



EXAMINATION OF TIN WHISKER GROWTH IN ELECTRONIC ASSEMBLIES

PHD THESIS

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Motivations and aims of the research

In the manufacturing of electronic assemblies, the electronic components are fixed onto the printed circuit board mainly by soldering. In order to gain good solderability, the leads of electronic components are coated with a thin layer of a certain metal. For many years, in the electronic industry solders and coatings were made of tin-lead alloys, due to their low melting temperatures and wide availability.

In the previous years, the European Union has adopted a directive (RoHS - Restriction of Hazardous Substances [1]) on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Restrictions on the use of lead forced most electronic part manufacturers to replace the traditionally used tin-lead finishes to lead-free finishes. Among these, tin electroplating became the most common method because of its good wettability, corrosion resistance, reliable solder joints, low cost and ease of storage. However, it soon became obvious that these platings form whiskers easily. Tin plated films containing more than 3% lead mitigate the formation of tin whiskers and this had been an industry accepted solution for over 50 years [2,3]. The absence of lead has resulted in a reliability issue by the formation of conductive tin whiskers, although it was not entirely an unknown phenomenon before. A tin whisker is a single crystal tin needle with typical diameters of 0.5 to 10 μm , and length of up to mm magnitude [4–7]. It is grown spontaneously on finished surfaces and grows across component leads can cause current leakage or short circuits, and ultimately the failure of electronic circuits. Although its mechanism is not completely understood, it is mainly theorized that such growth is caused by compressive mechanical stress gradients in the tin layer (such as residual stresses caused by electroplating; stresses caused by the diffusion of different metals, development of intermetallics or oxides, thermally induced stresses or mechanically induced stresses). In the presence of compressive stress the whiskers are extruded as a stress release mechanism [8, 9].

Minimizing the size of electronics and reducing the space between components significantly increases the probability of whisker bridging and creating a shortcut. It may be formed spontaneously after electroplating or during storage with an incubation time even up to years. Whiskers can be found on various parts of the electronic assemblies: components leads, printed wiring boards coatings, connectors, or even the metal packaging of components.

After reviewing the literature I found that although there is some research about the appearance of whiskers since the 1950's, the majority of the papers only began published in 2000's just before the electrical industry's transferring towards lead-free coatings. Therefore

the whisker growth mechanism is still not a fully understood process. After analysing the existing literature on the subject my conclusions are summarized in the following points:

- Currently in the literature there is a wide variety of accelerated life test methods to examine the whiskering properties of different coatings but, because of the diversity of the whisker growth factors, many test methods are waiting to be investigated.
- Although researchers are looking for a solution to prevent the formation of whiskers, the currently available methods are only partially effective. Additionally, in the literature only a few studies were found where the whiskering properties of the different grain structured tin layers are examined. No research has been made on enlarging or modifying the grain morphology after plating, nor about their effects on whisker growth.
- To inhibit the development of Cu_6Sn_5 intermetallic layer which conducts the formation of whiskers, in some cases, silver or nickel underlayer is placed between the copper substrate and tin coating. At these structures, the formation and the properties of the intermetallic layer between the tin-nickel and tin-silver are lacking the related literature; the existing models have not been verified with experimental results or calculations. No thorough research has yet been carried out regarding the effect of silver underlayers on whisker mitigation.
- Alloying tin with different metals change the whiskering properties of the layer, certain substances (e.g. lead, copper, etc.) change the number of whiskers on coatings. Currently there is only limited research on the effects of copper on whiskering on tin-copper alloy coatings which only examined alloys with a smaller percentage of copper (up to 3,7% Cu) on mainly electroplated coatings. The copper-alloyed coatings have not been aged in high humidity conditions; hence the effects of oxidation and corrosion on the alloys are unknown.
- The physical process of tin oxide formation and its growth parameters are not yet thoroughly understood. In addition, the role of the corrosion on whiskering formed on tin layers is not completely clear. All the observations about the effect of humidity, corrosion and the development of tin-oxides are in aspect of their effect on the tin layer, but there are no observations about the effect on the already developed whiskers.

