is α = 90° - φ

Use of Whisker Length Formula

In order to test consistency among multiple observers to use the above formula, 15 people have been selected, each to measure 15 whiskers. Out of 15 participants, only four have been previously exposed to whiskers, yet they have never used the above method for measuring whisker length. All participants received a presentation-format tutorial on measuring whiskers with one example of the measurement, instructions on how to use Image J software [69] to measure whiskers, a spreadsheet with the formula already embedded for ease of use, and 15 pairs of images showing whiskers from two views. Participants were encouraged to ask questions, but with no interaction amongst themselves.

The images provided for measurements had a stated tilt angle θ, and length was specified to be measured either by effective shorting distance method (JESD22-A121A) or sum of segments method (JESD22-A121). All length measurements done by participants were compared to measurements done by an experienced user of the formula. Whiskers were chosen of different lengths, ranging from 10μm to 1500μm. All provided images were taken using SEM, and no optical images were used.

The method by which whiskers were asked to measure is listed under “Measurement Type” column in Table 2. Straight line refers to a whisker that had no bends or twists in its length, and thus could be measured by a single line. Shorting length measurements as per JESD22-A121A were employed for some whiskers with multiple segments. Other whiskers with multiple segments were measured via

JESD22-A121 method, where sum of lengths of the segments were used. The average and standard deviation for each whisker measured by the participants and compared to measurements of the experienced user are presented in Table 2. All the images used for this exercise are presented in Appendix A.

Table 2: Average results for each of 15 whiskers measured by 15 participants

Whisker #	Measurement Type	Participants Avg ± STD (µm)	Experienced User (µm)
Whisker 1	straight line	132 ± 6	132
Whisker 2	3 segments	675 ± 43	671
Whisker 3	shorting length	54 ± 6	52
Whisker 4	straight line	12 ± 1	10
Whisker 5	shorting length	43 ± 7	51
Whisker 6	2 segments	54 ± 4	57
Whisker 7	straight line	304 ± 2	307
Whisker 8	shorting length	30 ± 1	29
Whisker 9	shorting length	129 ± 30	125
Whisker 10	10 segments	303 ± 24	294
Whisker 11	shorting length	108 ± 1	111
Whisker 12	straight line	1515 ± 30	1503
Whisker 13	2 segments	152 ± 17	147
Whisker 14	2 segments	50 ± 5	50
Whisker 15	straight line	48 ± 6	45

On average, 7% ± 3% error is observed among all the measurements done by the participants as compared to the experienced user. The distribution in average % error is given in Table 3.

Table 3 Average error in measurements for each participant, as compared to measurements done by an experienced user, using method proposed in this thesis

Participant #	Avg % error for each participant for 15 whiskers
Participant 1	8
Participant 2	3
Participant 3	4
Participant 4	5
Participant 5	9
Participant 6	11
Participant 7	9
Participant 8	4
Participant 9	9
Participant 10	8
Participant 11	9
Participant 12	9
Participant 13	10
Participant 14	5
Participant 15	8

The above results demonstrate consistency between different users to perform whisker length measurements. The accuracy and speed of these measurements would increase with more exposure. Time to take two images at slight tilt to each other would be mostly defined by the speed of beam scan in SEM, since tilting and locating the whisker is a matter of 10-30 seconds. This work has not assessed measuring whisker lengths based on optical images. Once the users are familiar with Image J, measurement of whiskers takes from less than a minute to several minutes, depending on how many segments of whiskers are being measured. To assist in measurement, the length formula may be imported in a spreadsheet, such that inputting measurements from Image J (or other measurement software) would quickly convert to final length values. The whisker length measurement thus takes just under few minutes.

To contrast this, seven participants were asked to employ JEDEC-suggested whisker measurement method. Here, a sample with three whiskers clearly identified to the participants, was placed under the SEM, and participants were asked to rotate and tilt the sample to align each of the whisker with the field of view. Each participant was an experienced SEM user, but had limited exposure to whiskers.

Among the three whiskers (whiskers can be seen in Appendix B), one was a straight line whisker with only one measurement required. One whisker was a three-segment whisker, where each segment needed to be tilted and rotated to get it perpendicular to the field of view. And the third whisker was a multi-segmented whisker measured via a shorting length method. The average and standard deviation across all the participants measuring length for each whisker is given in Table 4.

Table 4 Average results for each of the whiskers measured with JEDEC and IEC suggested methods

Whisker #	Measurement type	Participants Length Avg ± STD (µm)	Length as calculated from Formula (µm)
whisker 1	Straight line	440 ± 137	763
whisker 2-segment1	Segment 1 of 3-segment whisker	113 ± 11	124
whisker 2-segment2	Segment 2 of 3-segment whisker	175 ± 26	202
whisker 2-segment3	Segment 3 of 3-segment whisker	372 ± 97	464
whisker 2 (total)	Sum of 3 segments	643 ± 119	790
whisker 3	Shorting length	66 ± 6	70

Among the seven participants, the average % error was 20% ± 11% - compared to 7% ±3% as with the two-image and use of formula measurement. The average % errors for each participant are given in Table 5. Note the dramatic difference in measured and calculated length for whisker 1 – this whisker has a growth angle <5° from the surface normal, and would require a tilt exceeding 85° in order to be positioned perpendicular to the view. SEM stages are typically not equipped to be tilting this far, thus all of the observers had to stop short of locating the optimum. Rest of the whiskers had growth angles such that they could be positioned perpendicularly to the view with the SEM stage tilting.

Table 5 Average error in measurements done via JEDEC/IEC method for each participant, as compared to the length calculated from the formula

Participant #	Avg % error for each participant across 5 length measurements
Participant 1	20
Participant 2	20
Participant 3	5
Participant 4	33
Participant 5	6
Participant 6	32
Participant 7	21

A more significant advantage of measuring whisker length via two images instead of tilting the sample is time spent for the measurement. Instead of tilting the whisker by a designated angle to acquire a second image to be used with the formula, the observer is forced to the adjust position of each whisker in order to align the whisker perpendicular to line of inspection. Measuring lengths of three whiskers under SEM through tilting and rotating sample, participants spent 1.5 to 3hrs each on the task. As noted before, these were all experienced SEM users that did not require any additional SEM orientation. The same 1.5 to 3hrs was the range for the participants measuring 15 whiskers from two views of the whisker. That time also included getting familiar with the Image J software and reading instructions.

It is clear that the method currently proposed by JEDEC and IEC standards can be simplified in both time spent and effort utilizing the two images approach. More importantly, the accuracy of measurement can be greatly improved by using the two image approach.

Throughout this work, whisker lengths will be collected from different experiments in order to construct distributions of whisker length. The definition of whisker length (sum of segments or shorting distance) for each measurement set will be identified individually.

Length Distribution

Since whisker lengths may span across a large range, it is important to collect a significant number of whiskers for the proper identification of distribution parameters. The current practices of trying to locate only the longest whisker and measure do not give the full picture to the variety of whisker lengths present. Also, locating the maximum whisker on the specimen may be problematic, unless thorough inspection of all surface areas and proper whisker measurement techniques are employed. Collecting a set of whisker lengths and constructing a distribution, on the other hand, gives the probability that a certain length exists on the surface and allows for much more accurate predictions. Such distributions are also useful when attempting to virtually reconstruct whiskers on a surface. As an example, whisker risk assessment softwares utilize the distributions of lengths to see, whether whiskers of certain length may grow and possess shorting hazard, given geometry of electrical contacts.

Growth Angle

Growth angle is another important parameter in describing whisker growth. Just as whisker length distributions are needed to assess the risk of whisker shorting through simulations, growth angle is needed to determine the direction of growth. It is possible to have a situation where a whisker is of significant length that it can cause an electrical short, yet growing in a harmless direction away from a nearby conductive surface. Of course, as mentioned above, electrostatic forces or other external forces (e.g. air flow) may cause the whisker to bend substantially and make electrical contact, but this should be considered separate from the natural growth angle of the whisker.

Throughout this work, growth angle of the whisker shall be defined as angle between the whisker and the axis perpendicular to its surface of growth (denoted φ in Figure 20).

To help with identifying the growth angle, first we shall define height of the whisker – the vertical distance between the tip of the whisker and the plane from which it originates. Height can be calculated by the following formula, where all the nomenclature comes from Figure 20. Angle γ is the angle between plane in View 1 and the surface from which the whisker is growing. If View 1 was taken perpendicular to the whisker-growing surface, then $\gamma = 0°$. Also if $\gamma = 0°$, then Height = L_{bd} in Figure 20.

$$\text{Height} = \frac{\sin\left[\cos^{-1}\left(\frac{L_{cd}}{\frac{1}{\sin\theta}\sqrt{L_{cd}^2 + L_{ce}^2 - 2L_{cd}L_{ce}\cos\theta}}\right) + \gamma\right]}{\sin\theta}\sqrt{L_{cd}^2 + L_{ce}^2 - 2L_{cd}L_{ce}\cos\theta}$$

It can be easily shown, that the growth angle φ is calculated through the following formula, where all designations refer to Figure 20:

$$\varphi = \cos^{-1}\left(\frac{\text{Height}}{L_{ab}}\right) = \cos^{-1}\left(\frac{\sin\left[\cos^{-1}\left(\frac{L_{cd}}{\frac{1}{\sin\theta}\sqrt{L_{cd}^2 + L_{ce}^2 - 2L_{cd}L_{ce}\cos\theta}}\right) + \gamma\right]}{L_{ab}\sin\theta}\sqrt{L_{cd}^2 + L_{ce}^2 - 2L_{cd}L_{ce}\cos\theta}\right)$$

An issue comes up at the time of measuring the growth angle of the whisker with multiple segments. One of the two cases is then possible:

(1) Defining the growth angle as the angle between surface normal and the line of the effective shorting distance for the whisker as seen in Figure 21.

(2) Using the angle between surface normal and the first segment of the whisker that is closest to the root of the whisker as shown in Figure 22.

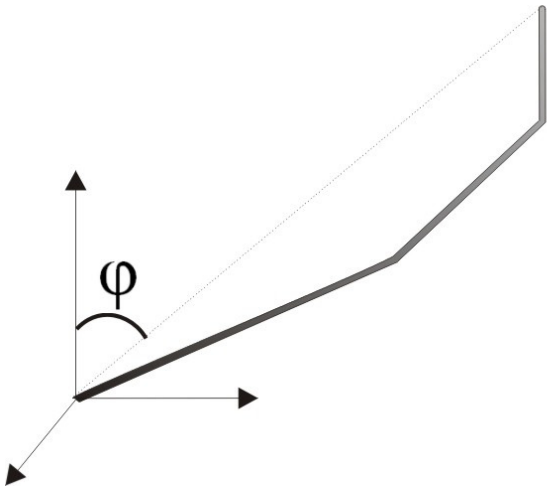


Figure 21 Growth angle measured as the angle between surface normal and the line of effective shorting length for the whisker

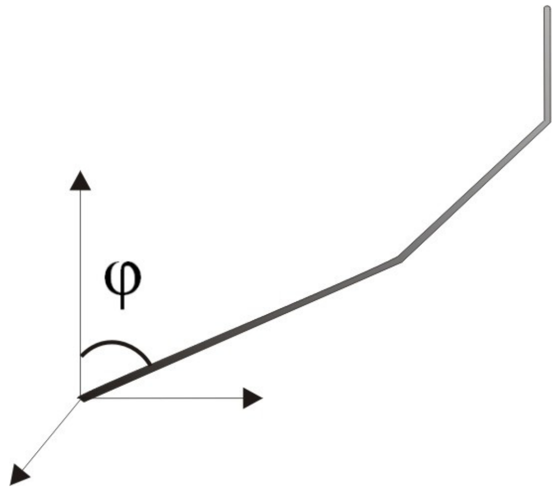


Figure 22 Growth angle measured as the angle between surface normal and the segment of the whisker closest to the root

In either case, it is possible to see that the growth angle would change if an additional kink in the whisker occurs, adding an extra segment that is oriented in a different direction from the previous segment.

Throughout this work, the case of measuring angle between surface normal and the line of effective shorting length shall be defined as the growth angle. While here the angle between surface normal and whisker has been chosen, there is currently no consistent manner in defining angle of growth. Hilty [70] defined the growth angle between the surface orthogonal and the whisker, while Fang [71] and Huang [72] measured the angle from the surface to the whisker.

Thickness (Diameter)

Along with whisker length, knowing whisker cross-sectional area would allows one to approximate the volume of material present in the individual filament. Of course, to do so, one would need the length of the whisker calculated via summation of all individual segments of the whisker (if it is multi-segmented) instead of using the shorting length. Note: the terms diameter and thickness will be used interchangeably in this work, as it will be approximated that whiskers have circular cross-sectional area.

While historically whiskers have been observed as having uniform diameter along their length, but that is not always the case In rare cases, filamentary whiskers may have a varying thickness, where part of the whisker has a significant change in thickness as compared to the rest of the whisker (Figure 23). Figure 24 shows a whisker that has a split along its length. Whiskers with gradual changes in thickness have also been observed. . For this discussion, thickness and diameter will be used interchangeably. Whisker cross-sections are not completely round but have been assumed round for the purposes estimating volume, fusing and strength properties.

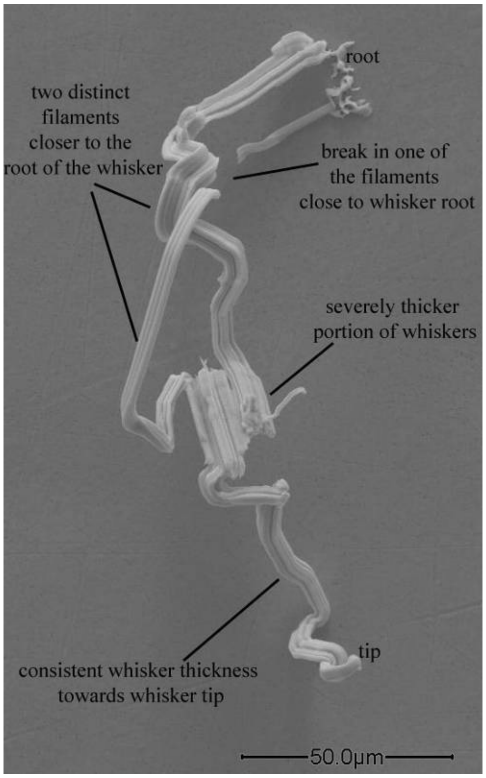


Figure 23 Example of a whisker with abrupt thickness changes along its length

Figure 24 Example of a whisker with a split on the end

It should be noted that tin growths are not always filamentary shapes. As examples, consider the nodule like tin growth in Figure 25 and odd shaped eruption of tin in Figure 26. These growths are not appropriate for diameter measurements as previously discussed.

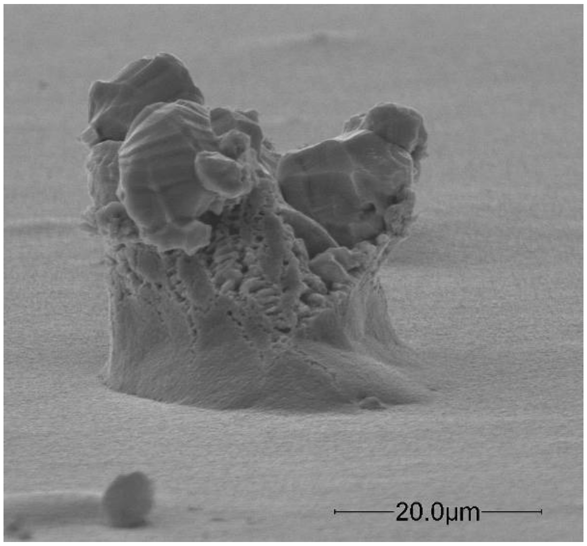


Figure 25 Example of a nodule with length: thickness ration less than 2:1

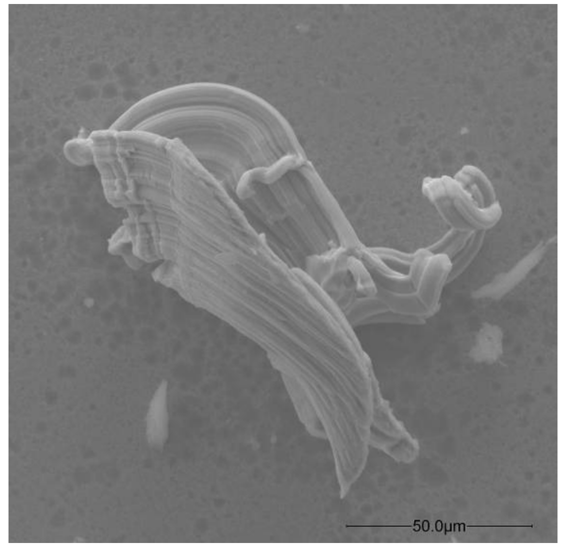


Figure 26 Example of a whisker with cross-section that can not be approximated as circular

For this work, measurement of whisker thicknesses were made from close-up views near the location where the whisker emerges from the surface. Whiskers were assumed to have a circular cross-section; therefore, their thickness would appear the same independent from the angle of view. The black line in Figure 27 is an example of how thickness of filamentary whisker has been measured for the purpose of this work. To ensure that the thickness is measured without capturing some distance along the length of a whisker, either software that outlines the boundaries perpendicular to the measurement was used, or a circle was fitted onto a whisker such that it touches the edges of the whisker without overhanging. The diameter of the circle is thus the diameter of a whisker (Figure 28).

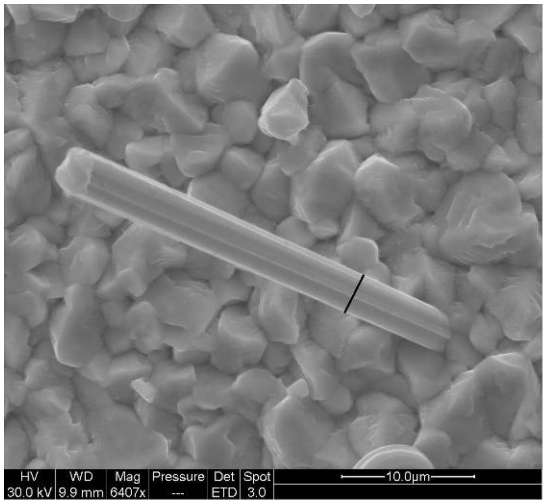


Figure 27 Example of thickness measurement for a filamentary whisker

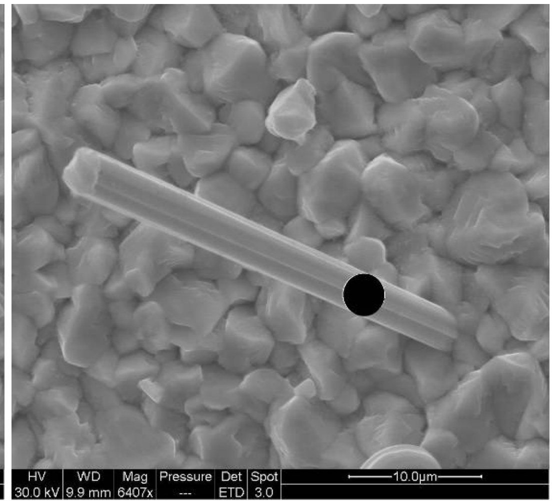


Figure 28 Fitting a circle onto a whisker for diameter measurements

Chapter 3: Evaluation of Environmental Tests

If you can look into the seed of time,
And say which grain will grow and which will not,
Speak then to me
W. Shakespeare, Macbeth (Act 1, Scene 3, Line 60)

The industry has put forward several documents as guidelines in assessing tin whisker growth on tin-rich finishes, namely

- JESD22-A121A [45] (issued by Joint Electron Devices Engineering Council - JEDEC)
- IEC 60068-2-82 [73] (issued by International Electrotechnical Comission - IEC)
- ET-7410 [74] (issued by Japan Electronics and Information Technology Industries Association - JEITA).

These documents define environmental testing conditions for assessing whisker growth. Limited knowledge, however, exists with regard to comparing the whisker growth in these short-duration stress tests to long-term ambient storage conditions.

All three documents require environmental storage as means of evaluating Sn coatings as whisker prone. The environmental conditions are summarized in Table 6.

Table 6 Summary of whisker environmental tests

Standard	IEC60068-82-2	JESD22-A121A (†)	ET-7410
Issue Date	2007/5	2008/7	2005/12
Optional Preconditioning	Soldering simulation Lead Forming	Reflow Lead Forming	Lead Forming
Ambient Storage	30°C, 60%RH 25°C, 55%RH 4000 hrs	30°C, 60%RH	30°C, 60%RH 4000 hrs
Elevated Temperature Humidity Storage (ETH)	55°C, 85%RH 2000 hrs	55°C, 85%RH 60°C, 87%RH (*)	55°C, 85%RH 2000 hrs
Temperature Cycling (TC)	Min: -55°C or -40°C Max: 85°C or 125°C 1000 or 2000 Cycles	Min: -55°C or -40°C Max: 85 (+10/-0)°C 1000 or 2000 Cycles	-40°C to 85°C 1000 cycles
Acceptance Criteria	50µm	--	--

(†) JESD22-A121A does not prescribe duration of tests or Acceptance criteria. JESD201 should be used for that
(*) Earlier version JESD22-A121, published May 2005

JEDEC has issued an additional acceptance requirements (JESD201 [47]) to go along with JESD22-A121A, which states accepted whisker lengths for different classes of products (ranged from most critical to least critical consumer hardware, 3 to 1) as a result of conducting environmental tests.

Given that these tests are designed to assess whether or not a certain tin coating (or coating process or coating system or set of materials and processes, etc.) is prone to whiskers, one would expect that these tests (like many accelerating reliability tests) would simply speed-up the process of whisker formation by minimizing the incubation time before the first whiskers grow and the time for whisker to reach a certain length as well. The test documents themselves, however, are not as optimistic: JESD22-A121A has a disclaimer that "these tests have not been correlated with longer environmental exposures of components in service"; IEC 60068-2-82 states that no quantifiable acceleration coefficient exists for the elevated temperature humidity storage as compared to some use conditions, while in applications where temperature cycling is present, the following acceleration conditions have been derived for Alloy42 (Fe-42%Ni) substrates:

$$\ln(n) = -2.8\ln\left(\frac{\Delta\vartheta}{1K}\right) + 22.2$$

where

n – is the number of cycles

$\Delta\vartheta$ - is the range between lower and upper temperature.

The equation was derived on assumption that the coefficient of thermal expansion (CTE) for the substrate material influences the growth of whiskers. As a result, material with CTE different from Alloy42 would produce different acceleration factor in temperature cycling test. No similar trend was defined for copper-based substrates, nor does the model provide any measurable properties of the materials involved.

