Investigations of Zinc (Zn) Whiskers using FIB Technology

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Abstract
Mitigation of tin whiskers on tin plated components is a critical issue that must be addressed by the electronics industry prior to the implementation of lead-free processing. The study of whisker formation and growth in alternative material systems may provide insight into mechanisms for whisker behavior in tin systems. This work focuses on the characterization of zinc whiskers grown from an electroplated zinc layer over carbon steel. Focused ion beam (FIB) technology and traditional metallography techniques are used to prepare cross-sectional views. Samples are examined using optical, scanning electron, and transmission electron microscopy. X-ray diffraction techniques are also used to characterize the electroplated zinc layer over steel. Intermetallic compounds do not appear to play a significant role in the generation of compressive stress within the electroplated zinc. Previous studies from the literature examining zinc whiskers and dislocation loops in zinc are reviewed. Characterization of the zinc over steel system provides a framework for further discussion of comparisons and contrasts between zinc and tin.

Introduction
Tin (Sn) whisker mitigation is of high importance to the electronics industry as the transition to lead-free manufacturing takes place. Consensus within the electronics industry on tin whisker mitigation and testing is difficult to achieve because the fundamental mechanisms for whisker formation and growth are not well understood. Without knowledge of the fundamental mechanisms, development of standardized, accelerated tests for whisker growth is almost impossible. Although tin (Sn) is the primary material of interest, zinc (Zn) electroplated coatings produce whiskers with similar characteristics to those seen in pure tin (Sn) coatings. Much can be learned by studying the “whiskering” behavior of alternative material systems, some of which may be applicable to increasing our understanding of tin whiskers. This work focuses on a preliminary study of zinc whiskers grown from electroplated zinc coatings on steel.

Whisker formation and growth is hypothesized to be a multi-stage process including: 1.) whisker nucleation, 2.) growth part I - atoms being added to the whisker, and 3.) growth part II - long range diffusion required for enough atoms to be present to result in the observed whisker lengths. Careful examination and characterization of material cross-sections will provide insight into these stages of whisker formation and growth. Focused ion beam (FIB) cross-sections of tin whiskers were first published by Xu et al. [1] and Baudry and Kerros [2] in 2001. Both studies reported similar microstructures. The FIB images showed that the root of the tin whisker grain was in contact with copper-tin intermetallic. See Figure 1. The tin finishes examined (in cross-section) by Xu et al. were matte tin and satin bright tin, with grain sizes of 2-3 microns and approximately 1 micron, respectively. Lee and Lee [3] correlated tin whisker growth with compressive stress as a function of storage time. The stress was attributed to the formation of an irregular intermetallic compound (IMC) at the tin grain boundaries.

Figure 1 - FIB cross-section of tin whisker (satin bright finish). The whisker grain is in contact with copper-tin intermetallic compound (IMC). [1] Courtesy C. Xu
While intermetallics add to the stress state in tin-copper metallurgical couples, the same does not appear to be true for electroplated zinc on steel. Zinc and iron can form several intermetallics as shown by the phase diagram in Figure 2.[4] These intermetallic compounds are an integral part of forming corrosion resistant coatings by the hot dip galvanizing process, where the intermetallics form rapidly at high temperature. The electroplating process, by contrast, occurs at lower temperatures and the formation of intermetallic compounds is less pronounced.

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Figure 2 - Equilibrium Fe-Zn phase diagram showing room temperature intermetallic phases. [4]

Experimental
The sample used in this study was a carbon steel substrate with an electroplated zinc coating. [5] The sample was removed from the underside of a raised access floor tile in a data center. The sample was thought to be 15 to 20 years old, although this information could not be confirmed. No additional information regarding the history of this tile was available.

The surface of the electroplated layer was first examined with optical and scanning electron (SEM) microscopy. FIB (focused ion beam) technology was then used to prepare cross-sectional views of both whisker-free and whisker-containing regions. The FIB uses gallium ions to impinge on the surface being studied. These gallium ions effectively mill away material without mechanical polishing or chemical etching. Successive images can be captured as material is removed. Additional characterization of the specimen was conducted using traditional metallography. X-ray diffraction was performed using a Bragg reflection diffractometer and CuKα radiation with a spot size of 500nm. The iron based substrate led to small levels of Fe fluorescence through the film, which were eliminated through background correction. A transmission electron microscopy (TEM) specimen was also prepared using FIB. A sputtered layer of platinum was used to protect the whisker during TEM sample preparation.