Consequently, there are still a lot of unclear issues in the field of tin whiskers. In order to minimize the appearance of this fault, the better understanding of the physical background of the phenomenon is necessary. Therefore, nowadays examination of whisker formation

has become particularly current. In light of the above, in this dissertation I have chosen the following main topics:

- Examining the whisker resistance of tin layers equipped with silver and nickel underlayers under accelerated life tests
- Analysing the intermetallic between tin-silver and tin-nickel layers and their effect on whisker growth
- Investigating the effect of tin oxide growth and tin corrosion on whisker formation
- Observing the impact of grain deformation due to recrystallization on the whisker formation
- Examining the increasing the percentage of copper in tin-copper alloys and their effect on whisker formation in high humidity circumstances.

Applied observation techniques

Normally, the formation of tin whiskers can be measured in years. I have aged the created samples with different accelerating environmental tests in order to develop the whiskers more quickly. A number of accelerating environmental test standard has spread, which are used to detect parameter changes, failures, and other phenomena that occur during the lifespan of electronic components within a shorter period of time. Some of the accelerated tests are such as HAST (Highly Accelerated Stress Test), HTSL (High Temperature Storage Life) and TS (Thermal Shock). During the reliability tests, the samples are stored in climatic chambers at temperatures higher than room temperature and/or combined use of high relative humidity conditions or subjected to sudden changes in temperature. This procedure called "aging" is a commonly used process in electronics for examination, where the above factors are influencing separately or combined.

According to the literature, the rising of temperature accelerates the diffusion processes occurring in the material, similarly to the formation rate of intermetallic alloys and the oxidation-corrosion processes, and it increases compressive stress necessary for the development of whiskers [10]. However, the higher temperature has a positive impact on the mechanical stress relaxation process as well. The increase of humidity accelerates the corrosion-oxidation processes. I have chosen the majority of the temperature and humidity settings for the accelerated life tests according to the JEDEC whisker test standard [4]. In the

different cases I have studied other special properties (such as tin-oxide growth), which are not suitable for these standard values.

Various surface analytical methods are necessary for examining the developed surface structures. I have investigated the surface of the samples and the shapes and sizes of the whiskers first by scanning electron microscope (SEM). Initially, lower magnification ($\times 150 - \times 300$) was used to observe and search the entire surface for whiskers and to identify the longest one. After, the whiskers were further inspected by using higher magnification (up to $\times 10,000$). In some cases, in order to find the correct length of the whisker, the sample had to be first rotated and tilted. I have applied FIB (Focused Ion Beam) technique for the cross-sectional observation of the layers by etching with a focused ion beam on the sample. By this, the cross-section of the area can be observed to up to $20 \mu\text{m}$ depth after tilting by $45-60^\circ$. FIB Scanning Ion Microscope (SIM) images offer better channelling contrast than SEM images, which are formed by differences in crystalline orientations. This provides a more detailed information of the cross-sectional structure, this way it is also possible to examine the grain structure of the layers. The chemical composition of the layers and element mapping can be determined with the use of EDS (Energy Dispersive X-ray Spectroscopy). EDS is a method suitable to determine elemental composition in mass or atomic percentage on a specific area of the material. The SEM/ EDS can be used to find the chemical composition of materials down to a spot size of around $1 \mu\text{m}$, and to create element composition maps over a much broader area. But for analysing the elements on the cross-section of the sample after etching by FIB, this spot size is too large. In this case transmission electron microscopy (TEM) EDS is used where the spot size is an ultimate small area of 5 nm so accurate analysis can be made. In order to do so, the TEM samples must be electron transparent which means that the thickness must be about 100 nm or less. If an exact position on the sample needs to be observed by TEM (e.g. the root of a whisker) FIB is used to mill very thin membranes from the specific area of interest.

New scientific results

Thesis Group 1: Whiskering Properties of Structures with Underlayers in Humid Environment

Thesis 1.1: I have proved that tin layers are more whisker resistant in the early stage with silver underlayers than layers with nickel underlayers, until the point when the tin diffuses into the silver layer and makes contact with the copper and forms Cu_6Sn_5 intermetallics which create additional stress in the tin layer. I have shown experimentally that the Ni_3Sn_4 intermetallics expand towards the tin layer instead of the nickel layer creating stresses initially inside the tin layer.

I have experienced that storing samples at 40 °C/ 95% RH, the first whiskers appeared early (at 2200 hours), and grew continuously on tin layers with nickel underlayers. The explanation of this phenomenon is that the Ni_3Sn_4 intermetallic layer grows towards the tin instead of the nickel layer, thereby creating compressive stress instantly in the tin layer, which is contrary to the statement of the existing literature [10]. Based on the results of my experiments, observing the intermetallic layer growth between the silver and nickel underlayer and the tin layer, I have found that the silver layer reacts faster with the neighbouring copper and tin layer compared to nickel, when stored for the same period of time. After storing for 4200 hours, I have investigated that while the nickel layer remained completely intact, the thickness of the silver layer decreased to nearly one third and at some parts the copper layer diffused through the layer, and formed Cu_6Sn_5 intermetallic rapidly after reaching the tin layer. This is the reason why the whiskering ability of the silver underlayered samples increased rapidly after 4200 hours compared to the nickel samples.