Since no data exists comparing long-term storage of tin-plated surfaces to the predictions of the environmental tests, the effectiveness of these tests are highly questionable. It is also not apparent how consistent are these tests in creating more dense growth than the tin surfaces that are stored in ambient for the same duration of time. The questions to be asked are:

- Do the environmental tests predict what whisker growth would exist, if this tin plating was stored in ambient conditions for several years?

- If comparing between whisker growth during environmental test and whisker growth during the same amount of time spent in ambient, is it correct to expect
    - either no growth anywhere (equivalent to non-whiskering tin)
    - or a far more prominent growth during environmental exposure as compared to ambient storage? In this case, either the environmental tests have hindered whisker growth, or statistical interpretation of results is needed to make sure that the tested tin finishes are equivalent to the ones stores in ambient.

This chapter presents three sets of experiments that will cover several objectives.

- Experiment 1 – involves commercially-plated copper coupons that have seen sequential environmental exposure. The span of the test is 5 years and compares the whisker growth in environmental exposure to long-term storage. This experiment also assesses the ability of Ni underlayer to mitigate whisker growth. The sequential environmental exposure is addressed in Chapter 4 as well. Data collected from whisker thicknesses and compared to whisker lengths will be explored in Chapter 5.
- Experiment 2 – involves copper coupons plated in laboratory with commercially-available electrolytes. Specimens have been subjected to environmental exposure and compared to ambient exposure as control. Additionally, Chapter 4 will describe part of this experiment concerning

different sequences of environmental exposures and their growth results as compared to single-exposure tests and ambient.

- Experiment 3 – looks at an experimental electroplating of tin over brass coupons. Specimens have been subjected to the environmental exposures and are looked at several years after the exposure to see long-term effect of the tests.

All temperature cycling (TC) experiments were conducted in temperature shock chambers, with dwell times of 10min at each temperature (-55°C and +85°C). All whisker growth that occurred during elevated temperature humidity (ETH) was not corrosion-related – no corrosion observed on any of the specimens.

Experiment 1

Keywords: long-term storage comparison, end-of-test ambient vs environmental, sequential environmental test, nickel barrier layer, plating thickness, whisker growth angle

Test coupons were prepared with a copper (Olin 194 Cu-2.4Fe-0.03P-0.1Zn) substrate to simulate the substrate material commonly used in electronics industry. Individual coupons measured 31.7x12.7x0.5mm. A single commercial vendor electroplated all coupons with Sn with half of the specimens first plated with a Ni layer.

Surface Sn grain size averaged 4µm with a standard deviation of 1 µm. Using X-Ray Fluorescence (XRF), the thickness of tin plating was measured to average 7.5µm with a standard deviation of 1.7µm – further discussion is provided in Plating Thickness section below. On samples containing Ni, the underlayer thickness averaged 1.4 with a standard deviation of 0.2µm, which is close to the 1.27µm suggested minimal Ni barrier thickness [75]. Summary of the specimen characteristics may be found in Table 7

Table 7 Specimen characteristics for experiment 1

Substrate	Olin 194 Cu-2.4Fe-0.03P-0.1Zn
Specimen Size	31.7x12.7x0.5mm
Plating Type	Commercial line plated Sn
Underlayer	1.4±0.2µm Ni
Surface Grain Sizes	2-5µm
Plating Thickness	7.5±1.7µm

After plating, samples were held in room ambient for 2.5 years. Over that period, no whisker growth was observed. Some samples were then put through sequential environmental testing, while others were left in ambient conditions as control (Table 8).

Table 8 Number of coupons in each category of the test

	Sn on Cu	**Sn on Cu with Ni underlayer**
Control (4 years of ambient exposure)	2	2
Test (sequential environmental exposure)	6	6

At the time of test initiation, only JESD22-A121 [76] (published May 2005) test conditions were available, and the test was conducted based on this standard:

- Temperature Cycling: -55°C to +85°C, 10min dwells, 3 cycles/hour
- Elevated Temperature Humidity: 60°C and 85%RH

Standards published later (including IEC 60068-2-82 and JESD22-A121A) have only changed the Elevated Temperature Humidity conditions to 55°C and 85%RH. Figure

29 below shows the flow diagram of environmental exposure that coupons went through during the test. Whisker growth parameters (length and density) were gathered prior to temperature cycling, at 500 and 1000 temperature cycles, after 1500hrs of elevated temperature humidity, and after 1 and two years of ambient storage after environmental testing. All whisker inspections were done using Scanning Electron Microscopy (SEM).

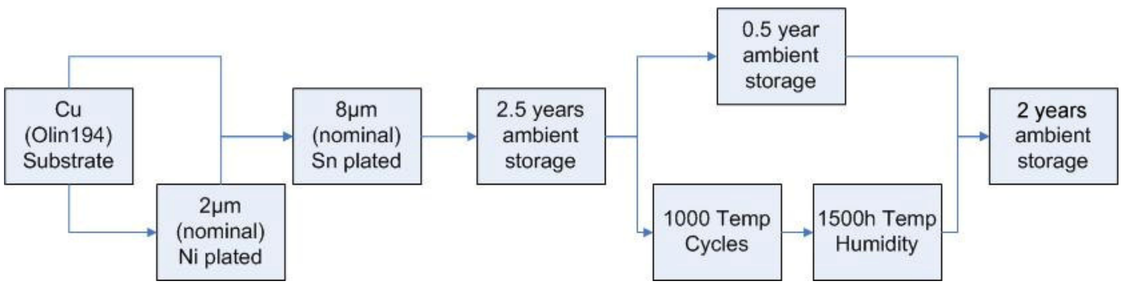


Figure 29 Flow diagram for Experiment 1

The length of a whisker was defined in accordance with JESD22-A121A with a single measurement of the effective shorting distance defining the whisker instead of the sum of lengths of the individual whisker segments.

For the density measurements, areas of 260μm by 220μm were randomly chosen across each coupon, with 11 areas analyzed per coupon (66 per condition). For the purpose of comparison, some – but not all – areas and whiskers were returned to at various stages of the test to visually record the progression of growth.

Upon completion of the environmental exposure, after 1000 temperature cycles and 2 months in elevated temperature humidity, both length and diameters of whiskers were measured.

For two years following test completion, coupons were stored in ambient environment. After one year, previously inspected areas of each coupon were re-examined to update whisker length and density measurements. Same was done after additional year, summing up to two years of ambient exposure after the end of environmental testing. We shall note here that no changes were observed on the coupons between the end of environmental stress test and the completion of two years in ambient storage.

Prior to the test, about 2.5 years after plating, no whiskers were found. After the sequential environmental exposure, whisker density and length distributions were recorded and are documented in Table 9 and Table 10.

As previously mentioned, no additional whisker growth was observed in two years of ambient storage following the end of the sequential environmental test for specimens both with and without Ni underlayer. Control coupons that were not exposed to sequential environmental testing have remained whisker-free for 5 years of ambient exposure.

Table 9 Whisker density (# whiskers/mm^2) mean ± standard deviation at various stages of the environmental stress test. Each datum point represents 66 density measurements

	Sn on Cu	**Sn on Cu with Ni underlayer**
500 temp cycles	2707 ± 1320	1535 ± 1392
1000 temp cycles	3216 ± 955	1906 ± 1524
2 months in elevated temp humidity	2987 ± 999	1864 ± 1480

Whisker length data was gathered from measuring 300-600 whiskers at different observation intervals. Whiskers were chosen from the areas used for density measurement.

Table 10 Whisker length mean ± standard deviation at various stages of the environmental stress test

	Sn on Cu (µm)	Sn on Cu with Ni underlayer (µm)
500 temp cycles	9 ± 5	9 ± 5
1000 temp cycles	12 ± 5	12 ± 7
2 months in elevated temp humidity	12 ± 6	19 ± 18

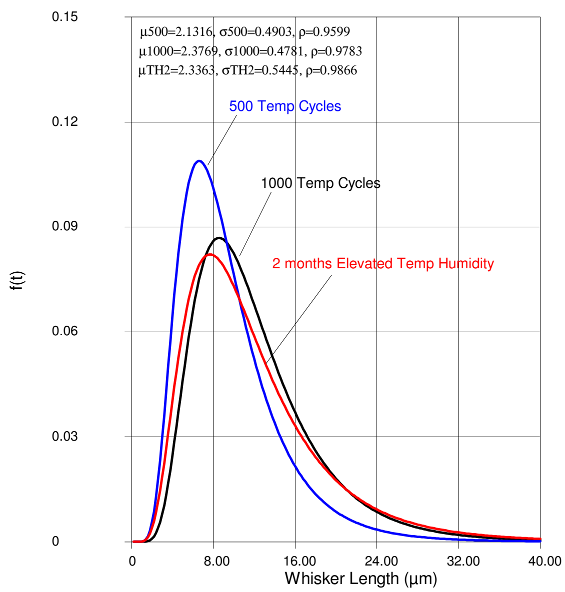


Figure 30 Whisker length distributions for Sn on Cu at three stages of the test

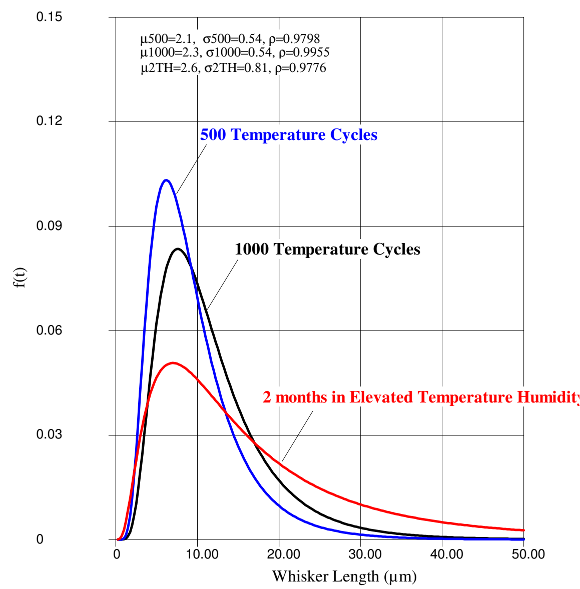


Figure 31 Whisker length distributions for Sn on Cu with Ni underlayer at three stages of the test

Consistent with observations made by Fukuda [77], the length data closely followed a log-normal distribution, with parameters displayed in Figure 30 and Figure 31.

Data collected for both whisker density and length seemed to progress forward from 500 to 1000 temperature cycles, however, have off-set back for 2-months of elevated temperature humidity that followed. This was most likely due to measurement uncertainties, where new areas and new whiskers were include in density and length data sets. Note that variance has increased with each consecutive set of measurements. ANOVA statistical analysis conducted on both sets of data (with Ni and with no Ni underlayer) for length and density between 1000 temperature cycles and 2 months of ETH are identified below in Table 11.

Table 11 ANOVA results of density and length of whiskers from Experiment 1 as compared between 1000 temp cycles and 2 months of ETH

	Sn over Cu	Sn over Cu with Ni underlayer
Density	No statistical difference	No statistical difference
Length	No statistical difference	Statistical difference present

It was noted previously that plating thickness of all samples was measured using X-Ray Fluorescence (XRF). Average thickness of tin across all 12 samples was 7.5µm with standard deviation of 1.7µm. The spread of values is indicative of the variations within a commercial plating process – the nominal plating thickness for the parts may not always be representative of the true values. A summary of plating thickness and whisker growth metrics is presented in Table 12.

Table 12 Plating thicknesses along with average length and density values for each sample at the completion of test

Sample#	Sample Description	Ni underlayer (µm)	Sn plating (µm)	Average Length (µm)	Max Length (µm)	Average Density (#/mm^2)
1	Sn on Cu, Ni underlayer	1.6	9.5	13	66	3573
2	Sn on Cu, Ni underlayer	1.6	8.5	14	50	1493
3	Sn on Cu, Ni underlayer	1.6	8.9	20	244	3337
4	Sn on Cu, Ni underlayer	1.3	4.5	30	214	126
5	Sn on Cu, Ni underlayer	1.3	4.5	30	256	185
6	Sn on Cu, Ni underlayer	1.3	9.1	22	213	2531
7	Sn on Cu		8.6	10	20	2556

Sample#	Sample Description	Ni underlayer (µm)	Sn plating (µm)	Average Length (µm)	Max Length (µm)	Average Density (#/mm^2)
8	Sn on Cu		6.8	14	39	2793
9	Sn on Cu		8.7	10	21	2192
10	Sn on Cu		7.2	12	27	3317
11	Sn on Cu		6.7	13	32	2984
12	Sn on Cu		7.5	12	24	3956

The whisker density and length appear to be related to plating thickness as can be seen in Figure 32 and Figure 33. Thicker plating does seem to induce more whisker growth, while average whisker length is greater for thinner coatings. Both whisker densities and lengths appear to be equally distributed along the higher plating thickness values (7-9µm), while a distinct difference exists at lower thickness (4.5µm). Maximum whisker lengths observed could be correlated to plating thickness: whiskers in 200-300µm range existed on both thicker and thinner plating, but not on medium-thickness finishes.

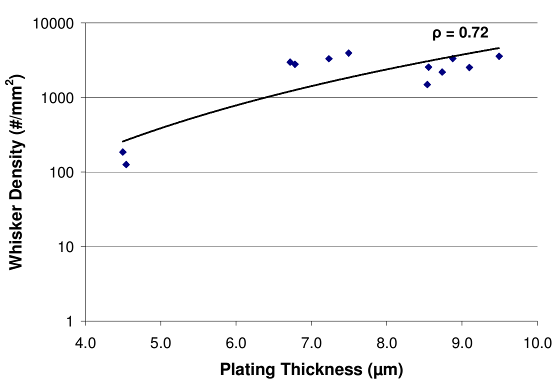


Figure 32 Correlation between whisker density and Sn plating thickness

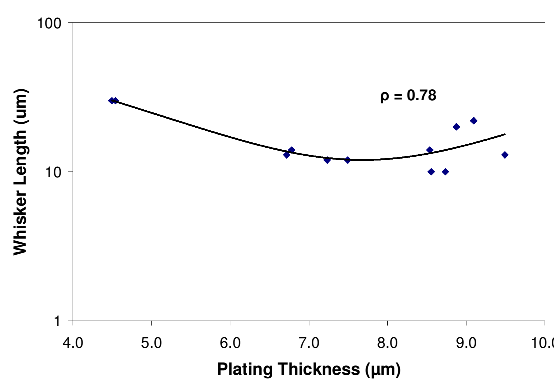


Figure 33 Correlation between whisker length and Sn plating thickness

As part of the study, 588 whiskers were selected for growth angle estimation. Not all whiskers used for the length distribution were incorporated in the growth angle distribution. The decision to ignore some whiskers was based on their shape – whiskers that generally were shorter than 10μm and at the same time ended up curling into an arc were ignored for angle calculations, due to the difficulty of assigning the growth angle for them. For the purpose of this work, the growth angle is defined to be between the effective shorting length line and an axis orthogonal to the surface, meaning that a whisker was first fitted with a single line to represent its length. The distribution of growth angles is given in Figure 34 with very few whiskers growing close to parallel to the surface in the 81°-90° range.

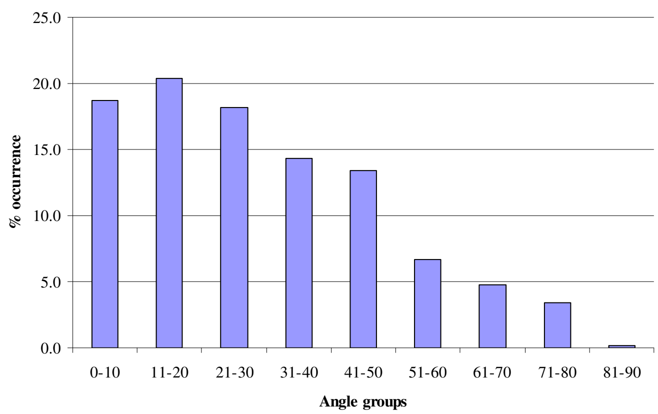


Figure 34 Growth angle distribution for 588 whiskers. Growth angle defined between the whisker effective shorting length and the axis perpendicular to the surface

These findings were consistent with previously reported observations of whiskers not having a preferential angle of growth and being less prone to grow parallel to the surface [64][65]. (Note: Hilty [64] defined the growth angle between the surface orthogonal and the whisker, while Fang [65] measured the angle from the surface to the whisker).

Angle of growth, however, is not necessarily a stagnant property of a whisker. As the whisker becomes longer and longer, it may change its orientation through addition of kinks or even by rotating a whisker without noticeable bends introduced along the length. Figure 3 demonstrates a whisker that has changed its growth angle during the 19-minute growth period without adding a kink. A more detailed video of this growth can be observed via CALCE tin whisker web page [80]. Similar effects are observed in Figure 46; it also compares two phenomena: addition of kink and an untraceable change of orientation as the whisker grows.

It is apparent that the Ni underlayer was not effective in preventing whisker growth during environmental exposures. To confirm the presence of Ni between Sn plating and base Cu, a Focused Ion Beam (FIB) section was conducted at the root of several whiskers (Figure 35). Continuous layer of Ni was found between the copper substrate and tin deposit under base of the whisker (Figure 36). To verify that Cu has not seeped through Ni underlayer, Sample 4 (with Sn thickness of 4.5µm) was analyzed under Electron Dispersive X-ray Spectroscopy (EDS). Using a 10kV accelerating voltage, and with the density of Sn at 7.3 g/cm^3, the penetration depth of the beam would be approximately 1µm [81]. At this depth, no Cu was detected, suggesting that Ni has prevented migration of Cu into the Sn.

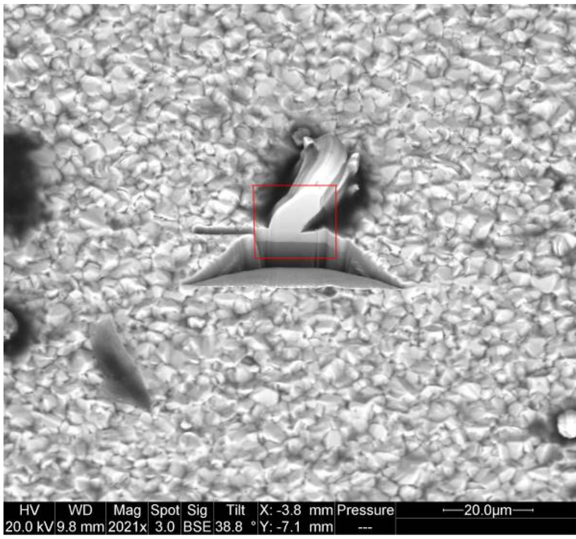


Figure 35 FIB section of a whisker on Sample 4 - Sn-plated Cu with Ni underlayer

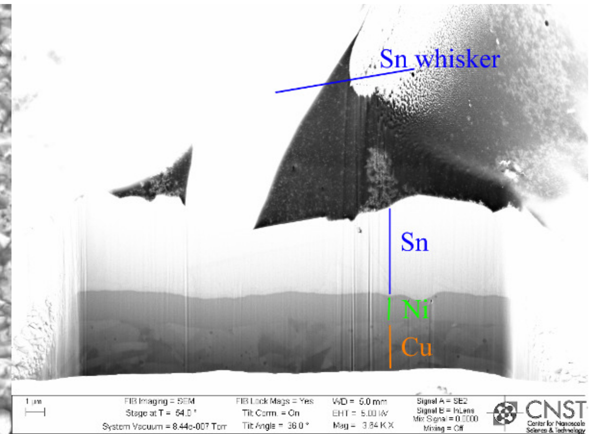


Figure 36 Magnified image from Figure 35, showing a continuous layer of Ni between Sn and Cu at the root of the whisker

The results of this test add to existing literature that does not confirm the benefit of Ni underlayer in whisker mitigation. While some [82][83] have shown that Ni underlayer has prevented whisker growth, others [84] [85][86] do not see its effects.

<u>*Experiment 2*</u>

Keywords: end-of-test ambient vs environmental

Experimental coupons were created from sheared 2.5cm x 2.5cm squares taken from a 0.8mm thick Cu plate (C11000, 99.9%Cu). Each coupon was polished with silicon carbide sandpaper and then with alumina powder down to 0.5µm particle size. Samples were then rinsed in water and later by alcohol to remove surface debris left by polishing and were ready for electroplating.

A 1.5L sulfuric acid-based Sn plating bath was prepared with commercially-obtained electrolytes (Caswell, Inc) and de-ionized water (resistivity 18.2MΩ cm). To ensure Sn deposition only on one side, the back of each sample was taped with an acidresistant tape. Samples were polished one day prior to electroplating. Immediately before plating, samples were immersed into 25% sulfuric acid for 5 sec, rinsed in de-ionized water, and then placed in the plating bath immediately. The bath was continuously agitated by a magnetic stirrer, while both the sample and the anode were placed vertically in the bath approximately 10cm apart. The plating set up can be seen in Figure 37. Plating was conducted at 23°C operating the bath at a constant current density of 3.5mA/cm^2. Plating efficiency at the given current density was calculated based on pre- and post-plating mass of the samples to be >90%.

To calculate plating efficiency, used Faraday's law of electrolysis:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

where

- m is the mass of the substance altered at an electrode
- Q is the total electric charge passed through the substance (multiply your current in Amps by the amount of time you spent plating in sec)
- F = 96 485 C mol^{-1} (same as Amp*sec/mol) is the Faraday's constant
- M is the molar mass of the substance (118.9 g/mol for Sn)
- z is the valence number of ions of the substance (electrons transferred per ion, 2 for Sn)

The formula thus becomes:

$$m = \left(\frac{Current[A] * Time[\sec]}{96485[A * \sec/mol]}\right)\left(\frac{118.9[g/mol]}{2}\right)$$

Compared this theoretical calculation to the mass gain from weighing specimens before and after plating, and determine the efficiency of plating:

$$\%eff = \frac{actualMass}{theoreticalMass} * 100\%$$

No hydrogen evolution was observed during the plating process. Samples were rinsed in de-ionized water and dried with a pressured stream of air promptly after plating. All 21 samples were electroplated individually within 2 days.