Results
SEM photos with examples of zinc whiskers observed in this specimen are shown in Figures 3a to 3c. Figure 3c shows an example of zinc whisker with a nodule at the base.

Figure 3a – Zinc whisker observed on electroplated layer.  
Figure 3b – Zinc whisker observed on electroplated layer. A TEM specimen was prepared from this whisker location. See Figures 7 and 8.
Figure 3c - Zinc whisker with a nodule at the base. FIB cross-sections of this whisker are examined in this study.

A FIB cross-section of the as-plated material is shown in Figure 4, revealing microstructures of both the electroplated zinc layer and the steel substrate. The steel substrate illustrates a non-equiaxed microstructure with grain ranging in size from 4 – 10 \( \mu m \). The electroplated zinc layer has a thickness of approximately 1 \( \mu m \) and appears to have a very fine grain (sub-micron) structure. A metallurgical cross-section of the zinc on steel structure reveals the thickness and morphology of the deposit. The zinc is nominally 1 \( \mu m \) thick. Since it is an electroplated layer, there are some fluctuations in the thickness as a function of location. The thickness variation is less than 20%. There is no obvious iron-zinc intermetallic formation visible in the traditional cross-sections.

Figure 5 shows a series of photos taken during the focused ion beam milling process. The whisker under examination is the same whisker shown in Figure 3c. Figures 5a-5c show the whisker as a function of time during the ion milling process. Figure 5d is a higher magnification photo of Figure 5c. The most striking difference between the tin whisker cross-sections published by Xu et al. [1] and the zinc whisker cross-sections shown in this study, is the fact that the zinc electroplated layer, and the zinc whisker itself, appear to be polycrystalline and fine-grained. Several additional FIB cross-sections were made in order to determine if this observation of a polycrystalline structure was repeatable and characteristic of the zinc electroplated layer. All cross-sections showed similar characteristics, including those prepared by traditional metallography techniques.
The grain size of zinc layer could not be determined from traditional metallurgical cross-sectioning. While individual grains cannot be seen in the FIB micrographs, the grain size is clearly submicron in size. When the grain size is less than about 0.1 µm, the term “particle size” is usually used. [6] X-ray diffraction can be used to approximate the particle size. Analysis of the two strongest independent peaks results in a particle size of 32nm. The x-ray diffraction pattern for this sample of zinc on steel is shown in Figure 6. The fine grain (or particle) size of this zinc plating will expedite mass transport and long range diffusion in the zinc layer.

Figure 5b - Photo showing the same whisker as in Figure 5a with additional material removed by ion milling.

Figure 5c - FIB cross-section of a zinc nodule and whisker grown from an electroplated zinc layer on a steel tile.

Figure 5d - Higher magnification photo of Figure 5c. A fine-grained, polycrystalline microstructure of the zinc layer is observed.

Figure 6 - X-ray diffraction pattern for zinc on steel. Powder diffraction peaks are indicated for zinc (red), iron (blue) and zincite, ZnO (green).
Figure 7 illustrates the use of FIB to prepare a TEM specimen of a zinc whisker. The original zinc whisker, prior to FIB sample preparation, is shown in Figure 3b. As mentioned, platinum was sputtered on the plating surface to protect the zinc whisker during the FIB process. The horizontal features seen in Figure 7 are platinum artifacts. Figure 8 shows a TEM image of an area at the base of a whisker. The grain structure of the steel substrate material is clearly seen. Dislocations can also be observed in the carbon steel substrate material. It is difficult to differentiate between the zinc electroplated layer and the actual zinc whisker; both appear to have a fine-grained structure. Dislocation structures, if present in the zinc layer, could not be resolved, perhaps due to the fine grain size of the material.

**Discussion**

Consideration of the similarities and differences between tin and zinc and their resulting whiskers, is useful in order to gain a greater understanding of whisker formation and growth.