In case of storing at 105 °C/ 100% RH, I have experienced longer whiskers to develop on the silver underlayered samples compared to the nickel underlayered samples. The longer whiskering property of the silver underlayer samples is due to the following: the moment when the copper diffused through the silver underlayer and formed intermetallic with tin was sooner at high temperature (105 °C) than at lower temperature (40 °C) as the diffusion rate is highly dependent on the temperature. Similarly, the Ni_3Sn_4 intermetallics expanded towards the tin layer creating stresses inside the tin layer. However the growth rate of Ni_3Sn_4 is much lower than the growth rate of Cu_6Sn_5 (as in case for the penetrated silver layer) and the material transport caused by the slowly generated stress can be blocked by the rapid oxidation in the case of the high temperature and high humidity condition (see Thesis 1.2). Longer whiskers are more likely to cause short circuits in electronic devices, so the lengths of whiskers are more important than the density in practical aspect of system reliability. Hence

coatings with silver underlayers may be more vulnerable to shorts created by whiskers than the coatings with nickel underlayers.

Thesis 1.2: I have proved that in case of an increased surface oxidation of tin, the longitudinal growth of whiskers is "converted" to the growth of the whisker density.

I have experimentally found that on the samples aged at 105 °C/ 100% RH the tin coating does not follow the known whisker formation process known in the literature [4], a novel mechanism for whisker growth occurs due to the formed thick oxide layer. The excessive oxidation evolving in this environment prevents the growth of the developing whisker. After a whisker had grown out, the hostile environment oxidized it quickly, which stops the growth. Additional stresses in the layer do not make the whisker grow longer; instead new whiskers grow out at the cracks of the surface beside the existing whisker. This way the whisker density grows instead of the length. In this case, the developed whiskers do not follow the usual whisker appearance, the developed whiskers are thicker ($>10\ \mu\text{m}$), and may grow in bundles (which are 30-40 μm large). In this connection I have discovered and interpreted the "whisker-on-whisker" phenomenon. In case there is a crack on the oxide layer of the whisker and additional stress in the tin layer causes tin atoms to diffuse into the whisker, I have observed that a new whisker may grow out of the existing whisker, which will grow until the appearing oxide layer on its surface causes it to stop.

Publications related to Thesis group 1: L1, L2, R1, R2.

Thesis Group 2: The Role of the Grain Structure of Tin for Whisker Growth

Thesis 2: I have proved that due to the recrystallization process, the transformation of the grain structure within the tin layer delays the development of whiskers.

I have examined the recrystallization (stretched by 5% and then annealed in 150 °C for 1 hour) as a new procedure to reduce whisker formation. The samples treated with this process were compared with samples treated by annealing (which is a whisker mitigating procedure applied by the industry), and untreated reference samples. I have examined the whisker growth properties of these samples with the following accelerated reliability tests: 105 °C/ dry, 50 °C/dry and temperature cycling. I have concluded that during aging, the pre-treatment methods (mainly recrystallization) result in a delaying effect in time of the first whisker appearance compared to the reference samples, which advantage will become negligible over time because of the additional intermetallic layer thickness growth and re-accumulation of tensions. The reason is as follows: in case of the annealing, the grain structure is not transformed, but the electroplating caused the initial stress to relax, so the

developing stress due to intermetallic layer formation occurs later. However, in case of the recrystallized samples a new grain structure is formed; instead of the original columnar grains, a mixed structure of semi-columnar and horizontal grains is formed, which is more resistant to whisker development. I have shown experimentally and explained theoretically that in case of a bright tin (grain size ≤ 500 nm) layer under a nodule or hillock, inside at the bottom of the columnar grains near the intermetallic region, large amount of voids develop. I have proven that the reason for this is that the tin diffuses from the grains into the large hillock or nodule, and the large quantity of mass transport void is formed at the bottom of the columnar grain.

Publications related to Thesis group 2: L3, R3.