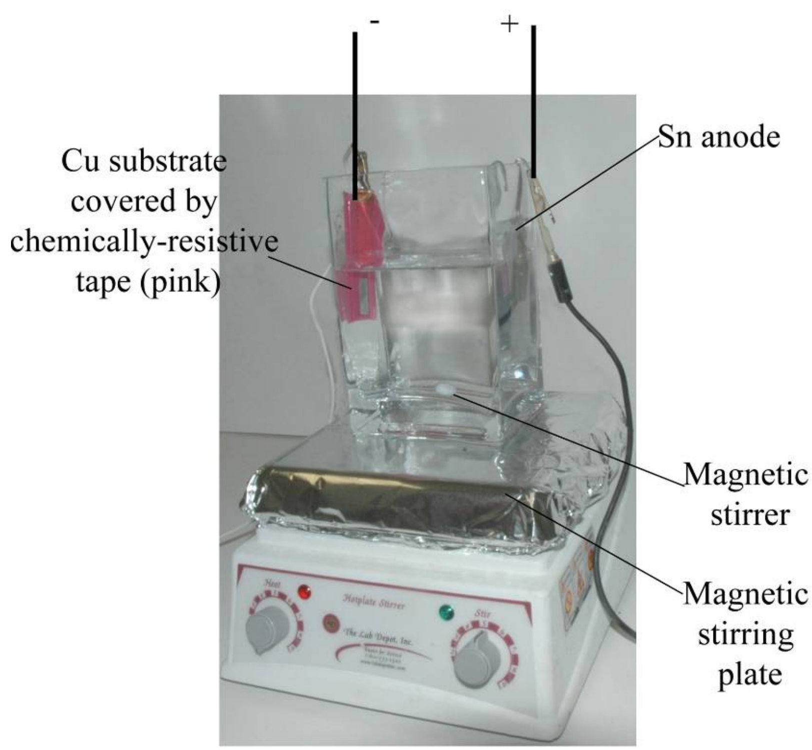


Figure 37 Electroplating bath set up for Experiment 2

Surface grain sizes were measured to be 2-5µm in diameter. Plated tin thicknesses were measured using X-Ray Fluorescence (XRF) and varied between 4 and 7µm from sample to sample. Summary of specimen characteristics may be found in Table 13.

Table 13 Specimen characteristics for Experiment 2

Substrate	C11000, 99.9% Cu
Specimen Size	2.5cm x 2.5cm x 0.8mm
Plating Type	Commercial Sn electrolytes plated in lab
Surface Grain Sizes	2-5μm
Plating Thickness	4-7μm

Samples were distributed into test sets between different environmental exposure conditions such that different thicknesses and order of plating would be equally distributed between the tests. The environmental exposures and the times of inspection are presented in Table 14.

Table 14 Environmental exposure conditions and inspection points conducted for Experiment 2. Each sample set consisted of three test coupons

Sample Set #	Environmental Exposure Condition	Inspection Points
1	Temp Cycles, -55°C/+85°C, 3 cycles/hr, 10min dwell, 1000 cycles	Pre-test, 500 cycles, 1000 cycles
2	Elevated Temp Humidity, 55°C/85%RH, 3000 hrs	Pre-test, 1000hrs, 2000hrs, 3000hrs
7	Ambient*	Days after plating: 0, 20, 44, 72, 83, 96, 119, 132, 149, 168, and 180

(*)Note: As will be discussed in Chapter 4, multiple inspections of ambient-stored samples were needed to compare to whisker growth for six different environmental tests.

Samples were held in ambient conditions thirteen days before distributing between different environmental exposures. A total of three samples were used per sample set. The conditions used for testing are identical with ones stated in JESD22-A121A.

- Temperature cycling (TC) was conducted in a shock chamber between -55°C and +85°C, with 10 min dwells, 3 cycles per hour
- Elevated temperature humidity (ETH) was a constant exposure to +55°C and 85%RH

- For control, ambient exposure was done at ~23°C and ~50%RH

All samples were examined under SEM prior to environmental exposures, and no whiskers were observed upon initial inspection. Throughout the test, all samples were examined for whisker growth with whisker length and densities documented at selected time intervals as indicated in Table 14. Whisker density was measured by examining 10 areas on each sample; this totals to 30 areas for each of the seven sets of samples. Each area was 0.23mm^2, and was selected by randomly generating X- and Y-coordinates on each sample, such that the results are not biased to the observer. Only tin growths with length to diameter ratios greater than two were considered. As an example, Figure 38 depicts whiskers (circled) and other post-plating formations.

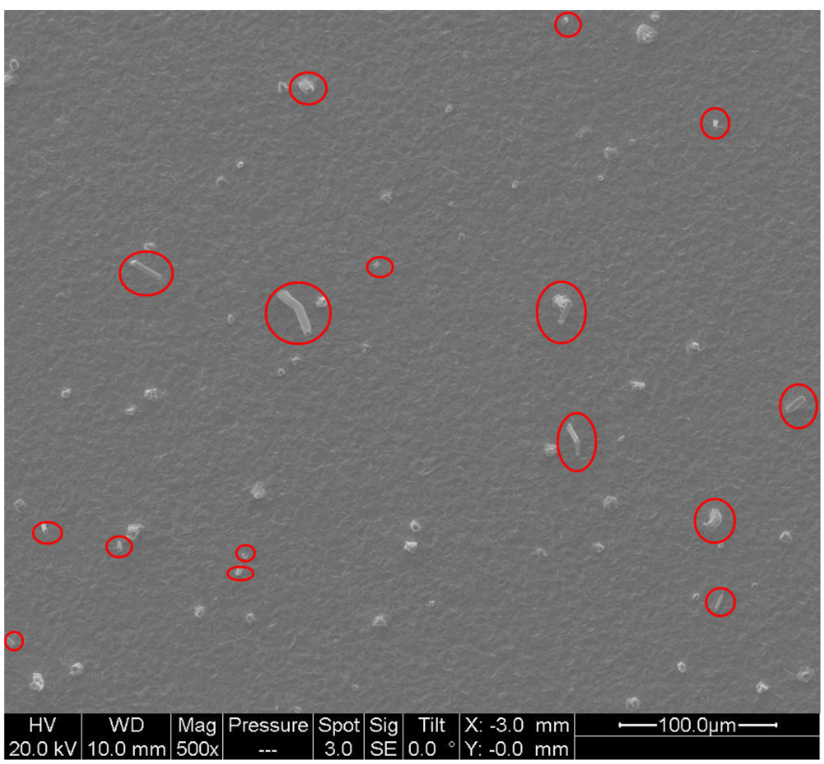


Figure 38 Example of whisker density count on ambient-stored sample after 168 days. Total of 16 whiskers present on area of 0.23mm^2

When whiskers were present on the documented area, at least five whiskers per area were documented for length. If less than five whiskers were present on a given area, all whiskers were measured. At least half of the areas on each sample were revisited at each inspection interval – the rest were randomly chosen locations. Special care was taken to try and capture the longest whisker on sample each time. For the purpose of this experiment, whisker length was defined as the sum of all individual segments of the whisker.

The end-of-test results are presented in Table 15 (more detailed results can be found in Chapter 4, Experiment 2 description). The lognormal-distributed lengths at end of respective exposures can be seen for temperature cycling in Figure 39, and for elevated temperature humidity in Figure 40.

Table 15 Summary of whisker density and length at the end of tests for Experiment 2

Exposure	Mean Density ± STD (whisker/mm2)	Mean Length ± STD (µm)	Maximum Observed Length (µm)
TC: -55°C/+85°C. 1000 cycles	12 ± 9	10 ± 4	33
ETH: +55°C/85%RH, 3000hrs	19 ± 1	11 ± 4	34
Ambient at 44 days (same as end of TC)	32 ± 16	14 ± 7	38
Ambient at 149 days (same as end of ETH)	41 ± 16	17 ± 10	49

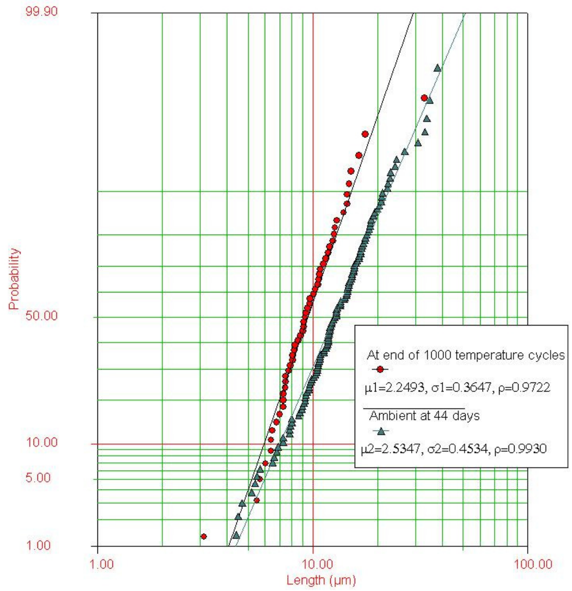


Figure 39 Lognormal cumulative probability distribution plot for whisker lengths after end of TC exposure and corresponding control 44 days in ambient

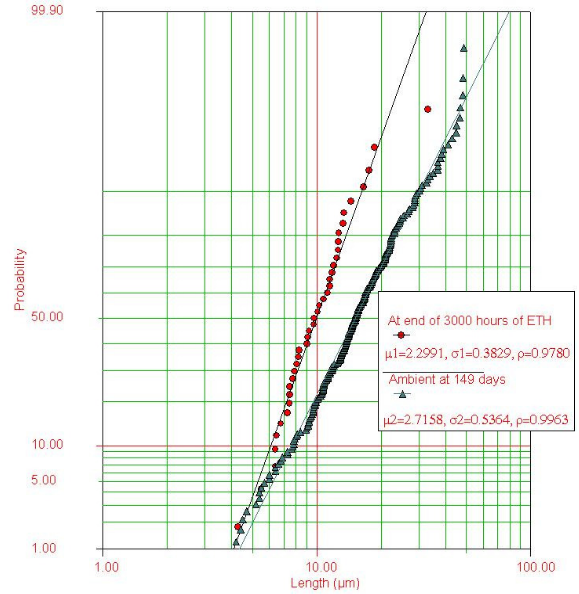


Figure 40 Lognormal cumulative probability distribution plot for whisker lengths after end of ETH exposure and corresponding control 149 days in ambient

It appears that the ambient exposure has produced somewhat more and longer growth than either of the environmental exposures, although this difference is not very pronounced. This is not consistent with the results of Experiment 1, where even if looking at specimens after temperature cycling exposure (and ignoring the sequenced elevated temperature humidity), they have produced considerable growth, compared to no growth for control specimens stored in ambient.

<u>*Experiment 3*</u>

Keywords: environmental vs long-term storage comparison

For this experiment, specimens were prepared from cartridge brass and later electroplated with tin. Brass (Cu-30%Zn) sheet of 1mm thickness was sheered into 2.5cm x 1.2cm individual coupons. An experimental electroplating bath with pulse reverse current deposition was used. Unlike the deposits in Experiments 1 and 2 which were done under direct current, this deposition used two different set current levels, a periodic reverse of current, and some off-time. During direct current stages of the plating (also known as cathodic modulation), tin would be reduced on the surface, and a potential for hydrogen evolution would also exist. However, during reversal of current (or anodic modulation), tin would be oxidized, and during this time, tin ions will be replenished around the cathode for subsequent cathodic pulses. Off-times are characterized by no current passing through the system, and this too serves to replenish tin ions in the vicinity of the cathode. More information on this plating procedure and the theory behind it can be found in the original publication [87]. The specimens described herein have been characterized as "low tensile stress" specimens by the manufacturer.

The electroplating was done in a methanesulfonic acid (MSA) based bath consisting of:

- 240 mL/L of MSA
- 107 g/L of tin (II) methanesulfonate
- 300 ppm Triton-X

Electroplating was carried out at 37°C using a rotating cathode. Each coupon was plated to 9μm of Sn and had plated area of 100mm^2. A total of 6 specimens were prepared as having 'low tensile stress' in tin plating. Summary of specimen properties may be located in Table 16.

Table 16 Specimen properties for Experiment 3

Substrate	Brass 260 (Cu-30Zn)
Specimen Size	2.5cm x 2.5cm x 0.8mm
Plating temperature	37°C
Plated Area	100µm^2
Plating Type	Experimental electrolytes plated in lab
Surface Grain Sizes	2-8µm
Plating Thickness	9µm

After plating, specimens were stored in ambient environment for 4 months. Beyond that, three of the specimens have been subjected to temperature cycling (TC), and three to elevated temperature humidity (ETH). Upon completion of the test, specimens were stored in ambient environment to be revisited later on (Figure 41). The details of the exposure can be found in Table 17 below.

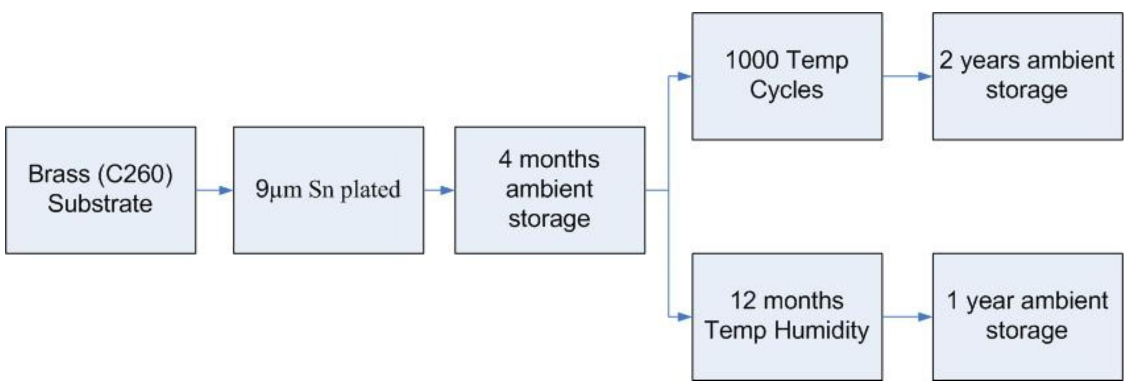


Figure 41 Flow diagram for Experiment 3

Table 17 Details of environmental exposure for Experiment 3

	Temperature Cycling (TC)	**Elevated Temperature Humidity (ETH)**
Environmental conditions	-55°C to +85°C, 10-min dwells, 3 cycles per hour	60°C / 85% RH
Duration of exposure	1000 cycles	12 months
Whisker inspection intervals	Pre-test, 500 cycles, 1000 cycles, 1 year after TC, 2 years after TC	Pre-test, 5 months, 9 months, 12 months, 1 year after ETH
Total time since plating	~ 2.5 years	

Examination of each sample included whisker density collection on at least five areas, and if whiskers were present, at least five were documented on each area, with the exception of areas that had fewer that five whiskers, in which case – all of the whiskers present were documented. Upon revisiting the samples at different inspection intervals, same areas were looked at as during prior observations, and additionally several new areas were added. Whisker lengths for this experiment were defined as the shorting length between whisker root and point furthest on the whisker.

The results at different intervals throughout the test can be seen in Table 18. Note that the inspection intervals of 2 years after TC and 1 year after ETH actually refer to the same point in time: ~2.5 years after samples were electroplated. No whisker growth was observed on any specimens during the 4-month ambient storage prior to the test. For specimens in temperature cycling, no whiskers grew during the environmental exposure or for one year of ambient storage after it. However, an additional year in ambient has produced extensive whiskers, with some exceeding 4mm in length (Figure 42).

Specimens that went through ETH exposure showed numerous whisker growths at the end of five months of exposure. The density of whiskers (# of whiskers per mm^2) was almost unchanged throughout additional seven months of ETH and a subsequent one year in ambient. Whisker lengths did see a slight increase between five and nine months in ETH, but almost no changes occurred beyond that (Figure 43). After 12 months in ETH, specimens were placed in ambient environment, and revisited only a year later. By locating the exact areas used for whisker observations after 12 months in ETH inspection, it was apparent that no whisker growth has occurred during a year of ambient storage that followed it.

Table 18 Whisker growth results for Experiment 3

Exposure	**Inspection Interval**	**Whisker density (#/mm2)**	**Whisker length (µm)**	**Maximum whisker length observed (µm)**
		Mean ± STD	**Mean ± STD**	
TC	Pre-test	No whiskers		
	500 cycles	No whiskers		
	1000 cycles	No whiskers		
	1 year after TC	No whiskers		
	2 years after TC	24 ± 12	125 ± 181	4143
ETH	Pre-test	No whiskers		
	5 months	246 ± 41	18 ± 18	161
	9 months	285 ± 135	31 ± 28	194
	12 months	281 ± 147	31 ± 26	194
	1 year after ETH	281 ± 147	31 ± 26	194

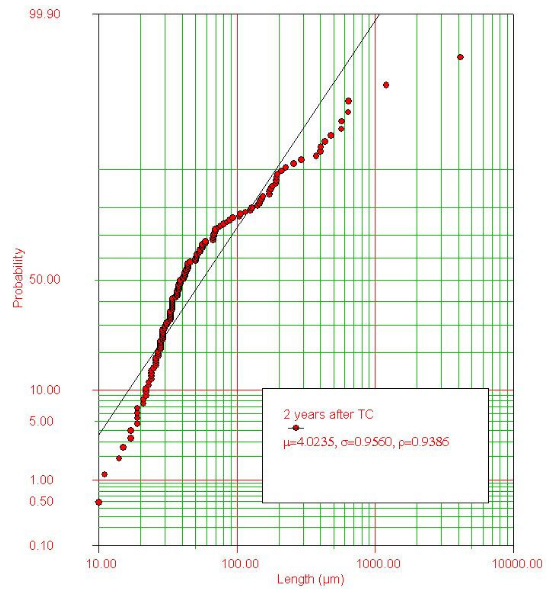


Figure 42 Lognormal cumulative probability distribution plot for whisker lengths 2 years after TC

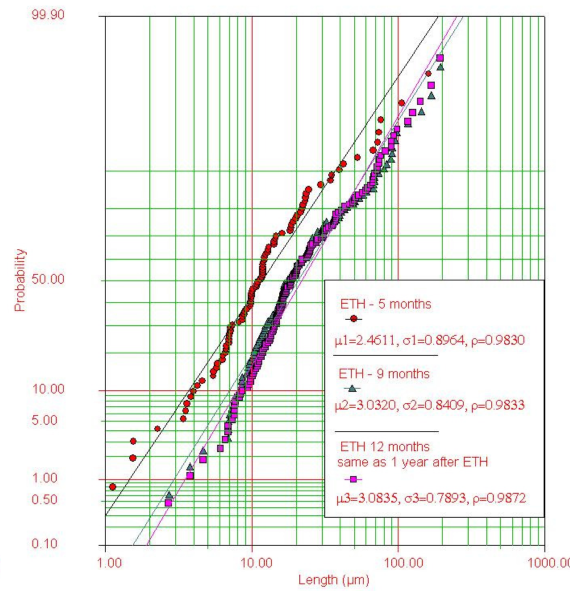


Figure 43 Lognormal cumulative probability distribution plot for whisker lengths at 5, 9, and 12 months of ETH and 1 year after ETH

Looking at the whisker growth on specimens that underwent temperature cycling, it is unclear whether the environmental exposure has contributed to the whisker growth. However, given that no whiskers have appeared on surface one year after the exposure, it is likely, that its effect was minimal. In that case, the growth that was observed two years after the exposure may be attributed to the time in ambient exposure alone. On the other hand, the specimens that underwent ETH have not gathered any new growth in the two years since the exposure. Perhaps emergence of whiskers during ETH had an impact on future whisker growth. Nevertheless, the whisker density and lengths seen during ETH are not predictive of the growth seen after 2 years of ambient exposure.

<u>*Summary*</u>

The three experiments presented above have shown different outcomes. All three experiments utilized similar environmental exposures to promote tin whisker growth.

Experiment 1 had Sn-plated Cu specimens (with and without Ni unerlayer) stored for a period of 2.5 years prior to the environmental exposure, with no whisker growth. During the sequence of 1000 temperature cycles (-55°C to +85°C, 10 min dwells, 3 cycles an hour) followed by 2 months in elevated temperature humidity (60°C, 85%RH), whisker growth in thousands per mm^2 was evident, with whisker lengths up to 250µm. However, no further whisker growth occurred in the following two years of exposure, nor did any whiskers grow on the control specimens stored in ambient environment for five years. The whiskers appear to be induced by the environmental exposures. Ni barrier layer was shown insufficient in preventing whisker growth, furthermore, longer whiskers were evident on specimens with Ni underlayer as compared to just Sn-plated Cu.

Experiment 2 also dealt with Sn-plated Cu (different Sn electrolytes) specimens that saw environmental exposure soon after plating. At the end of temperature cycling and elevated temperature humidity exposure, whisker growth was similar to that observed on ambient-stored specimens that were stored in ambient for time equal to that of environmental stress tests. It appears that environmental exposure did not have an effect on whisker growth as compared to ambient exposure.

Experiment 3 addressed an experimental electroplating process with Sn-plated brass specimens. Whisker growth was apparent during elevated temperature humidity (ETH) exposure, but no additional growth was seen once the specimens were out in ambient for one year after completion of ETH. On the contrary, the specimens in temperature cycling test have shown no growth during the test or for an additional one year of ambient storage after. However, between year one and two of ambient exposure after the test, a massive amount of whisker growth was apparent, far exceeding the whisker lengths seen in ETH, but with an order of magnitude lower density.

From these results, it can be concluded that the existing temperature cycling and elevated temperature humidity tests may over-predict, under-predict, or have no effect on whisker growth as compared to ambient storage. Environmental conditions alone are thus not the single driving factors behind whisker growth. As was mentioned in Chapter 1, tin whisker growth is a function of many macro-scale parameters, and temperature and humidity are just some of them. It is important to develop an understanding how other factors play a role, and how they act in collaboration with environmental exposures in whisker formation.

Chapter 4: Evaluation of Sequential Environmental Tests

If we knew what we were doing,
It would not be called Research
A. Einstein

As Chapter 3 has shown, the environmental tests conducted in accordance with existing testing standards do not have consistent predictive value with short-term or long-term tin whisker growth in ambient storage. This chapter explores the possibility of sequential environmental tests providing such a prediction. Experiments 1 and 2 will be revisited from Chapter 3, this time with a closer examination of the effects of sequencing temperature cycling (TC) and elevated temperature humidity (ETH) exposure. Results will provide an answer as to whether some combination of environmental tests should be used for whisker promotion, as compared to a single environment exposure.