Several studies have provided evidence that tin whiskers appear to grow from the base. [7-9] Lindborg [10] suggests that, “Since the general morphology with striations along the whisker and frequent formations of nodules at the base is quite similar for tin, cadmium and zinc whiskers it is most likely that spontaneous cadmium and zinc whiskers also grow from the base.” Lindborg goes on to point out, however, that although the substrate and [external] stress effects are pronounced for tin, these effects do not appear to be as strong for zinc and cadmium. These comments are consistent with observations from this study. Iron-zinc intermetallics [substrate effects] do not appear to play a significant role in the generation of compressive stress within the electroplated zinc. Intermetallics were not observed in either the FIB images, or the x-ray diffraction spectra.

An intriguing similarity between zinc, cadmium and tin is that each of these materials demonstrates anisotropic thermal expansion behavior. The coefficient of thermal expansion (CTE) varies significantly between the “c” axis and the “a” axis for zinc, cadmium and tin as shown in Table 1. [11] Zinc and cadmium both have hexagonal close packed crystal structures while tin has a body centered tetragonal crystal structure. The CTE values for Mg are shown for comparison. This difference in expansion, as a function of grain orientation, may explain why texture appears to significantly influence the propensity for whisker formation within electroplated metal layers of tin and zinc. Honeycombe [11] describes how this anisotropic CTE behavior can result in a stress build up during thermal cycling.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal Structure</th>
<th>CTE “c” axis</th>
<th>CTE “a” axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>BCT</td>
<td>30.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Zn</td>
<td>HCP</td>
<td>63.9</td>
<td>14.1</td>
</tr>
<tr>
<td>Cd</td>
<td>HCP</td>
<td>52.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Mg</td>
<td>HCP</td>
<td>27</td>
<td>25</td>
</tr>
</tbody>
</table>

Texture: Lindborg [10] suggests that the texture of the zinc layer has a significant influence on
the propensity for whisker formation. Lindborg claims that strong crystallographic texture in the (110) orientation favored whisker growth, regardless of the steel substrate thickness. Results from the current study show that orientations of (102), (101) and to a lesser extent (103) were dominant. The (110) peak is at 70.6605 degrees and is close to the (103) peak at 70.0563 degrees and the spectra shows a preference for the (103) orientation over the (110) orientation.

Role of Recrystallization: The melting temperatures of tin and zinc (232°C and 419.6°C, respectively) are relatively low compared to other metals. Due to these lower melting temperatures, the three stages of annealing, recovery, recrystallization and grain growth, will occur more readily at room temperature. Recrystallization is a nucleation and growth process and is defined as “the formation of a new, strain-free grain structure from that existing in cold worked metal, usually accomplished by heating”. Boguslavsky and Bush suggest that electroplated tin deposits, containing lattice defects such as dislocations and vacancies, resemble bulk materials after plastic deformation and apply fundamental recrystallization principles to possible explanations for whisker growth in tin. Other researchers have also suggested that the recrystallization and [abnormal] grain growth play roles in the fundamental mechanism of tin whisker formation and growth. Hales et al studied zinc films and their results suggest that excess vacancies, necessary for growth of a “vacancy-type” dislocation loop, in zinc are produced as metal atoms move to the surface and participate in an oxidation process. Although Hales’ study was not focused on whisker growth, the observations made regarding the injection of vacancies into zinc films, compliment discussions of dislocation models for whisker growth. In addition, this proposed mechanism for vacancy creation via an oxidation process, is consistent with experimental observations, that humidity has a strong effect on whisker growth. Although no direct evidence of dislocation structures has yet been documented, the authors of the current work believe that it is likely that dislocations play a role in the formation and growth of metallic whiskers.

Summary

Insight into the formation and growth of tin whiskers can be gained by investigations of alternative material systems. This work provides a preliminary characterization of zinc whiskers. Examination of an electroplated zinc layer with whiskers using FIB technology has provided a framework for discussion of differences and similarities between zinc and tin. Iron-zinc intermetallics do not appear to play a significant role in the generation of compressive stress within the electroplated zinc.

Tin and zinc both exhibit anisotropic thermal expansion behavior which may account for the influence of plating texture on propensity for whisker formation.

Acknowledgments

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References

1. C. Xu, C. Fan, A. Vysotskova, J. Abys, Y. Zhang, L. Hopkins, and F. Stevie,
4. Landolt-Bornstein, Group IV Physical Chemistry - Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys, Volume 5
5. Courtesy of J. Brusse/QSS Group @ NASA Goddard
10. U. Lindborg, Met. Trans. 6A, 1581 (1975)