Thesis Group 3: The Whiskering Properties of Tin-Copper Alloys in Various Humidity Conditions

Thesis 3.1: I have proved that the two main influencing factors of whisker growth for tin-copper alloys were the level of oxidation and the copper content of the alloys. I have established that in case of 85 °C/ 85% RH conditions, the higher copper content of the alloys caused higher whisker density, but the first appearance of whiskers occurs later in time.

I have investigated the whisker growth differences of two high humidity conditions (85 °C/ 85% RH and 105 °C/ 100% RH) on pure tin and tin-copper alloys. In the case of the 85 °C/ 85% RH test condition, the level of oxidation was much less than in the case of 105 °C/ 100% RH because of both the higher temperature and humidity. Additionally, the diffusion rate within the whisker grain is lower in case of 85 °C/85% RH test condition, as it is highly dependent on the temperature. In relation with this, the whiskering behaviour of the alloys was very different during the different tests. The higher copper content of the alloys caused higher average whisker density and length in the case of both test types. In the case of 85 °C/ 85% RH test although the humidity was high, severe corrosion did not occur, therefore the whisker density was low but the developed whiskers were longer. During this test condition, it was also proven that the higher copper content of the alloys caused higher whisker density. Since the high copper content has a higher corrosion rate, the additional stresses due to the tin and copper oxides accelerates the whisker growth after the first appearance. The larger the copper content is in an alloy, the more stress will develop due to the corrosion of the alloy coating. Since melting points of alloys with higher copper content increase rapidly, grain growth due to recrystallization in these alloys cannot be so efficient and develop slower. Hence the first appearance of whiskers occurs later in time. But since

the high copper content has a higher corrosion rate, the additional stresses due to the tin and copper oxides accelerate the whisker growth after the first appearance.

Thesis 3.2: I have shown experimentally and explained theoretically that in case of extreme high temperature and humidity conditions (105 °C/ 100% RH), a new phenomenon develops in tin-copper alloys, called the copper-oxide whiskers.

I have proved that the major force for copper-oxide whisker growth on tin-copper alloy surface finishes in highly oxidizing 105 °C/ 100% RH environment is because of the corrosion of the Cu_6Sn_5 intermetallic layer. I have experienced that the two main influencing factor of the whisker growth was corrosion and the copper content of the alloys. On pure tin coatings, an even layer of SnO_x oxide layer develops on the surface of the layer, but on tin-copper alloy coatings, spots of Cu_xO will develop within the SnO_x layer. Storing the samples in elevated temperature generates a large mass of Cu_6Sn_5 intermetallic within the coating. During the localized corrosion of the tin (and tin-copper alloy) coating, water and oxygen easily reaches to the Cu_6Sn_5 intermetallic. Tin is anodic to copper and copper alloys and to the intermetallic compounds formed between tin and copper in most aqueous environments and hence the corrosion of the coating accelerates inwards in the layer. Because the developed SnO_x (and traces of Cu_xO) rust is precipitated as a result of secondary reactions, it is porous and absorbent which encourages further corrosion. Hence, due to the meeting of water and Cu_6Sn_5 , oxygen atoms diffuse into the Cu_6Sn_5 layer, break up the intermetallic material and enrichment of Cu_2O occurs. When SnO_x is formed from the Cu_6Sn_5 , the volume expands and compressive stress is generated, which is the driving force for copper-oxide whiskers. In case of tin-copper alloys, weak spots of Cu_xO are found on the oxide layer which is needed to relieve the developed internal compressive stress as copper-oxide whisker formation. If no Cu_xO is developed on the surface of the samples in early stage (such as in case of pure tin coatings), separation also occurs underneath the corrosion spots, but due to hardness of the tin-oxide it is impossible for the copper-oxide to break through, hence no copper-oxide whiskers develop.

Publications related to Thesis Group 3: L4, R4.

The Application of the Results

The results discussed in the thesis are mainly considered as basic research. Their fundamentality can be subject to the future whisker- research and hopefully provide direction towards the solution of the phenomenon. Currently, the whisker is a failure which still occurs in the industry very often, and decreases the lifespan of products.

The examinations described in **Thesis Group 1** have been developed for the order of the automotive electronics manufacturing company Robert Bosch Ltd. The measurement results show that high humidity conditions develop whiskers more strongly. Furthermore, it is clear that the extremely high corrosion conditions stop the growth of whiskers due to the inhibitory effect of tin-oxide.