Experiment 1

This experiment has already been described as Experiment 1 in Chapter 3, where the specimens were commercially tin-plated copper. With a total of 16 specimens: eight that have Ni underlayer between Sn and Cu, and eight without the underlayer. Specimen properties may be reviewed in Table 7. All specimens were stored in ambient for 2.5 years with no whiskers growing on the surface. After 2.5 years of ambient exposure, four specimens (two with underlayer and two without) were kept in ambient as control, and the rest were subjected to sequential environmental load:

- 1000 Temperature Cycles: -55°C to +85°C, 10min dwells, 3 cycles/hour
- 2 months of Elevated Temperature Humidity: 60°C and 85%RH

After environmental loading, an additional two years of ambient storage have brought the life of specimens to five years since plating (review flow diagram of specimen exposure in Figure 29). During this time, the control ambient-stored specimens have produced no whisker growth. The growth seen on environment-stressed specimens was confined to the time of environmental exposures, and no whiskers grew prior or after it. The growth progression can be seen in Figure 44 for specimens with Ni underlayer and in Figure 45 for specimens without Ni.

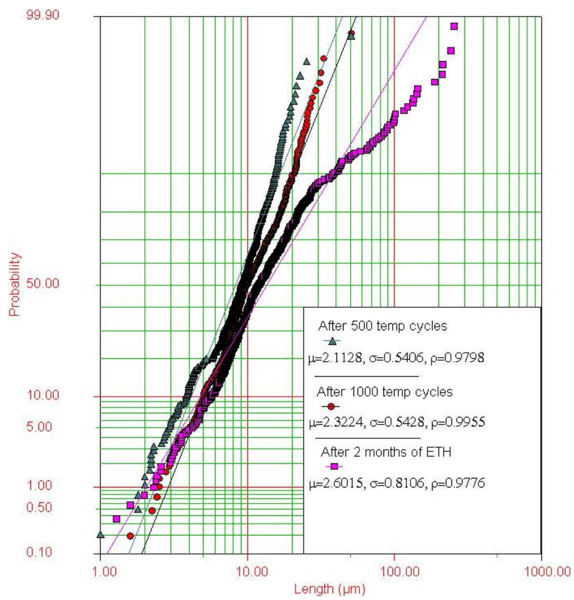


Figure 44 Lognormal cumulative probability distribution plot for whisker lengths on specimens with Ni underlayer in Experiment 1

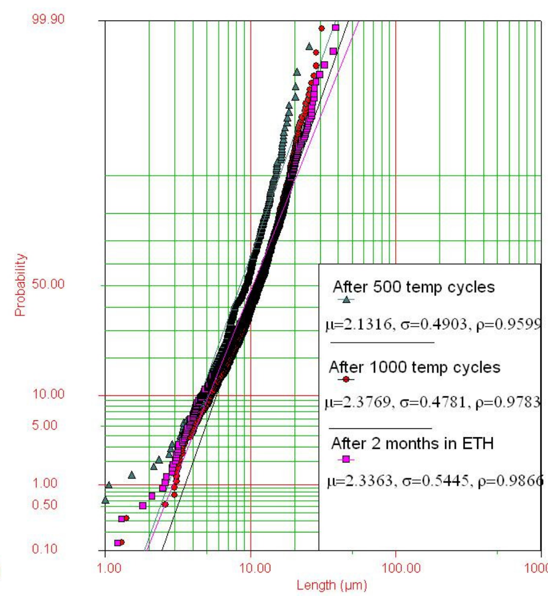


Figure 45 Lognormal cumulative probability distribution plot for whisker lengths on specimens without Ni underlayer in Experiment 1

The results of this experiment show a massive growth of shorter (<50µm) whiskers during TC, and little additional growth during consecutive ETH. However, some specimens have produced significantly longer whiskers during ETH (>200µm).

Experiment 2

Experiment 2 was initiated at the end of Experiment 1, when the data for TC and ETH was gathered. It was of interest to see the contribution of TC and ETH to the growth of whiskers in sequential environmental exposures. And perhaps devise a test where a combination of exposures would serve as an active whisker promoter. At the time, it was unknown that specimens from Experiment 1 would not add any growth in the two years following the environmental exposure.

Experiment 2 specimens were prepared by plating Sn over Cu substrates to a thickness of 4-7µm. (More details on specimen preparation can be found in Table 13) Specimens were distributed into test sets between different environmental exposure conditions such that different thicknesses and order of plating would be equally distributed between the tests. The test sets are presented in Table 19. Each specimen set received three test specimens.

Table 19: Environmental exposure conditions and inspection points conducted during the test. Each specimen set consisted of three test coupons

Specimen Set #	Environmental Exposure Condition	Inspection Points
1	TC (1000 cycles)	Pre-test, 500 cycles, 1000 cycles
2	ETH (3000 hrs)	Pre-test, 1000hrs, 2000hrs, 3000hrs
3	TC (1000 cycles) followed by ETH (3000 hrs)	Pre-test, 500 cycles, 1000 cycles, 1000hrs, 2000hrs, 3000hrs
4	ETH (3000 hrs) followed by TC (1000 cycles)	Pre-test, 1000hrs, 2000hrs, 3000hrs, 500 cycles, 1000 cycles
5	TC (500 cycles) followed by ETH (3000 hrs) followed by TC (500 cycles)	Pre-test, 500 cycles, 1000hrs, 2000hrs, 3000hrs, 1000 (total) cycles
6	ETH (1500 hrs) followed by TC (1000 cycles) followed by ETH (1500 hrs)	Pre-test, 1000hrs, 1500hrs, 500 cycles, 1000cycles, 2000 (total) hrs, 3000 (total) hrs
7	Ambient*	Days after plating: 0, 20, 44, 72, 83, 96, 119, 132, 149, 168, and 180

(*)Note: Control specimens left in ambient exposure were inspected each time an inspection was conducted on environmentally exposed specimens in order to obtain a baseline for comparison.

Specimens were held in ambient conditions thirteen days before distributing to different environmental exposure conditions. The conditions used for testing are identical with ones stated in JESD201 [47].

- Temperature cycling (TC) was conducted in a shock chamber between -55°C and +85°C, with 10 min dwells, 3 cycles per hour
- Elevated temperature humidity (ETH) was a constant exposure to +55°C and 85%RH
- For control, ambient exposure was done at ~23°C and ~50%RH

All specimens were examined under a Scanning Electron Microscope (SEM) prior to environmental exposures, and no whiskers were observed upon initial inspection. Throughout the test, all specimens were examined for whisker growth with whisker length and densities documented at selected time intervals as indicated in Table 14. Each inspection point during the test collected 30 locations of $0.23mm^2$ each on every specimen set for whisker density distribution. At least five whiskers were collected from each location to be used for whisker length distribution. If less that five whiskers were present, all whiskers at that location were measured. Summary of whisker density and length for each test condition at the end of all the tests can be found in Table 15. Detailed comparisons can be seen in Appendix C. In this experiment, the ambient control produced the longest whiskers and the densest growth. This finding implies that Temperature Cycling, Elevated Temperature Humidity or any sequence of the environmental exposures does not accelerate whisker growth for the specimens under test.

Table 20 Summary of whisker density and length at the end of tests

Set #	Exposure	Mean Density ± STD (whisker/mm^2)	Mean Length ± STD (μm)	Maximum Observed Length (μm)	# whiskers measured
1	TC	13 ± 8	10 ± 4	33	53
2	ETH	13 ± 12	11 ± 4	34	74
3	TC – ETH	24 ± 24	11 ± 4	30	97
4	ETH – TC	12 ± 12	12 ± 4	24	81
5	TC – ETH – TC	5 ± 13	17 ± 12	39	23
6	ETH – TC – ETH	11 ± 12	11 ± 4	21	62
7	Ambient 180 days	42 ± 18	18 ± 10	61	240

Table 21 and Table 22 below illustrate the progression of whisker length and density on the ambient-stored specimens. Captured whisker lengths were found to fit a Lognormal distribution.

Table 21 Lognormal parameters of whisker lengths at different inspection intervals of ambient-stored specimens

Time in Ambient (days)	m	s	ρ	# whiskers measured
20	2.37	0.47	0.9821	58
44	2.53	0.45	0.9930	123
72	2.63	0.49	0.9923	125
83	2.67	0.51	0.9924	159
96	2.68	0.52	0.9927	170
119	2.69	0.53	0.9950	188
132	2.70	0.54	0.9963	200
149	2.72	0.54	0.9963	219
168	2.71	0.54	0.9974	236
180	2.72	0.54	0.9967	240

Table 22 Normal parameters of whisker densities at different inspection intervals of ambient-stored specimens

Time in Ambient (days)	mean	STD	ρ
20	22	10	0.9750
44	32	16	0.9855
72	32	16	0.9837
83	39	19	0.9863
96	37	18	0.9825
119	40	15	0.9749
132	41	17	0.9770
149	41	16	0.9825
168	42	18	0.9815
180	42	18	0.9763

To compare the effects of environmental exposures, ANOVA analysis was conducted on whisker densities and lengths between all the specimen sets at the end of the test as well as to respective end-of-test ambient control. Two sets of whisker density (or length) data were considered identical, if $F < F_{critical}$. They were considered different otherwise. Results can be seen in Table 23.

Table 23 Results of whisker density and lengths ANOVA analysis on the different specimen sets of Experiment 2.
First number: density correlation, second number: length correlation
1 - data sets are considered identical. 0 - data sets are considered different

	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
Set 1 – end of test		11	11	11	00	11
Set 2 – end of test			01	11	00	11
Set 3 – end of test				01	00	01
Set 4 – end of test					00	11
Set 5 – end of test						10
Set 6 – end of test						
Ambient 44 days	00					
Ambient 149 days		00				
Ambient 168 days			00			
Ambient 180 days				00	01	00

In general, the environmentally-stressed sets seem to be similar to each other, with the exception of set 5 (TC-ETH-TC). The environmentally-stressed sets are identified as different from the ambient-stored specimens. However, Table 20 shows that this difference is not profound, as has been seen in Experiments 1 and 3 from Chapter 3. A time-lapse version of whisker growth in ambient over a period of approximately 400 days can be observed in Figure 46, where the same whisker was captured on 11 different occasions. All images were taken perpendicular to the surface of the specimen, meaning that any change in view of the whisker is due to a change in growth angle of the whisker. Note how images from 20 to 119 days show a straight filament whisker, and yet its orientation is changing. A more drastic change of orientation is introduced at day 132, where a kink (or bend) has been added into the whisker. This shows two different ways in which whisker may change its orientation during growth. While a kink in a whisker is a permanent feature that may result in a change in growth direction, the time lapse images indicate that a kink is not required for a whisker to change direction. Thus, direction of growth is not necessarily fixed and can be time dependent.

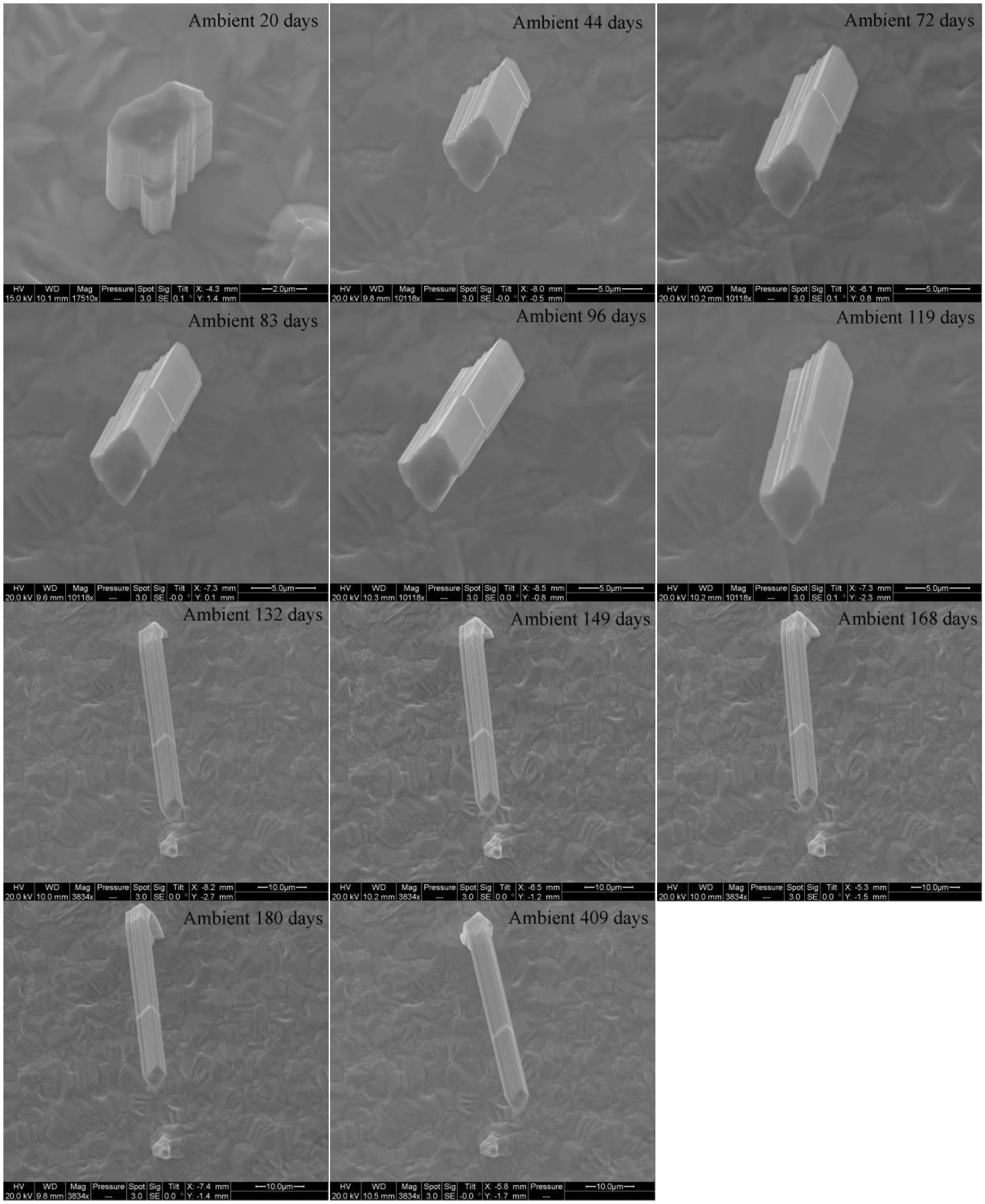


Figure 46 Example of growth progression of a whisker in ambient storage conditions captured at 19, 43, 72, 84, 96, 119, 132, 149, 168, 180, and 409 days after plating

In summary, Experiments 1 and 2 have demonstrated lack of consistency in the way that sequential environmental tests influence the growth of whiskers. While Experiment 1 showed abundant whisker growth during the sequence of temperature cycling and elevated temperature humidity, no whisker growth occurred during five years of ambient storage used for control. On the contrary, specimens stored in various sequences of environmental conditions in Experiment 2, have retarded whisker growth, as compared to ambient-stored control specimens. The results indicate that sequential environmental testing is no more reliable at predicting growth than single environmental testing. Factors other than environment may be playing a larger role.

Chapter 5: Length and Thickness of Whiskers

While the length of the whiskers has been widely addressed, their thickness has not been so vigorously reported. From early reports it became obvious that tin whisker thicknesses are typically in 1-5µm range [88][89]. Same holds true for cadmium whiskers [3]. The fluted-shape of whiskers, however, does not make them necessarily circular in cross-section. As has been shown by Sakuyama [90], the whisker cross-section is rather irregular at the edges (Figure 47). For ease of the following calculations, however, whiskers will be approximated as cylinders, and terms 'thickness' and 'diameter' will be used interchangeably.

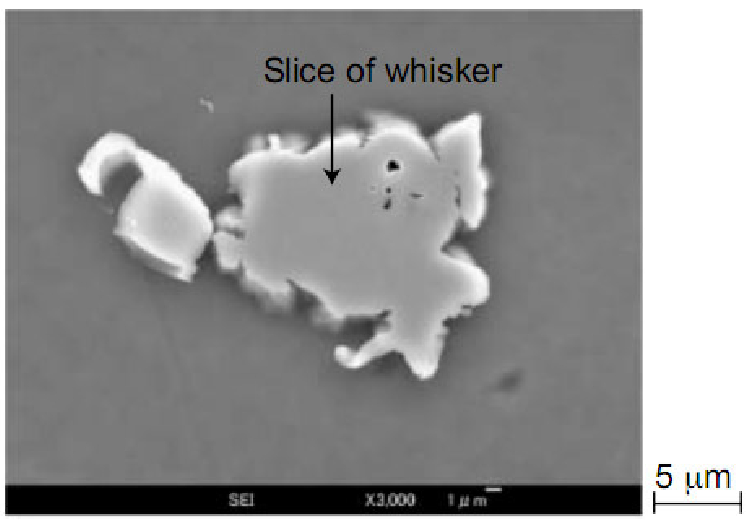


Figure 47 Cross-section of a whisker [90]

The objectives of this chapter are to present quantitative analysis of a large group of whisker thicknesses, as well as to assess whether they are related to whisker lengths. The first objective gives the opportunity to do probabilistic modeling of whiskers penetrating conformal coatings and predicting melting currents for whiskers.

Whisker thickness is important when considering the ability of a whisker to penetrate a conformally coated surface. It has been previously shown that the ability of an existing metal whisker to penetrate a layer of conformal coating on an adjacent conductor and come in contact with that conductor is hindered by whisker buckling **Error! Reference source not found.** when in contact with the coating as seen in Figure 48.

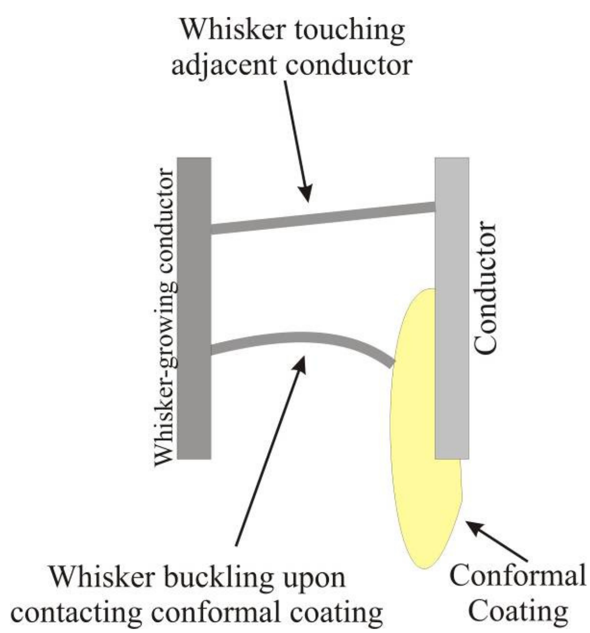


Figure 48 Schematic representation of two whiskers: one growing from a surface and buckling upon contacting conformal coating applied on a second conductor, and another whisker creating mechanical contact with the adjacent surface on an area with no conformal coating

The force required to buckle a metal whisker is estimated to be [42]:

$$F_B = \frac{\pi^2 EI}{(KL)^2} \approx \left(\frac{\pi^3 E}{32}\right)\left(\frac{d^4}{L^2}\right)$$

E = Young's Modulus of whisker material

I = Area moment of Inertia. For a circular cross-section $I = \frac{\pi d^4}{64}$

L = Length of whisker

d = diameter or thickness of whisker

K = Column effective length factor.

K=0.5 for whiskers fixed at both ends.

K=0.7 for whiskers fixed at one end, and pinned at the other

Whisker thickness is also important when estimating the electrical current level required to melt a whisker. The theoretical current in vacuum [91] required to melt a whisker is defined as:

$$I_{melt,vacuum} = \left(\frac{2\sqrt{Lz}T_0}{R_0}\right)\cos^{-1}\left(\frac{T_{amb}}{T_{melt}}\right) = \left(\frac{2\sqrt{Lz}T_0}{4\rho L / \pi d^2}\right)\cos^{-1}\left(\frac{T_{amb}}{T_{melt}}\right)$$

L_z = Lorenz number, ~2.45×10^{-8} $(V/K)^2$

T_0 = reference temperature

T_{amb} = ambient temperature

T_{melt} = melting temperature

R_0 = whisker resistance at reference temperature

For a circular-cross-section, $R_0 = 4\rho L / \pi d^2$

where $\rho = \rho_0$ = resistivity of material at reference temp T_0

L = Length of whisker

d = diameter or thickness of whisker

Experimental Sets and Goals of the Analysis

To quantify whisker thickness, two different sets of samples were used for collecting whisker thickness distributions:

Set 1 – Sn-plated Cu, and Sn-plated Cu with Ni underlayer as described in Chapter 3 under Experiment 1. All of the samples have spent 2.5 years in ambient environment, then went through 1000 temperature shock cycles from -55°C to +85°C (3 cycles per hour), and then an additional two months in 60°C and 85%RH. Upon completion of environmental exposure, whisker thicknesses and lengths (as shorting-distance measurements) were collected for 877 whiskers from all the samples. A smaller sub-set explored the correlation of whisker thicknesses to the sum-of-segments lengths of whiskers.

Set 2 – Sn-plated brass (Zn-30Cu) plated to a thickness of 6-7µm and stored in office ambient environment for ~11 years. Tin grain size for this set is of sub-micron surface dimensions and finish has a shiny luster to it. Many whiskers with lengths exceeding 1mm are present on the surface.

The two sets of samples have whisker growth in two completely different settings. Set 1 had whiskers growing only during the environmental exposure, and no whisker growth while in ambient storage prior to or after the test (see Chapter 3 for more details). For Set 2, however, all the growth occurred during ambient exposure.

Self diffusion of tin is responsible for the supply of tin atoms to the base of the whisker. The long-range transport of atoms trough grain boundaries has been attributed to growth of whiskers without visibly apparent or significant depletion of Sn layers in the vicinity of the whisker [92]. The terminology ‘long-range’ should be interpreted in context of individual atoms, where traveling 200μm in the direction parallel to the surface, as was demonstrated by Woodrow [92], is at least 10^6 times greater than the Angstrom-size atom itself.

Two questions are set to be answered with this work:

(1) If a correlation exists between whisker thickness and whisker length, can the diameters of whiskers be measured at some point before they reach their growth saturation, and estimate the maximum length it would grow to?

(2) Is it possible that the amount of Sn supplied to each whisker growing on a single surface is somewhat the same? If that were true, then the total volume of individual whiskers would be the same, creating a length to diameter dependency as $L \propto \frac{1}{d^2}$. As a result, thicker whiskers will remain shorter, and longer whiskers will have smaller cross-sections.

Set 1 – Environmentally-Induced Whiskers

For the 877 whiskers measured from Set 1, the distribution of thicknesses fits a lognormal distribution (Figure 49). As presented in Figure 50, the lognormal distribution holds even when separating the whiskers by substrate (410 whiskers on samples with Ni underlayer and 467 whiskers on samples with no Ni underlayer).

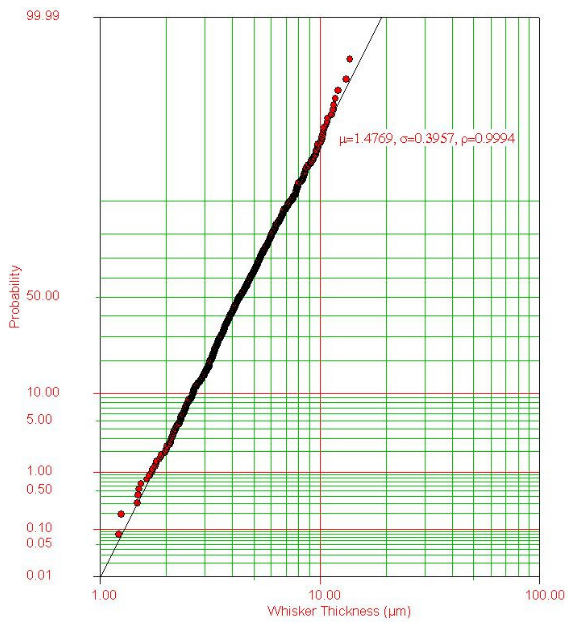


Figure 49 Lognormal cumulative probability distribution plot for whisker thickness from Set 1

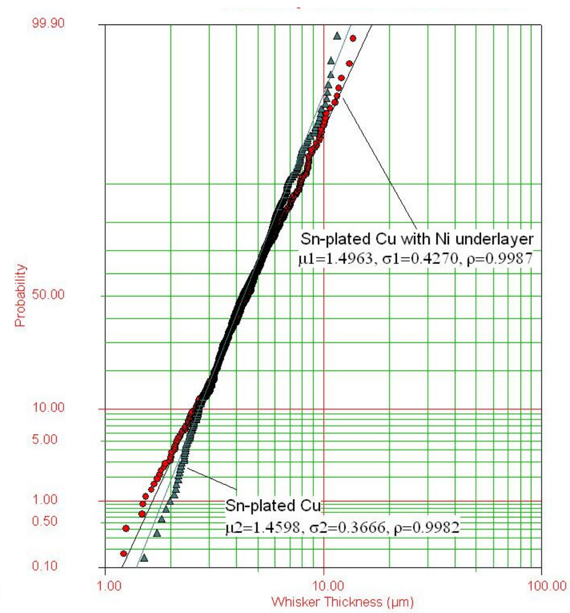


Figure 50 Lognormal cumulative probability distribution plot for whisker thickness from Set 1: Separation by presence of underlayer

The lognormal distribution parameters for Set 1 are listed in Table 24.

Table 24 Lognormal distribution parameters for whisker thicknesses of Set 1

	# of whiskers used	μ	σ	P
Set 1: All whiskers	877	1.48	0.40	0.9994
Set 1: Ni underlayer	410	1.50	0.43	0.9987
Set 1: No Ni underlayer	467	1.46	0.37	0.9982

The two sets of whiskers used above for thickness distributions are now correlated to the lengths of whiskers. Note, for this part of the work, the whisker length is defined as the sum of individual segments making up the whisker. This is different from the length definition used in Chapter 3, where the length was defined as the effective shorting distance between whisker root and the point furthest away from it. True length of the whisker is used here to see whether volumetric consistency exists amongst whiskers.

The distribution of whisker shorting lengths for Set 1 can be seen in Figure 51. The lognormal distribution parameters for the sum-of-segment lengths are given in Table 25.

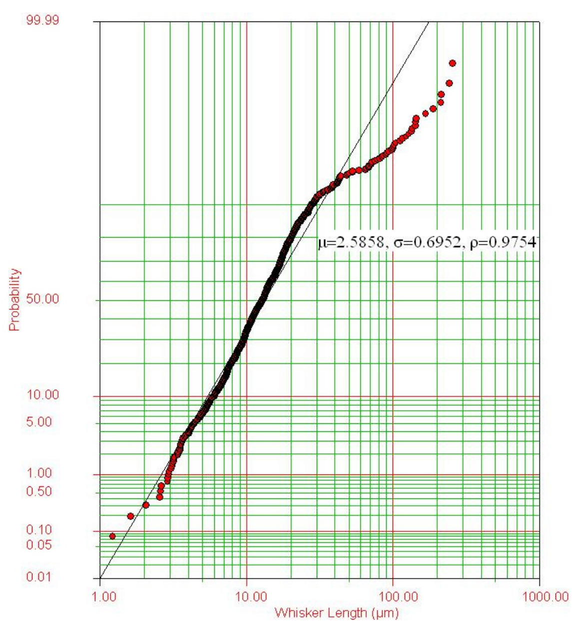


Figure 51 Lognormal cumulative probability distribution of whisker lengths for Set 1. Whisker length measured as sum of lengths for individual segments of the whisker

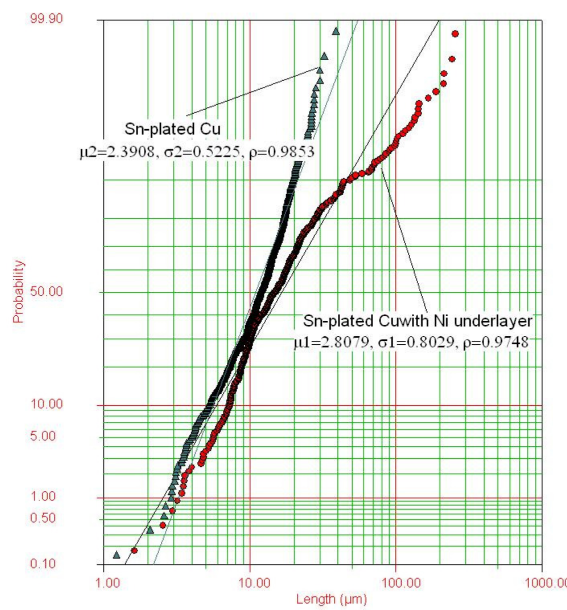


Figure 52 Lognormal cumulative probability distribution of whisker lengths for Set 1: Separation by presence of Ni underlayer

Table 25 Lognormal distribution parameters for whisker lengths of Set 1

	# whiskers used	μ	σ	ρ
Set 1: All whiskers	877	2.59	0.70	0.9754
Set 1: Ni underlayer	410	2.81	0.80	0.9748
Set 1: No Ni underlayer	467	2.39	0.52	0.9853

The scatter plots with correlations of whisker length and diameters are presented in Figure 53, Figure 54 and Figure 55. No correlation exists between whisker length and whisker thickness based on these results. These figures were constructed by combining data for the thickness distributions in Figure 49 and Figure 50 and the length data from Figure 51 and Figure 52. The correlation coefficient for all of the data from Set 1 (for samples with both Ni underlayer and without the Ni underlayer) is -0.06.

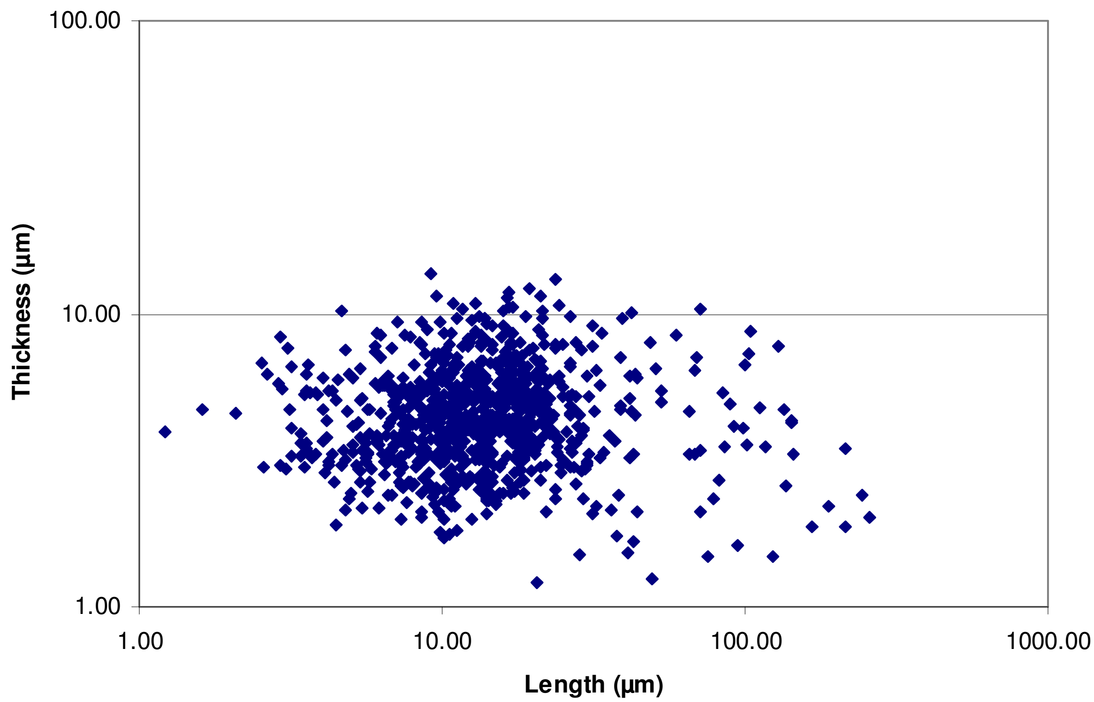


Figure 53 Scatter plot of whisker length vs. thickness for all of Set 1 Correlation coefficient -0.06

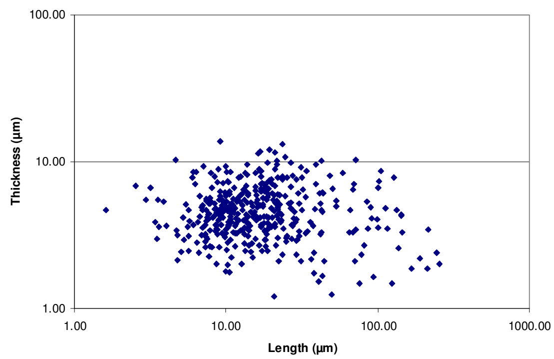


Figure 54 Scatter plot of whisker length vs. thickness for Set 1 samples with Ni underlayer Samples with Ni underlayer. Correlation coefficient -0.12

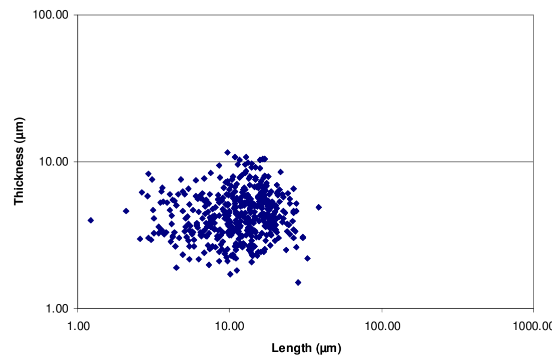


Figure 55 Scatter plot of whisker length vs. thickness for Set 1 samples without Ni underlayer. Correlation coefficient 0.06

As mentioned before, the samples used in Set 1 for the length to thickness correlation have seen temperature cycling and elevated temperature humidity exposure, during which all the whiskers grew, with no whiskers appearing during ambient storage prior to or after the exposure. Such whiskers were therefore induced by the environmental exposure, and perhaps have not reached their maximum lengths, meaning that if more environmental exposures were to be done, more and longer whiskers could have grown.

As mentioned before, the whisker lengths for Set 1 were measured as the shorting distance (straight line between whisker root and the point furthest away from the root on the whisker). This approximation may not provide the best assessment of total volume of whiskers. For more accurate predictions, whiskers of length:thickness ratio greater than 4:1 were chosen from the specimens with Ni underlayer present to be re-measured using the sum-of-segments method. This way, if a trend existed for thinner whiskers to grow longer, while thicker whiskers stay shorter, then, perhaps it would be more evident here. A total of 124 whiskers were re-measured in the sum-of-segments method. The relationship between whisker length and thickness is given in Figure 56. As before, no noticeable correlation exists for these environmentally-induced whiskers.

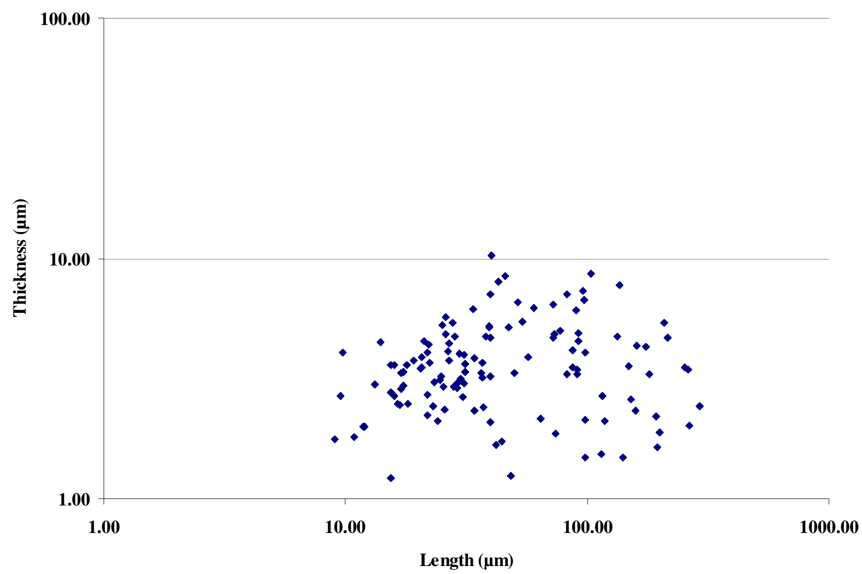


Figure 56 Scatter plot of whisker length vs. thickness for Set 1: Samples with Ni underlayer, length measured as sum of segments, only whiskers with length:thickness ratio of 4:1 or greater. Correlation coefficient -0.01

Set 2 – Long-term Ambient Growth

To contrast the above analysis, an 11-year old sample was selected for whisker length and thickness measurements. In this case, tin-plated brass of plating thickness 6-7 microns was used. The sample had ~10cm^2 exposed surface area of tin and has been stored in office ambient environment for over 11 years. During this time, whiskers of lengths exceeding 1mm have grown on it. The growth on the specimen, however, has not saturated, as can be seen by comparing the same area on the specimen after 9.5 and 11 years of ambient storage (Figure 57 and Figure 58). Among 30 areas thus compared between 9.5 and 11 years of ambient exposure, no new whisker initiations have been noticed, but a handful of whiskers did add in length.

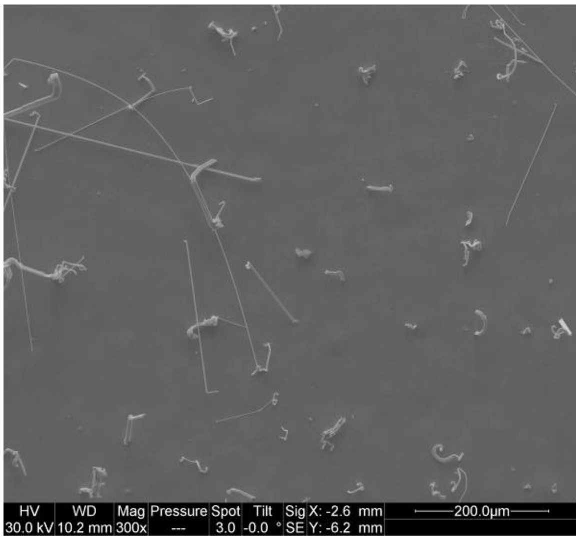


Figure 57 Area on Set 2 specimen after 9.5 years of ambient exposure

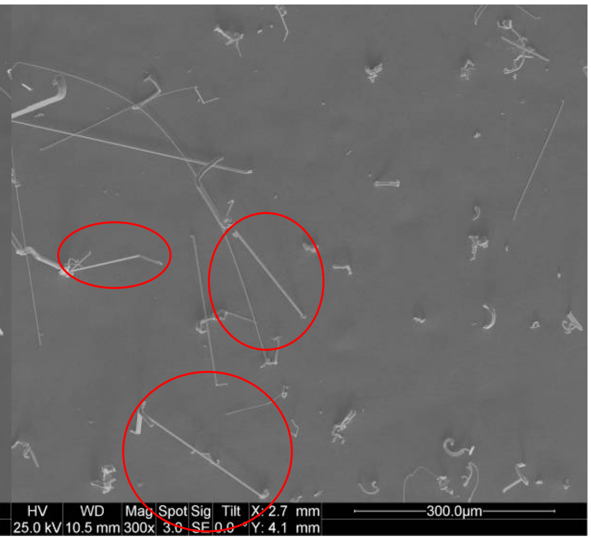


Figure 58 Same area as Figure 57, after total of 11 years of ambient exposure. The whiskers with significant change have been circled

It is obvious that these specimens have not reached saturation as of 9.5 years of ambient storage. The only way to find out whether current 11-year timeframe has achieved saturation would be to compare existing growth with what will be seen later on. Nevertheless, if saturation does exist, these specimens are now closer to it than ever before. And if some relationship between whisker's saturated (or maximum) length and thickness exists, it would be more prominent now than before.

Whisker length and thickness data for 187 whiskers at random locations throughout the 11 year old sample were collected. Both lengths and thicknesses of Set 2 whiskers followed lognormal distributions as seen in Figure 59 and Figure 60. Lengths were measured as a sum of individual whisker segments.

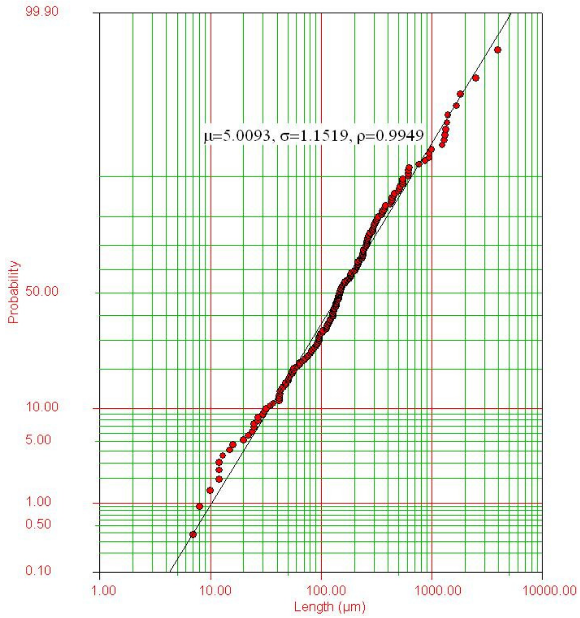


Figure 59 Lognormal cumulative probability distribution of whisker lengths for Set 2

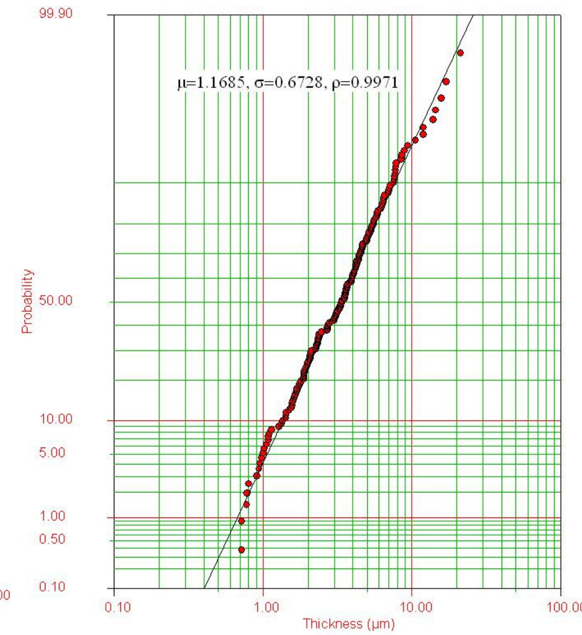


Figure 60 Lognormal cumulative probability distribution of whisker thicknesses for Set 2

The lognormal distribution parameters are listed in Table 26 below.

Table 26 Lognormal distribution parameters for whisker lengths and thicknesses of Set 2 (total of 187 whiskers) after 11 years of office ambient exposure

	μ	σ	ρ
Length	5.01	1.15	0.9949
Thickness	1.17	0.67	0.9971

As with the Set 1, no correlation between whisker length and thickness for Set 2 whisker growth on 11 year old Sn plating exposed to office ambient environment. The correlation coefficient is -0.137, and the data can be visualized in Figure 61.

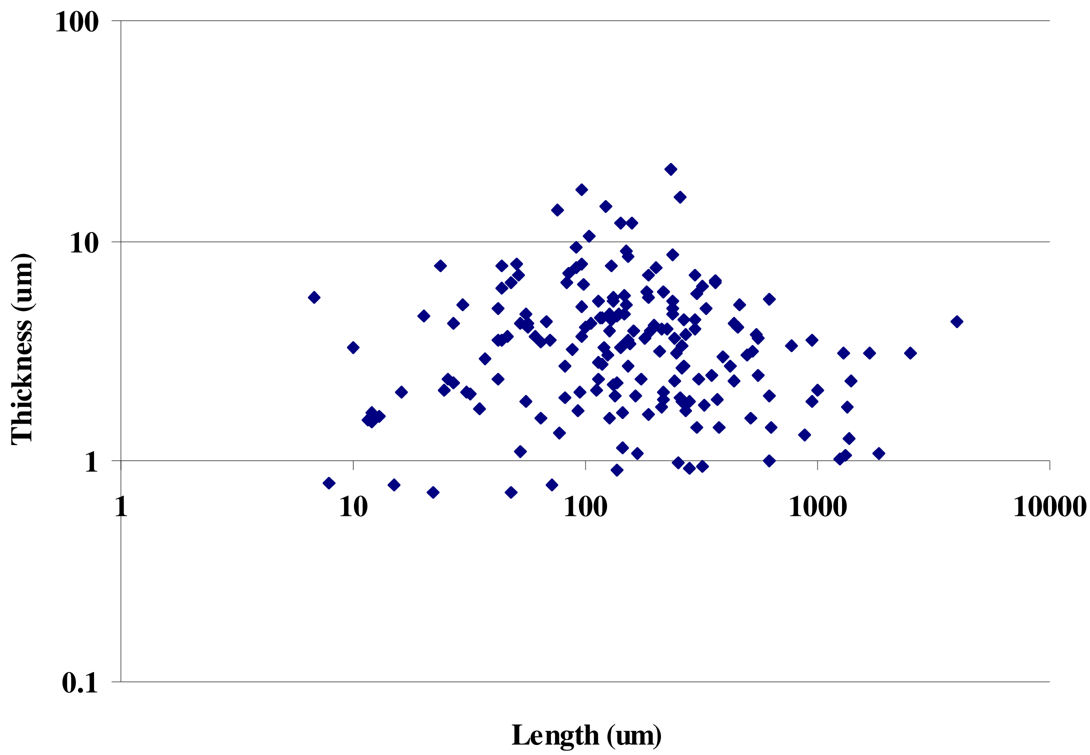


Figure 61 Scatter plot of whisker length vs. thickness for Set 2 (Sn-plated brass after 11 years office ambient storage). Correlation coefficient: -0.137

From the two sets of data presented above – one from whisker growth during environmental exposure and second from 11-years in office ambient conditions – it is clear that whisker lengths and thicknesses are unrelated. Therefore, it is incorrect to assume that only thinner growths will produce long whiskers or that thick growths will remain short However, data from Set 2 did show that whiskers with thicknesses greater than 10µm existed only for whisker lengths of 70-300µm. It is unclear whether this will hold true for all whiskers, or whether it comes from the limitations of sampling.