The results of **Thesis Group 2** show that with the use of the recrystallization process gives the possibility to delay the formation of whiskers in a new way, thereby extending the lifespan of electronic devices. The experiments were carried out with the cooperation of National Institute for Materials Science (NIMS) located in Japan.

In **Thesis Group 3**, I discovered a new type of fault, the copper-oxide whiskers. During the collaboration with NIMS, I have explained the physical background of this phenomenon and I have proved it by experiments. Additionally, I have investigated the whiskering ability of tin-copper alloy coatings, which is an important factor for describing the reliability of these kinds of surface finishes.

All of the work is connected to the scientific program of the “Development of quality-oriented and harmonized R+D+I strategy and functional model at BME” project. This project is supported by the New Hungary Development Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002). The work reported in the dissertation has been developed in the framework of the project „Talent care and cultivation in the scientific workshops of BME” project. This project is supported by the grant TÁMOP - 4.2.2.B-10/1--2010-0009.

Thesis Related Publications

Papers published in international or Hungarian journals in English:

- L1. **B. Horváth**, B. Illés, G. Harsányi, T. Shinohara: “Effects of Humidity on Tin Whisker Growth – Investigated on Ni and Ag Underplated Layer Construction”, *Thin Solid Films* 520, 2011, pp. 384–390
- L2. B. Illés, **B. Horváth**, G. Harsányi: “Effect of Strongly Oxidizing Environment on Whisker Growth form Tin Coating” *Surface & Coatings Technology* vol. 205 , 2010, pp. 2262–2266
- L3. **B. Horváth**, B. Illés, T. Shinohara, G. Harsányi: “Whisker Growth on Annealed and Recrystallized Tin Platings”, *Thin Solid Films* 520, 2012, pp. 5733–5740
- L4. **B. Horváth**, B. Illés, T. Shinohara, G. Harsányi, “Determining Whiskering Properties of Tin-Copper Alloy Solder-dipped Platings”, *Periodica Polytechnica – Electrical Engineering* 54/3-4, 2010, pp. 107-110

Papers published in proceedings of international conferences in English:

- R1. **B. Horváth**, T. Shinohara, B. Illés, G. Harsányi: "Tin Whisker Growth at High Humidity Environments – Investigated on Ni and Ag Underlayered Leadframes" Proceedings of 57th Materials and environment debate – Japan Society of Corrosion Engineering, Okinawa, Japan, 2010, pp. 304-307.
- R2. **B. Horváth**, B. Illés, G. Harsányi: „Investigation of Tin Whisker Growth: The Effects of Ni and Ag Underplates" Proceedings of 32nd ISSE conference, Brno, Czech Republic, 2009, pp. 1-5.
- R3. **B. Horváth**, B. Illés, T. Shinohara, G. Harsányi: "Microstructure of Sn thin films and its effect on whisker growth after stretching and annealing", Proceedings of 3rd Asian Materials Data Symposium (AMDS2012), Naha, Japan, 2012
- R4. B. Illés, **B. Horváth**, T. Shinohara, G. Harsányi: "Tin Whisker Growth from Sn-Cu (0-5 wt%) Surface Finishes", Proceedings of 17th SIITME conference, Timisoara, Romania, 2011

Further Scientific Publications

Papers published in proceedings of international conferences in English:

- R5. B. Illés, **B. Horváth**, B. Lipák, "Investigating Whisker Growth on Annealed and Recrystallized Tin Platings", Proceedings of 34th ISSE2011 conference, Tatranska Lomnica, Slovakia, 2011
- R6. B. Illés, **B. Horváth**, B. Lipák, A. Géczy "Investigating Whisker Growth on Immersion Tin Surface Finishing", Proceedings of 35th ISSE conference, Bad Aussee, Austria, 2012
- R7. **B. Horváth**, G. Harsányi: "Mechanical stress induced whiskers", Proceedings of 15th SIITME conference, Gyula, Hungary, 2009. pp. 389-393.
- R8. **B. Horváth**, "Review on problems of tin whiskers after RoHS changes", Proceedings of 14th SIITME conference, Predeal, Romania, 2008. pp. 145-149.
- R9. **B. Horváth**, "The directive on RoHS, and the examination of the restricted materials with XRF machine", Proceedings of 31st ISSE conference, Budapest, Hungary, 2008, pp. 130-133.

Other Publications:

- E1. **B. Horváth**, „Az ólommentes forrasztás környezeti hatásai”, ElectroNet magazine, 2008/5

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