Due to a lack of observed depletion of tin near whiskers, it has been proposed and stated that whisker form due to long range diffusion [92][93]. The material that constitutes whiskers is supplied by the surrounding tin plating layer. If we assume a whisker 500µm long with a diameter of 2µm, it takes up the volume of ~1500µm^3. ($V = L * \pi * d^2/4$). For a plating thickness of 5µm, this whisker would have to completely deplete all of the tin around it in the radius of 10µm in order to make up the whisker. However, in general no material depletion is observed in the area immediately surrounding a whisker.

Let us calculate percent of plating volume used up by whiskers on a given area with whisker growth. For the 11-year old Sn-plated specimen outlined above in Set 2, plating thickness was measured as ~6.5µm. The density of whiskers was measured to be 35 ± 12 whiskers per mm^2. The length and thickness lognormal distribution parameters are given in Table 26 above. Monte Carlo simulations of whiskers on an area of 1mm^2 were performed to compare total volume of tin in whiskers to the volume of plating in 1mm^2 area. Total of 1000 areas, 1mm^2 each, were simulated, and cumulative volume of all whiskers present on each area was compared to the amount of Sn available (6.5µm thick Sn on area of 1mm^2, results in 6.5×10^6µm^3).

The results of the total Sn volume used up by whisker as a percent of volume available within 1mm^2 area with 6.5µm thickness has a median of 0.24% and can be seen in Figure 62. Such a small percentage of tin used up in whisker growth easily accounts for lack of visual indication of material depletion on the surface, as was seen in images of this specimen (Figure 57, Figure 58). Woodrow's proof [92] that long range diffusion of tin supplies material to the forming whiskers coupled with the overall small percentage of tin consumed in formation of a field of whiskers easily accounts for the lack of visual evidence of depleted zones of tin.

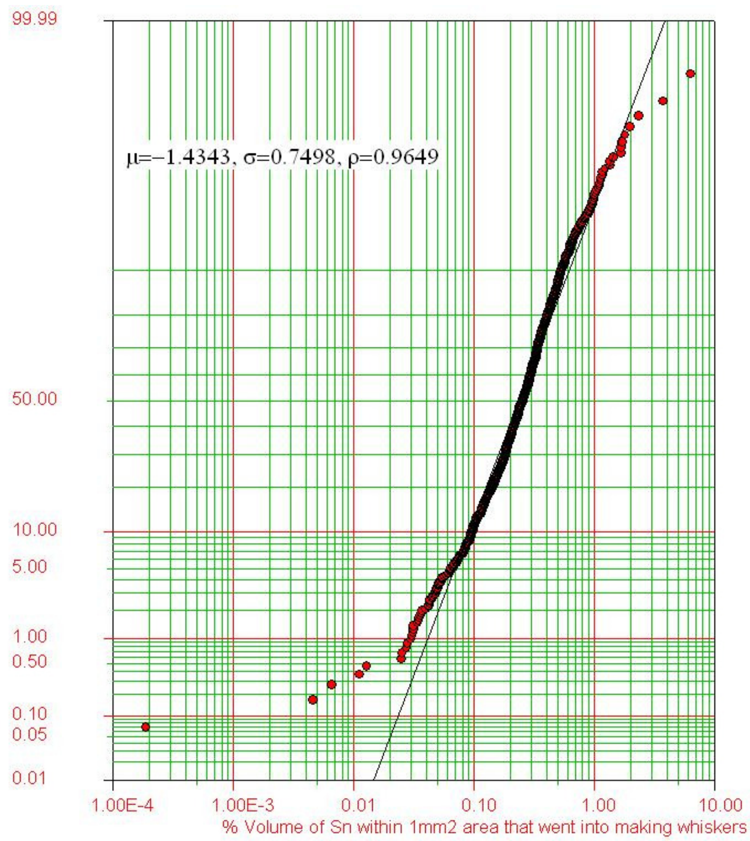


Figure 62 Cumulative probability plot (fit to Lognormal distribution) of Percent Volume of Sn available within 1mm^2 area that went into making whiskers. Result of simulating 1000 areas 1mm^2 each

Examples of Whiskers with unusual Thicknesses

The whiskers presented above have ranged in thickness between 0.7µm to ~21µm. This range, however, is not all-encompassing. On rare occasions, whiskers that are significantly thinner or thicker have been observed. Examples of tin and zinc whiskers that are far beyond the "usual" are presented below.

Figure 63 depicts a 200nm-thick whisker found on surface of Sn-plated brass. Figure 64 shows tin growths on Sn-plated beryllium-copper with a measured thickness of 30µm. A 70µm thick whisker growing on Sn-plated copper can be seen in Figure 65.

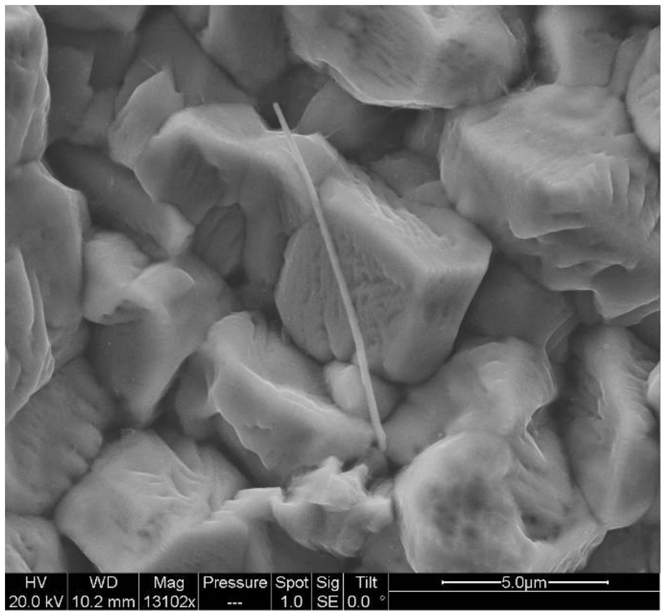


Figure 63 Tin whisker of ~200nm thickness on surface of Sn-plated brass

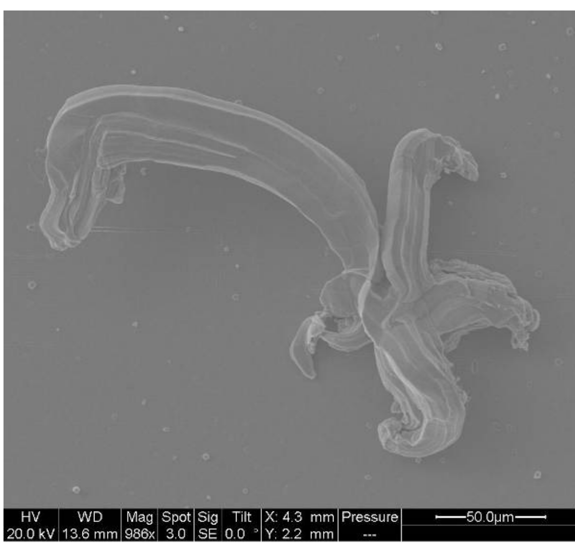


Figure 64 Tin whisker of ~30µm thickness on surface of Sn-plated beryllium-copper

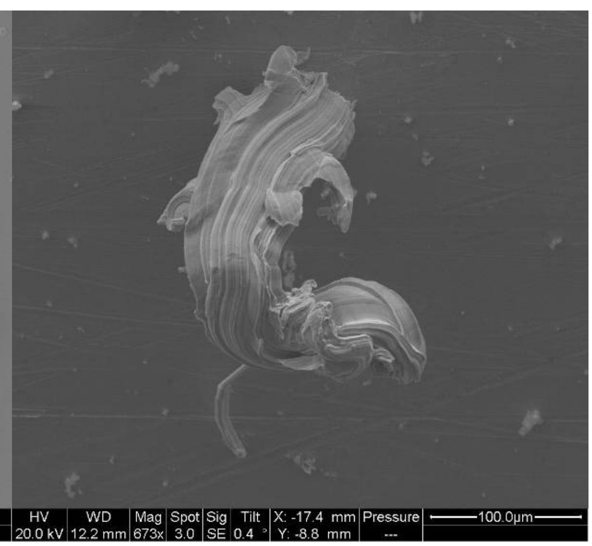


Figure 65 Tin whisker of ~70µm thickness on surface of Sn-plated copper

Thicker whiskers have also been observed on steel surfaces coated with hot dip galvanized (HDG) zinc. There whiskers with thickness of up to 35µm (Figure 66 and Figure 67) have been observed, while still in presence 1-10µm thick whiskers.

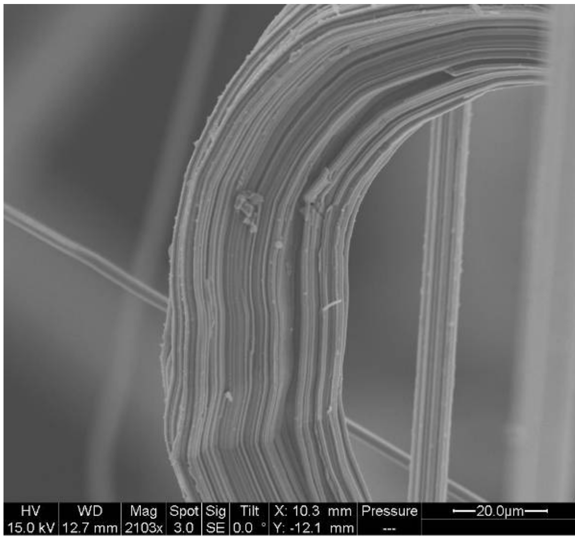


Figure 66 Zinc whisker ~35µm thick on HDG steel

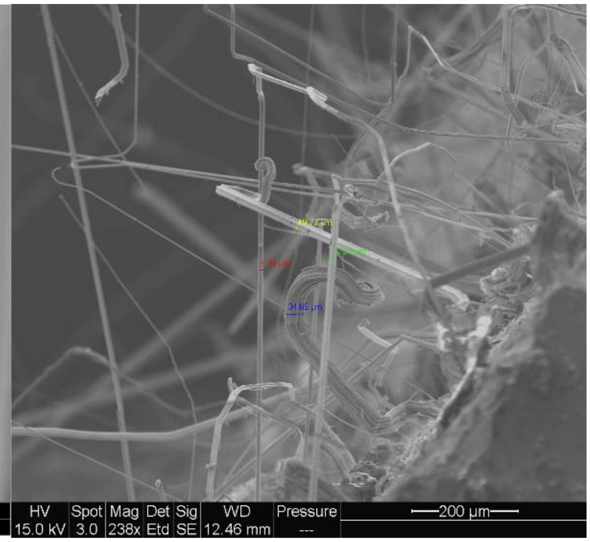


Figure 67 Zinc whiskers of 10µm, 13µm, 20µm, and 35µm thickness on HDG steel

Thicker whiskers present a greater threat. Since the melting current of a whisker is proportional to the square of whisker's diameter, a thicker whisker will melt under much higher current, and thus sustain an undesired electrical short for much longer. A thicker whisker will also penetrate a layer of conformal coating much further without buckling, limiting the benefits of conformal coating as a mitigator against electrical short circuits induced by whisker bridging between adjacent conductors.

Chapter 6: Tin Oxide Possible Future Use

An experiment is a question which science poses to Nature,
And a measurement is the recording of Nature's answer
M. Planck

Background on Metal Oxide Gas Sensors

Like many metals, tin forms a layer of oxide on the surface when exposed to air. Tin whiskers are not an exception, and similar oxides are formed on them. As a result, whiskers that make mechanical contact, do not necessarily create an electrical short, until the dielectric of the oxide film is broken [94][95].

A booming topic in research nowadays is the use of semiconductor properties of metal oxides in gas sensing. Materials such as SnO_2, Co_3O_4, Fe_2O_3, TiO_2, ZnO, and others act as chemiresistors, which means that they operate on the basis of surface reactions [96]. The ultimate goal of this research trend has been to create a single unit with multiple gas sensors and intelligent recognition of various gases. The choice of metal oxide is complicated by many factors, including among others their surface properties, electro-physical responses, and stability in sensing [97]. The principle of gas sensing lays in the changing properties of metal oxides when exposed to gases in as little as ppm range. Surface reactions with the gases cause electrons to transfer from surface states back into semiconductor's interior, creating conductive channels. If continuously electrically measuring a gas-sensing nanowire, this change will become apparent as a drop in resistance.

Experimental

In a series of experiments, tin-finished surfaces with whiskers growing on them were heated in a small enclosed space to temperatures exceeding the melting temperature of tin. Typically, the measured temperature on surface of specimens was achieved to be 280-300°C. Within the span of 10-30min, whiskers appeared to partially or completely expunge the metal back into the Sn film, leaving behind an oxide “shell” or “skin”. An example of this phenomenon is demonstrated in Figure 68, where a whisker heated at 280°C for 20min has been completely freed of Sn. If the whisker burst open, the remnants of Sn that have splashed on the surrounding surfaces would be evident. However, upon close examination of the areas surrounding such a whisker, no changes in surface were observed. It was thus assumed that Sn from the whisker has sunk back into the plating.

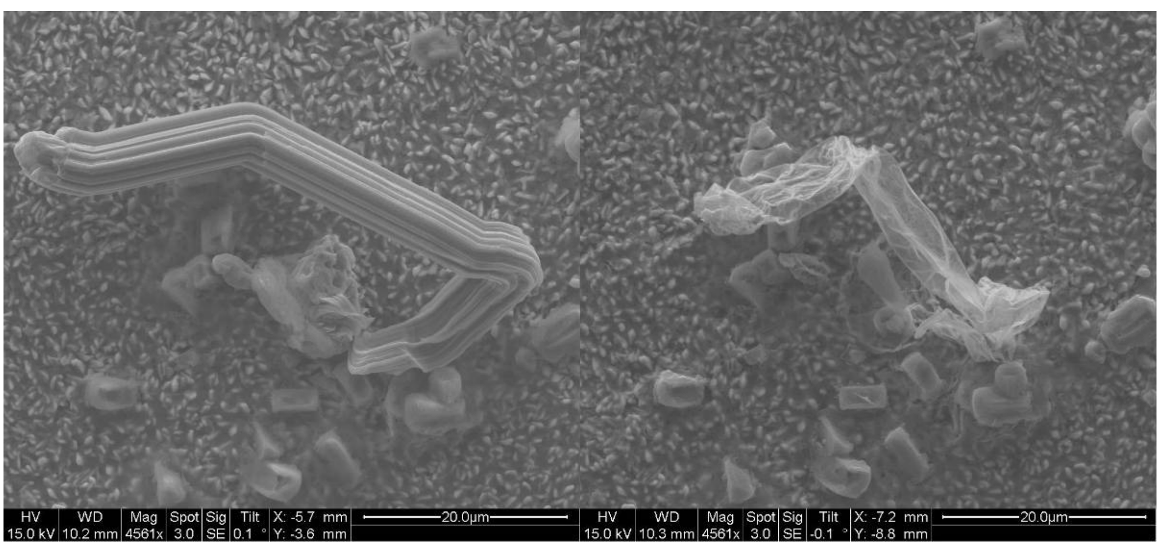
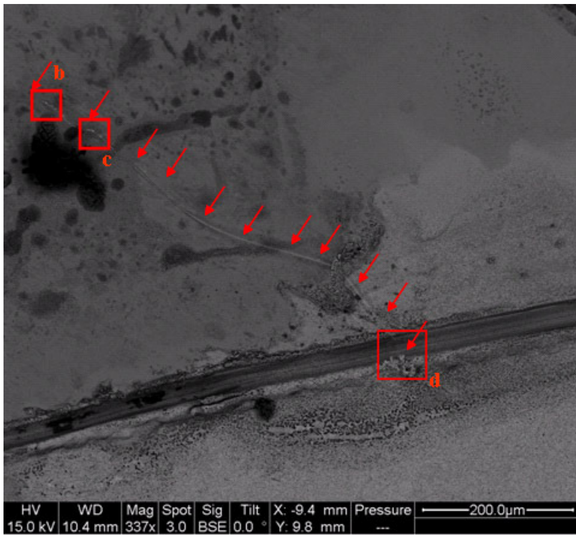
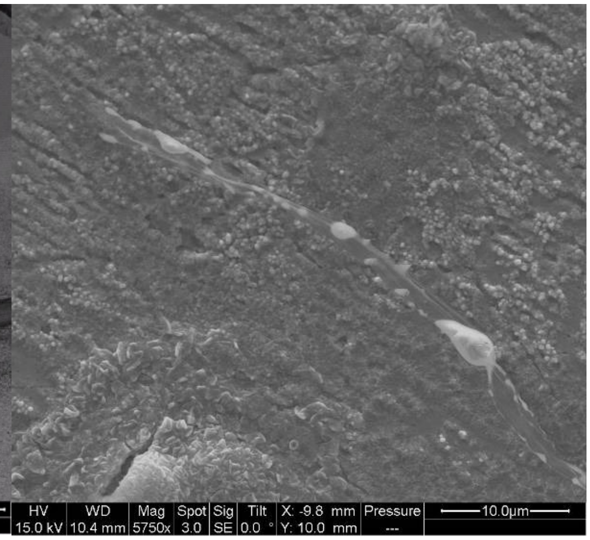


Figure 68 Whisker before (left) and after (right) heating a Sn-plated brass specimens at 280°C for 20min

To confirm the idea of Sn metal flowing from the whisker back into the plating, Sn-plated brass specimen was heated at 260°C for 15min. A whisker with length over 600μm was documented to almost expunge all metal, with just a few droplets of Sn remaining (Figure 69). Remaining tin is seen to form distinct droplets within the tube of tin oxide, and the droplets appear to have directionality, suggesting that the metal was flowing down the length of a whisker towards the root.

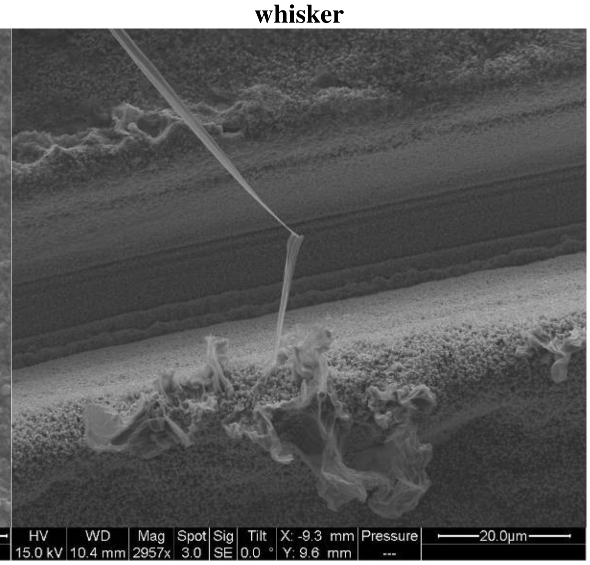


(a) Tin whisker devoid of metal. The shell is outlined with arrows



(b) Sn droplets solidified closer to the tip of the whisker

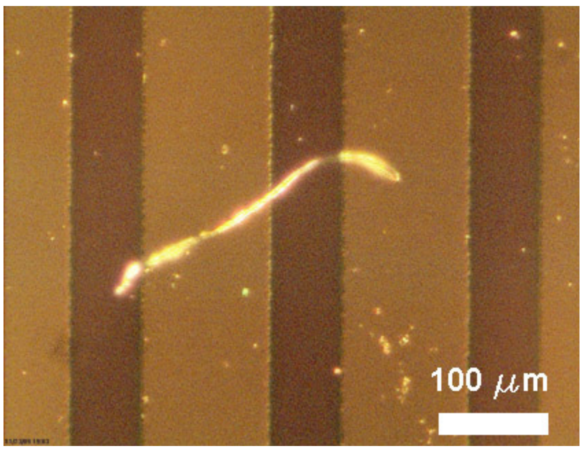
(c) Partially expunged part of whisker, with Sn solidified in form of droplets. Note the empty, almost-transparent collapsed shell and the directionality of the droplets, suggesting out-flowing of the metal



(d) base of whisker with no Sn evident

Figure 69 Tin whisker (>600μm) heated to 260°C for 15min showing clear distinction of metal still remaining inside the tin-oxide shell and solidified in form of droplets whose directionality suggests that tin was flowing down the length of the whisker

To test the electrical properties of the oxide shells, tin whisker while still attached to the Sn-plated surface, was heated at 280°C in air for 30min to expunge Sn. The remaining oxide shell was then removed and placed across chromium (Cr) contacts. The structure was then annealed at 500°C in air for 1hr to convert any remaining metallic tin into tin-oxide. P current-voltage (I-V) measurements were carried out at room ambient temperature and atmosphere. The optical image of the shell used in this experiment and the characteristic I-V curve can be seen in Figure 70. The slight non-ohmic behavior is due to Schottky barriers between Cr contacts and the nanowire of tin-oxide.



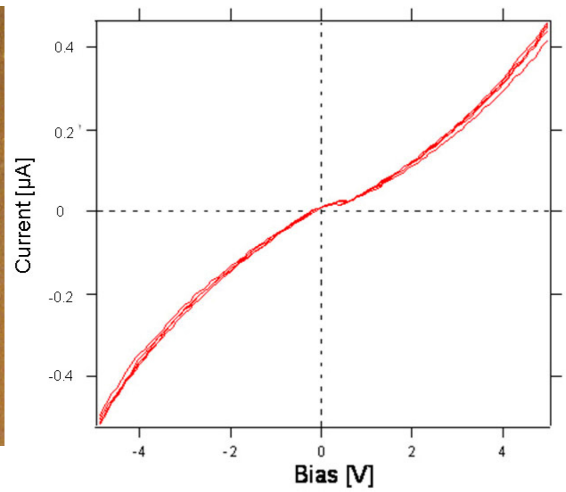


Figure 70 Electrical testing of whisker oxide shell. Left - tin oxide shell laying across Cr contact. Right - Current-Voltage curves

These preliminary results are consistent with those shown for tin-oxide nanowires [98]. Further investigation is needed to look into the behavior of the whisker shells in carbon monoxide environments. The potential benefit of this work may be the ease of sensor manufacturing from tin whiskers. Current methodologies for nanowire gas sensor construction commonly involve vapor deposition of metal oxide in high-pressure chambers [99], or growth of metal nanowires through electrodeposition, and converting them into semiconductors under high temperature annealing [100].

Summary and Conclusions

The work presented in this thesis is aimed to assess the predictability of existing environmental tests for tin whisker growth as compared to long-term ambient storage. Through this work, whisker measurement techniques were documented and improved. Three sets of tin finishes were assessed in accordance with environmental exposure tests, and compared to ambient storage. In addition to single environmental exposures, tests included sequencing existing environmental tests to determine effectiveness at promoting whisker formation. Results from testing demonstrate the unreliability of environmental exposure to produce meaningful predictions of whisker growth. Finally, no correlation between whisker thickness and length was observed.

As part of this work, extensive measurements of whisker growth were required. While measurements procedures may seem obvious, this work provided an opportunity to define procedures and techniques for whisker. To ease the work load required by this work in measuring whisker lengths, an easier way of measuring whiskers has been put forward. Instead of tilting and rotating the whiskers to align them perpendicular to the field of view as has been suggested previously, whiskers are tilted by a known angle, and then their true three-dimensional length is calculated from two views off-set by a known angle. This method has been shown to be more repeatable in terms of whisker length results among different participants as compared to aligning whiskers perpendicular to the field of view to obtain measurements.

For Experiment 1, tin whisker growth on tin-finished copper specimens with and without a nickel underlayer was evident exclusively during a sequence of environmental exposures. No whisker growth was observed in two and a half years prior to the exposure, nor in two years following it. In addition, no growth was observed on the specimens stored in ambient conditions throughout the five-year storage period. Nickel underlayer was shown not to be effective in retarding whisker growth, even though it is present as a continuous layer throughout the specimens. Within the sequential tests, temperature cycling was responsible for a large amount of whisker growth, while elevated temperature humidity added significantly only to the maximum whisker lengths.

Within Experiment 2, whisker growth on tin-finished copper coupons was compared for a number of different environmental sequences and single-condition environmental loads as well as ambient storage. Results show little appreciable difference between whisker growth among the set of sequenced, single environmental exposures, and ambient whisker growth. The whisker growth in Experiment 2 was overall significantly lower than growth observed in Experiment 1.

Results of Experiment 3 compare whisker growth on tin-plated brass during temperature cycling and elevated temperature humidity to the growth seen on the same specimens after one-to-two years of ambient storage following the environmental tests. While abundant whisker growth was present during elevated temperature humidity storage, no additional growth was observed on these specimens in the following year of ambient storage. On the contrary, specimens that showed no growth through temperature cycling tests followed by one year of ambient storage had substantial growth in the second year of ambient storage. Growth seen after elevated temperature humidity was denser, but shorter than that seen after two years post temperature cycling.

In an attempt to see whether similar amount of tin is present in all whiskers, making thinner whiskers grow longer, while thicker whiskers stay shorter, two sets of whiskers were measured to compare their lengths and thicknesses. One set was taken from whisker growth that occurred exclusively within the span of an environmental test, the other was collected after 11 years of ambient storage. The thicknesses of whiskers appeared to follow lognormal distribution, and no correlation was found to exist between the lengths and thicknesses. Unfortunately, this also meant that given a set of whiskers with different thicknesses, one can not predict how long they can possibly grow in the future. It is also shown that total volume of tin that goes to make whiskers in an area of $1mm^2$, is only fractions of one percent of total volume of tin available in that area, explaining why no noticeable depletion of material is seen.

It has also been demonstrated, that heating up a tin whiskers at temperatures above its melting point, will allow the metal to drain out of the whisker over a period of several tens of minutes. This leaves behind a tin-oxide “shell” that has the potential to be utilized as a carbon monoxide sensor. Preliminary experimental results of current-voltage relationship on such “shell” have followed a typical path observed for tin-oxide nanowires. Further investigation would reveal how these structures behave in carbon monoxide environment.

Contributions

As part of this work, a more reliable, accurate and time-efficient method of whisker length measurement compared to existing industry protocol has been put forward. The method involves capturing two images of a whisker where each image is tilted relative to the other by a known angle. The true length of the whisker is computed by taking measurements from each image and entering them into the trigonometric function derived herein. With this new method it has been demonstrated that a number of different operators can quickly and accurately measure whisker lengths with minimal variation in results amongst operators. In contrast, the methodology recommended by existing industry standards of positioning a whisker perpendicular to the field of view has been shown to be far more time-consuming and yields large variations in measured whisker length among different operators.

Environmental tests for whisker growth based on temperature cycling and elevated temperature and humidity have been compared to ambient storage of tin finishes. The results indicate that the tests may severely over-predict, or under-predict the whisker growth as compared to long-term ambient storage, or have little appreciable effect. This indicates that use of environmental tests for whisker growth is not reliable in assessing future whisker growth. In addition, sequencing of different environmental tests does not show any consistent results either.

Whisker thicknesses have been shown to follow lognormal distribution. However, no correlation exists between whisker lengths and thicknesses, disproving that whiskers of different sizes may have similar total volume; or that their lengths may be predicted based on the thickness.

First potential practical use of whiskers has been demonstrated by creating tin-oxide "shells" to be used as carbon monoxide sensors. This could serve as another method of manufacturing quasi-one-dimensional tin-oxide structures for gas sensors that will change from semiconductors to conductors upon release of an oxygen atom in a surface reaction with carbon monoxide.

Future Work

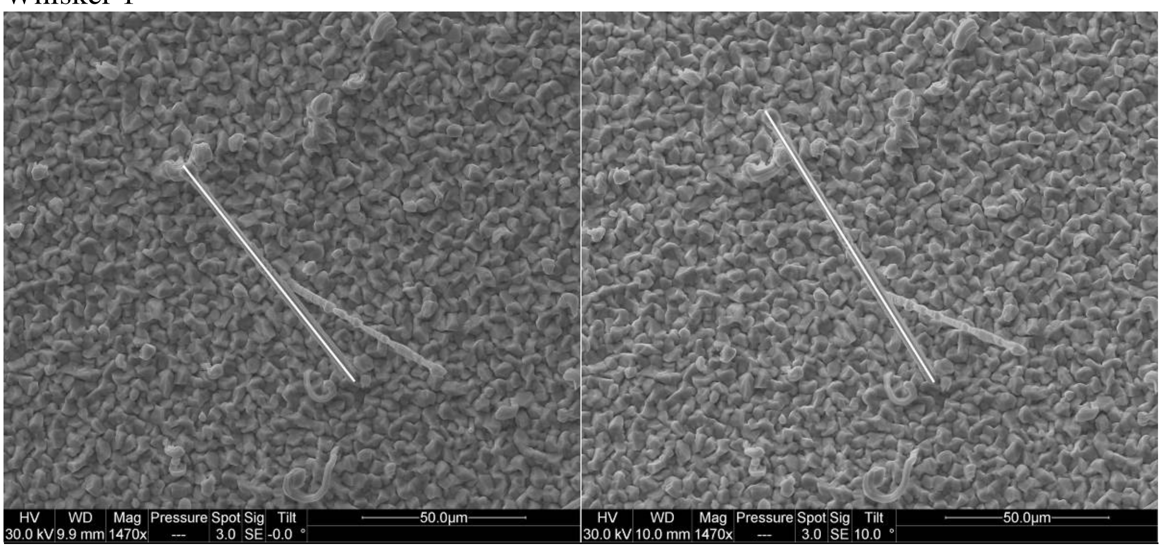
From this work, current environmental exposure conditions for whisker growth as well as sequential application of these environmental conditions cannot be used to determine future whisker growth. Based on these findings, it is clear that new test methods are needed to assess whisker growth propensity. Since plating process, plating chemistries, substrate, and deposit properties play a role, correlation with measurable plating properties with environmental conditions may be required to understand the confounding results that have been observed to date. Alternatively, full description of whiskering phenomenon from materials science perspective may explain the relationship between different parameters we observe to effect whisker growth on macro-scale level and aid in true acceleration of whisker growth.

Additionally, further investigation is needed into tin-oxide “shells” left behind, when the metallic tin is melted out of a whisker. The shells resemble current-voltage behavior of tin-oxide nanowires that can be used for carbon monoxide gas sensing. Additional research into how the shells remaining behind whiskers act in carbon monoxide exposure is imperative for further progress. If successful, this may be an additional manner in which carbon monoxide sensors may be manufactured.

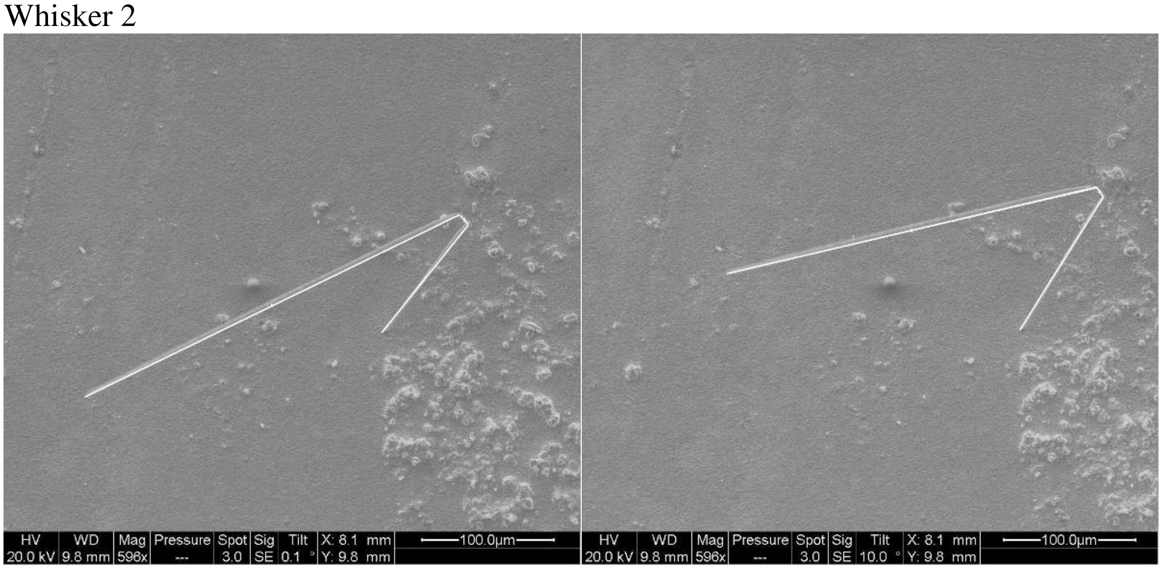
Appendix A: Whiskers for Length Measurements from Two Images

The following 15 pairs of images were given to the participants along with simple instructions on measurement of three-dimensional lines and the formula described in Chapter 2.

Whisker 1

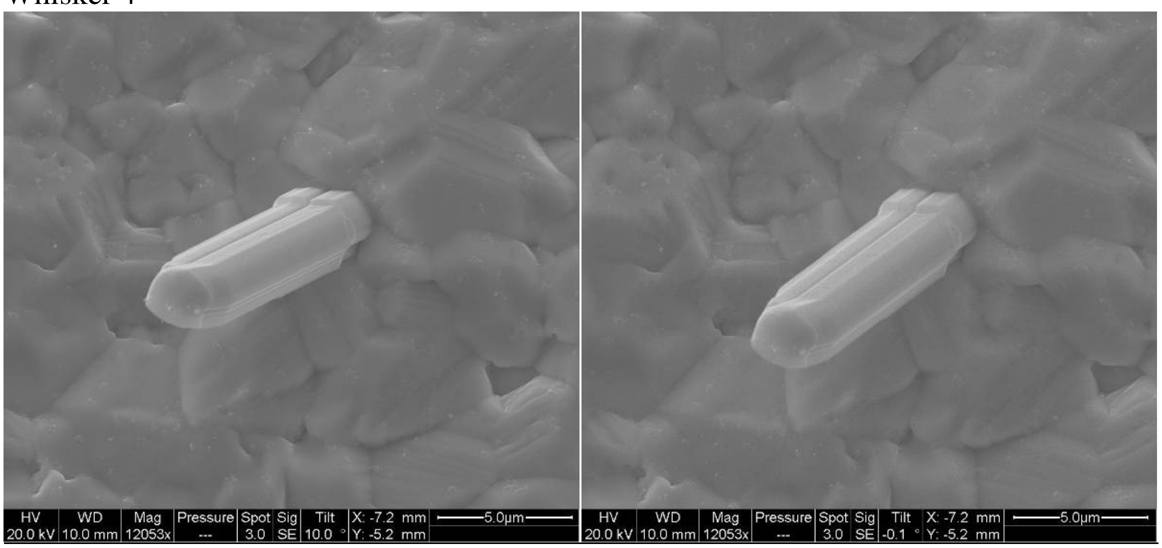


Whisker 2

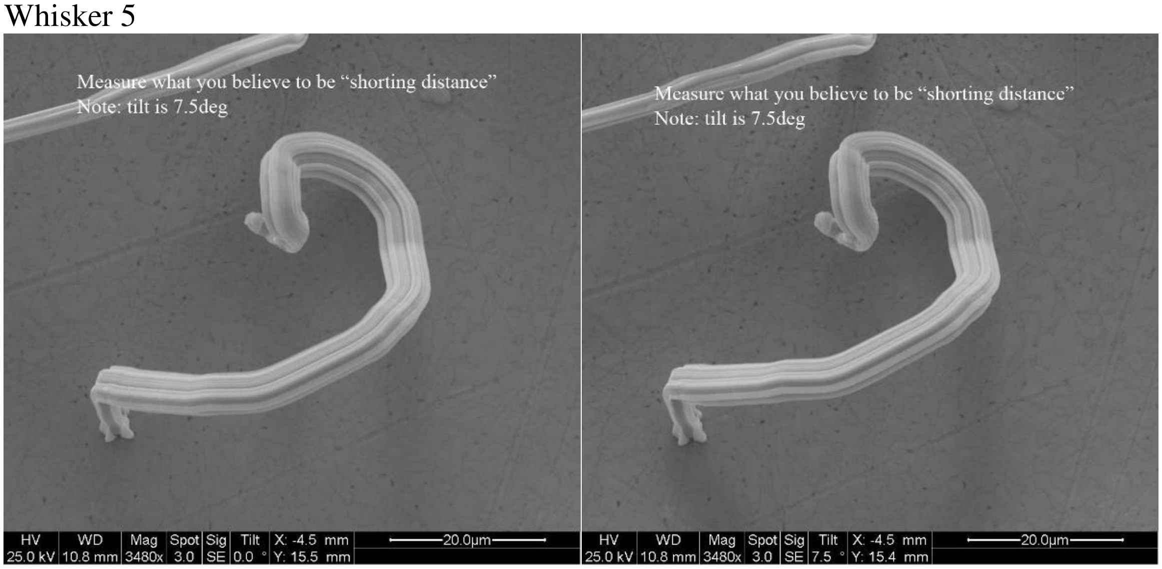


Whisker 3

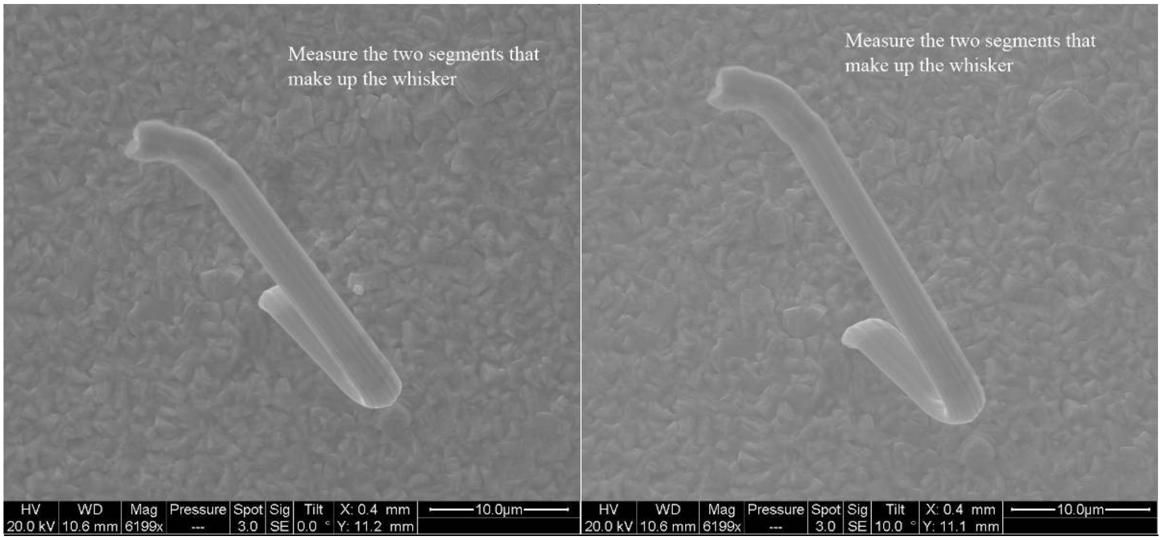
Whisker 4



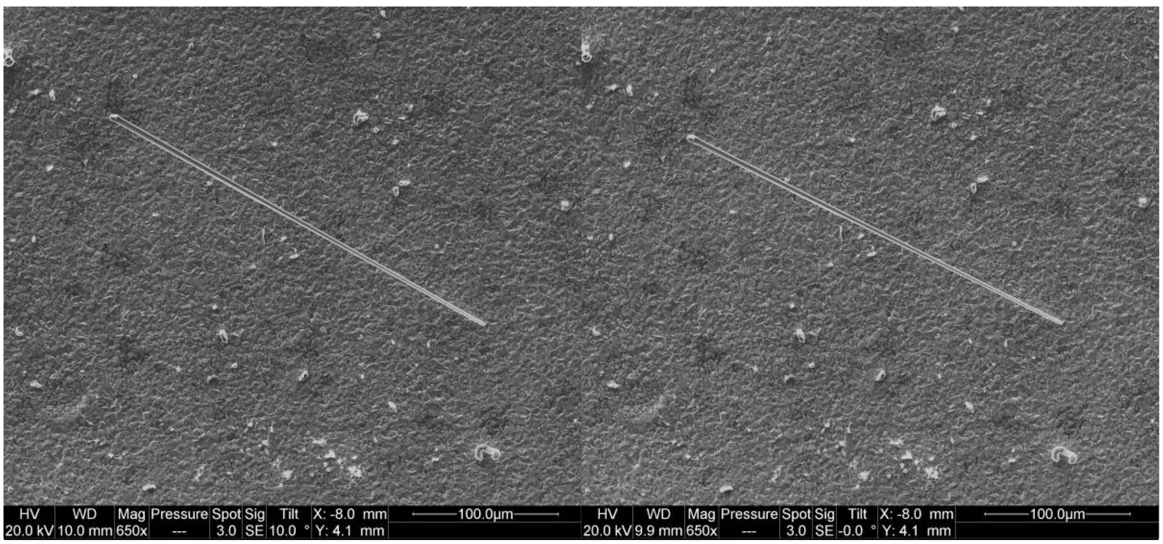
Whisker 5



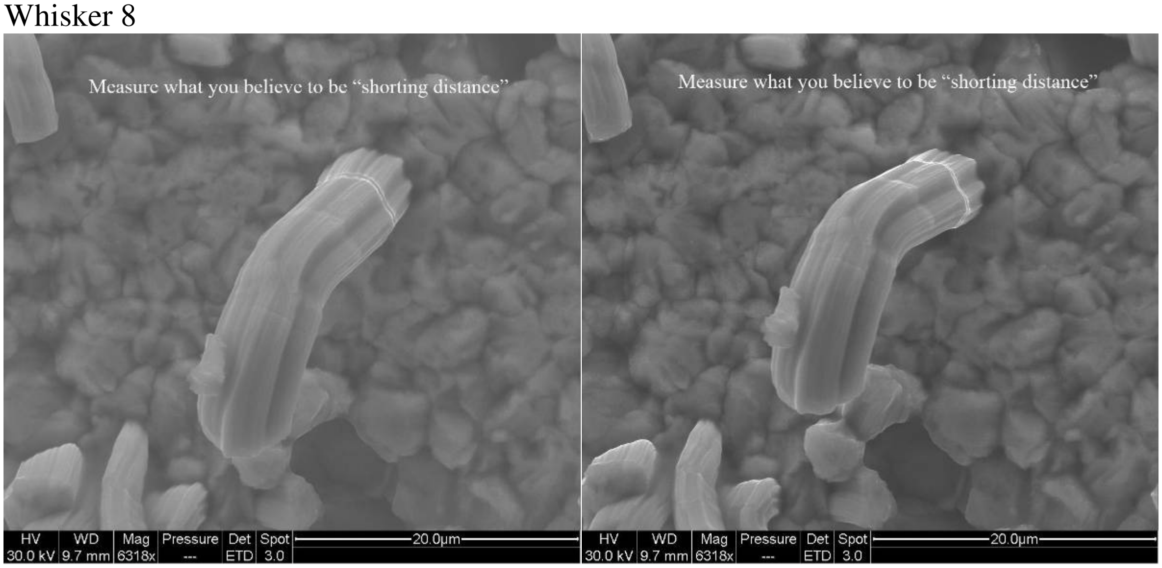
Whisker 6



Whisker 7

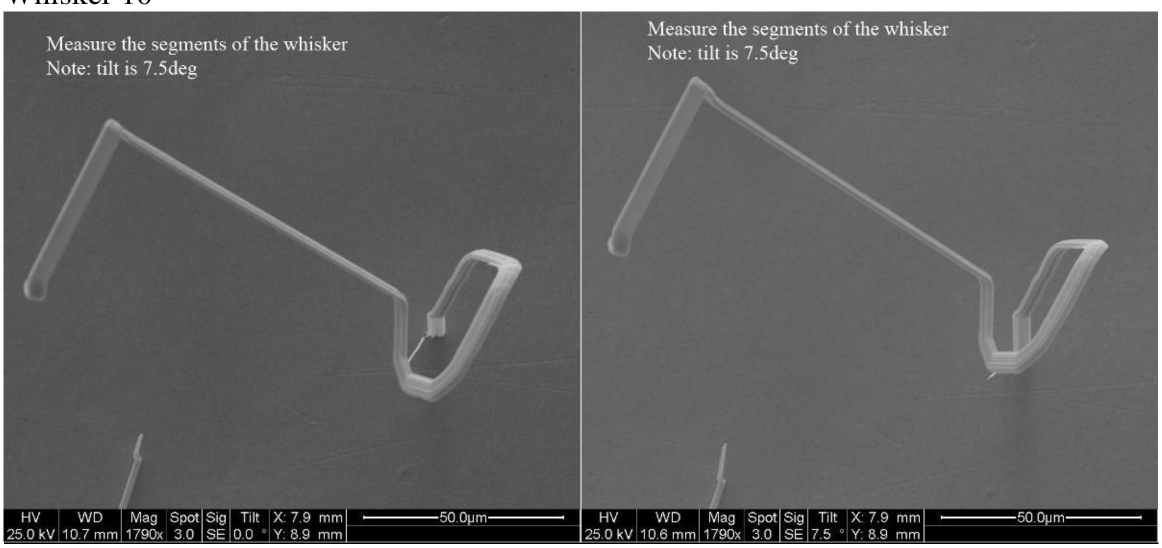


Whisker 8

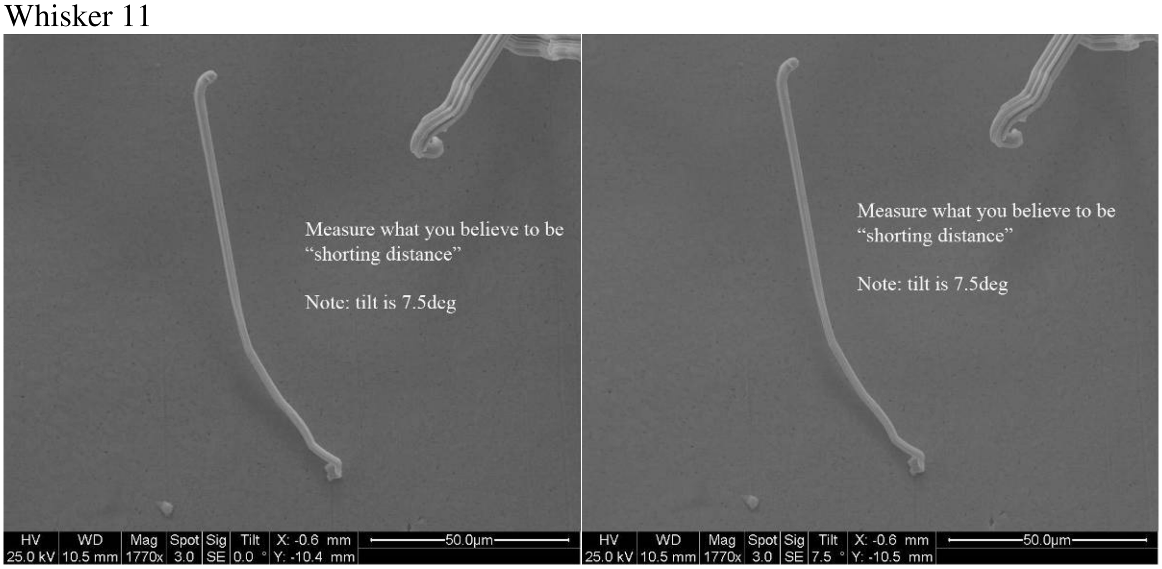


Whisker 9

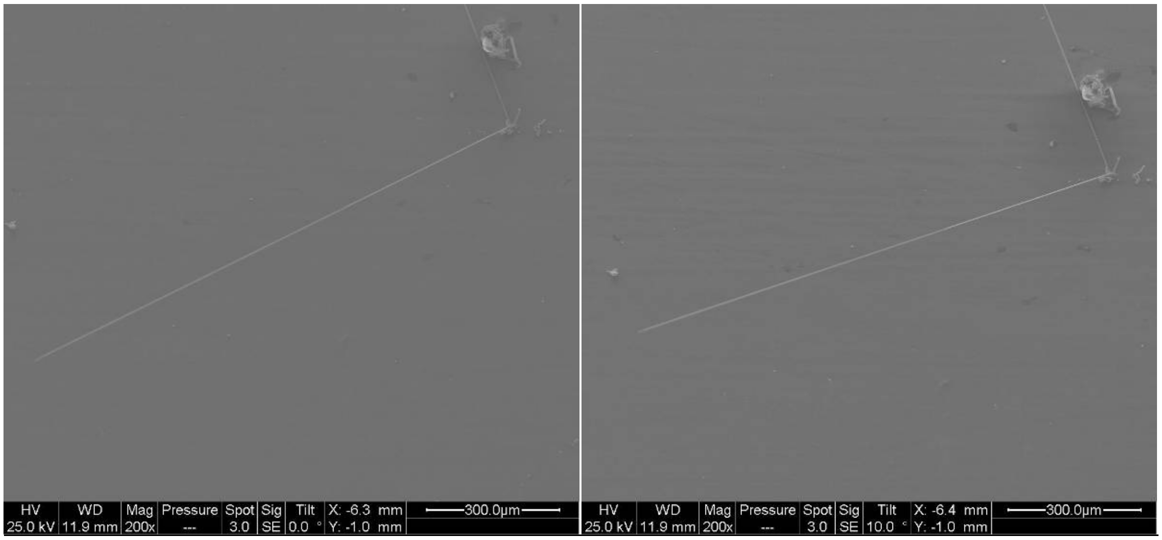
Whisker 10



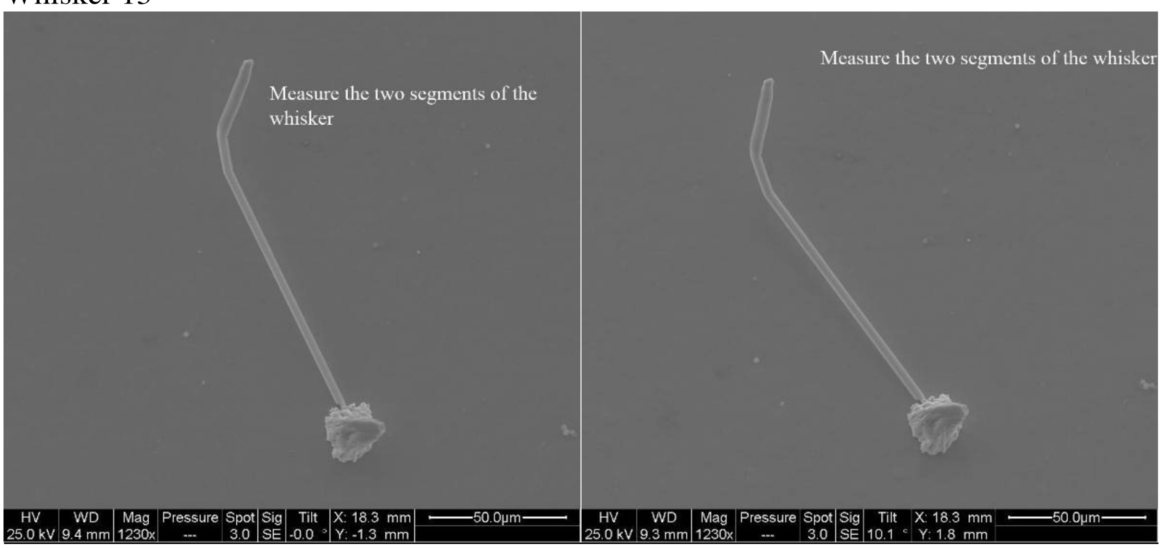
Whisker 11



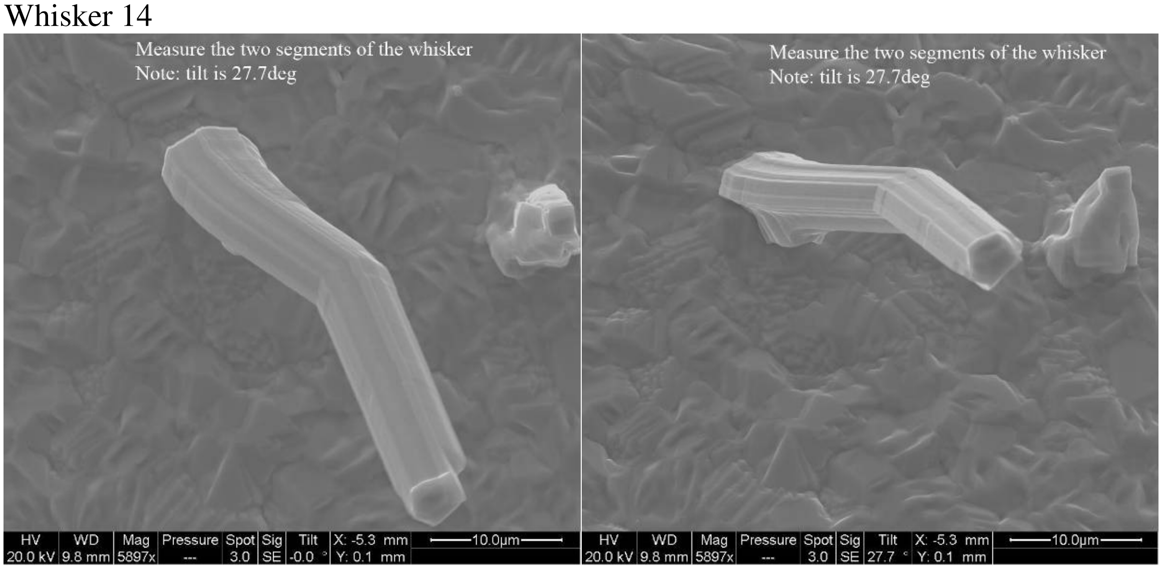
Whisker 12



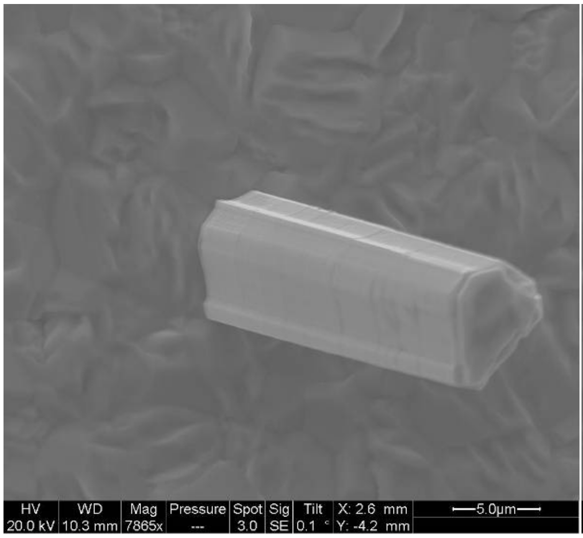
Whisker 13



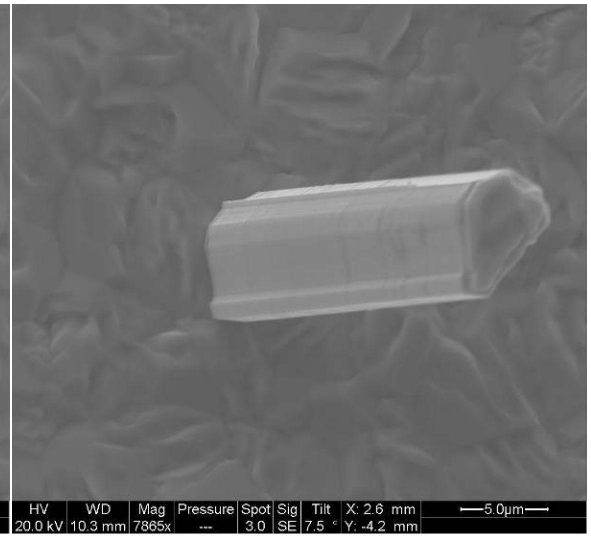
Whisker 14



Whisker 15


HV
20.0 kV
WD
10.3 mm
Mag
7865x
Pressure

Spot
3.0
Sig
SE
Tilt
0.1 °
X: 2.6 mm
Y: -4.2 mm
5.0µm

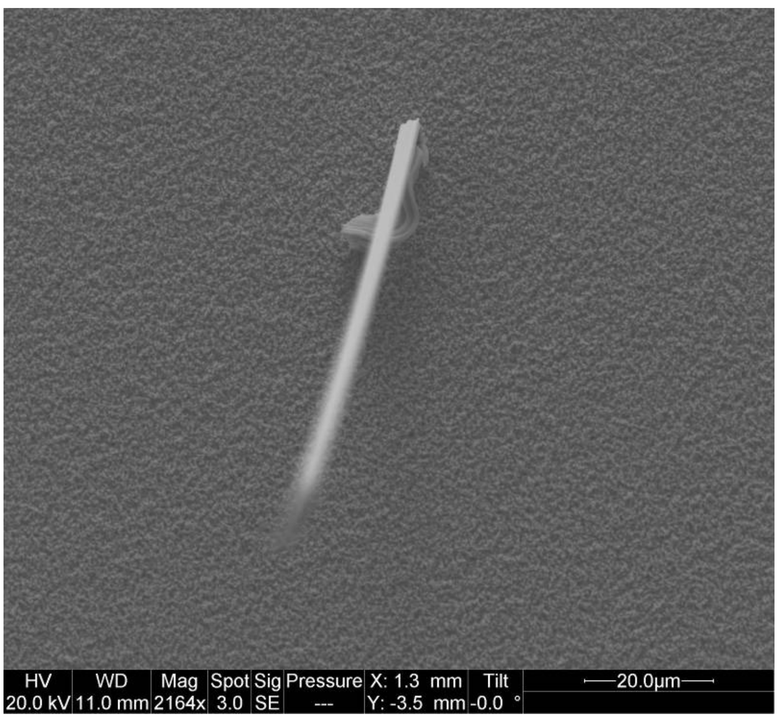

HV
20.0 kV
WD
10.3 mm
Mag
7865x
Pressure

Spot
3.0
Sig
SE
Tilt
7.5 °
X: 2.6 mm
Y: -4.2 mm
5.0µm

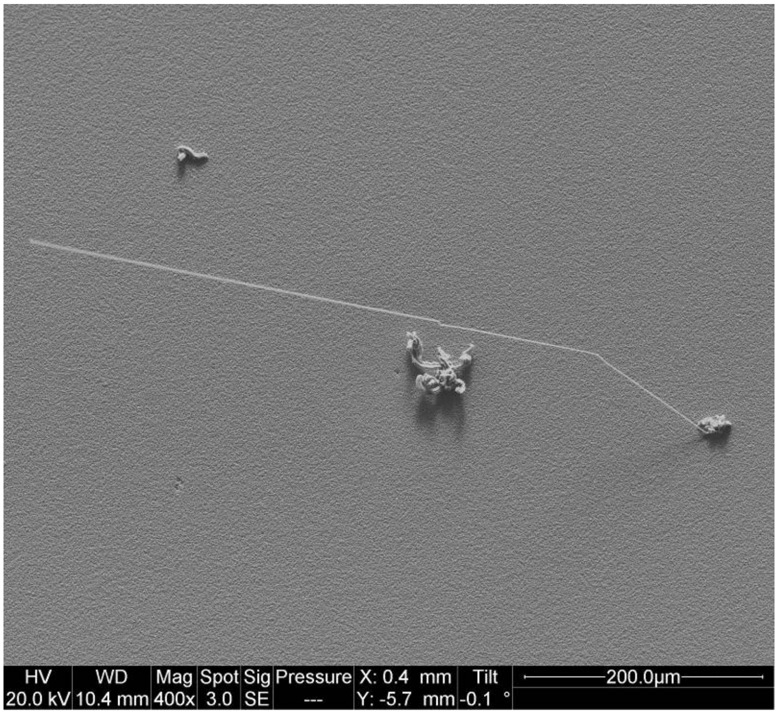
Appendix B: Whiskers for Length Measurements from Tilting under SEM

The following three whiskers were measured by seven participants. Measurements were done under SEM by tilting and rotating the whiskers such that they are aligned perpendicular to the field of view. These measurements were then compared to calculated whisker lengths using the tilting method.

Whisker 1: single filament



Whisker 2: three-segment whisker, length measured as sum of three segments



Whisker 3: multi-segment whisker measured as shorting-length distance

Appendix C: Whisker length and Density Distribution Parameters for Experiment 2

Table 27 Normal parameters of whisker density at different inspection intervals of Experiment 2 as compared to ambient

Set1

mean

TC500	12	18	*20days*
TC1000	13	29	*44days*

std

TC500	9	12	*20days*
TC1000	8	17	*44days*

Set2

mean

TH1000	13	29	*44days*
TH2000	14	36	*96days*
TH3000	13	41	*149days*

std

TH1000	11	17	*44days*
TH2000	10	18	*96days*
TH3000	12	16	*149days*

Set3

mean

TC500	27	18	*20days*
TC1000	24	29	*44days*
TH1000	25	37	*83days*
TH2000	24	40	*132days*
TH3000	24	42	*168days*

std

TC500	29	12	*20days*
TC1000	26	17	*44days*
TH1000	25	20	*83days*
TH2000	25	17	*132days*
TH3000	24	17	*168days*

Set4

mean

TH1000	8	29	*44days*
TH2000	12	36	*96days*
TH3000	12	41	*149days*
TC500	12	42	*168days*
TC1000	12	42	*180days*

std

TH1000	11	17	*44days*
TH2000	12	18	*96days*
TH3000	12	16	*149days*
TC500	12	17	*168days*
TC1000	12	18	*180days*

Set5

mean

TC500	2	18	*20days*
TH1000	9	29	*72days*
TH2000	4	38	*119days*
TH3000	5	41	*149days*
TC1000	5	42	*180days*

std

TC500	4	12	*20days*
TH1000	20	18	*72days*
TH2000	8	16	*119days*
TH3000	13	16	*149days*
TC1000	13	18	*180days*

Set6

mean

TH1000	5	29	*44days*
TH1500	5	29	*72days*
TC500	10	36	*96days*
TC1000	10	38	*119days*
TH2000	11	40	*132days*
TH3000	11	42	*180days*

std

TH1000	7	17	*44days*
TH1500	7	18	*72days*
TC500	10	18	*96days*
TC1000	12	16	*119days*
TH2000	12	17	*132days*
TH3000	12	18	*180days*

Table 28 Lognormal parameters of whisker length at different inspection intervals of Experiment 2 as compared to ambient

Set1

m

TC500	2.3	2.4	*20days*
TC1000	2.3	2.5	*44days*

s

TC500	0.4	0.5	*20days*
TC1000	0.4	0.5	*44days*

Set2

m

TH1000	2.5	2.5	*44days*
TH2000	2.5	2.7	*96days*
TH3000	2.3	2.7	*149days*

s

TH1000	0.3	0.5	*44days*
TH2000	0.3	0.5	*96days*
TH3000	0.4	0.5	*149days*

Set3

m

TC500	2.5	2.4	*20days*
TC1000	2.4	2.5	*44days*
TH1000	2.4	2.7	*83days*
TH2000	2.4	2.7	*132days*
TH3000	2.4	2.7	*168days*

s

TC500	0.4	0.5	*20days*
TC1000	0.4	0.5	*44days*
TH1000	0.4	0.5	*83days*
TH2000	0.4	0.5	*132days*
TH3000	0.4	0.5	*168days*

Set4

m

TH1000	2.4	2.5	*44days*
TH2000	2.4	2.7	*96days*
TH3000	2.4	2.7	*149days*
TC500	2.4	2.7	*168days*
TC1000	2.4	2.7	*180days*

s

TH1000	0.4	0.5	*44days*
TH2000	0.4	0.5	*96days*
TH3000	0.4	0.5	*149days*
TC500	0.4	0.5	*168days*
TC1000	0.4	0.5	*180days*

Set5

m

TC500	2.4	2.4	*20days*
TH1000	2.3	2.6	*72days*
TH2000	2.4	2.7	*119days*
TH3000	2.6	2.7	*149days*
TC1000	2.6	2.7	*180days*

s

TC500	0.4	0.5	*20days*
TH1000	0.3	0.5	*72days*
TH2000	0.5	0.5	*119days*
TH3000	0.7	0.5	*149days*
TC1000	0.7	0.5	*180days*

Set6

m

TH1000	2.5	2.5	*44days*
TH1500	2.5	2.6	*72days*
TC500	2.4	2.7	*96days*
TC1000	2.4	2.7	*119days*
TH2000	2.4	2.7	*132days*
TH3000	2.4	2.7	*180days*

s

TH1000	0.3	0.5	*44days*
TH1500	0.3	0.5	*72days*
TC500	0.4	0.5	*96days*
TC1000	0.4	0.5	*119days*
TH2000	0.4	0.5	*132days*
TH3000	0.4	0.5	*180days*

Table 29 Normal parameters of whisker length at different inspection intervals of Experiment 2 as compared to ambient

Set1

mean

TC500	11	12	*20days*
TC1000	10	14	*44days*

std

TC500	4	6	*20days*
TC1000	4	7	*44days*

Set2

mean

TH1000	13	14	*44days*
TH2000	13	17	*96days*
TH3000	11	17	*149days*

std

TH1000	4	7	*44days*
TH2000	4	9	*96days*
TH3000	4	10	*149days*

Set3

mean

TC500	13	12	*20days*
TC1000	11	14	*44days*
TH1000	11	16	*83days*
TH2000	11	17	*132days*
TH3000	11	17	*168days*

std

TC500	5	6	*20days*
TC1000	4	7	*44days*
TH1000	4	9	*83days*
TH2000	4	10	*132days*
TH3000	4	10	*168days*

Set4

mean

TH1000	11	14	*44days*
TH2000	12	17	*96days*
TH3000	12	18	*149days*
TC500	12	17	*168days*
TC1000	12	18	*180days*

std

TH1000	4	7	*44days*
TH2000	4	9	*96days*
TH3000	4	10	*149days*
TC500	4	10	*168days*
TC1000	4	10	*180days*

Set5

mean

TC500	11	12	*20days*
TH1000	11	16	*72days*
TH2000	13	17	*119days*
TH3000	17	18	*149days*
TC1000	17	18	*180days*

std

TC500	4	6	*20days*
TH1000	3	8	*72days*
TH2000	6	10	*119days*
TH3000	12	10	*149days*
TC1000	12	10	*180days*

Set6

mean

TH1000	12	14	*44days*
TH1500	13	16	*72days*
TC500	11	17	*96days*
TC1000	12	17	*119days*
TH2000	11	17	*132days*
TH3000	11	18	*180days*

std

TH1000	4	7	*44days*
TH1500	4	8	*72days*
TC500	4	9	*96days*
TC1000	5	10	*119days*
TH2000	4	10	*132days*
TH3000	4	10	*180days*

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