SURFACE MORPHOLOGY OF WHISKER CRYSTALS OF TIN, ZINC AND CADMIUM

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Summary. The surface morphology of whisker crystals of tin, zinc, and cadmium formed spontaneously on electroplated finishes has been examined by scanning electron microscopy. Whiskers representing a variety of plating conditions, substrate-finish combinations, and exposure environments have been evaluated. The surface features are described in detail and their implications for possible mechanisms of whisker formation discussed.

I. INTRODUCTION

The spontaneous formation of metal whiskers from electroplated tin, zinc, and cadmium finishes should be very familiar to electronic components designers today since they were first reported on electrical components in 1946[1] and have been observed on a wide variety of electrical components since then[2]. These whiskers are single crystals of the metal finish involved and are usually about 2µm in diameter and up to about 10mm in length. Current carrying capacities of up to 10mA have been reported[3] for whiskers which indicates their potential hazard to low voltage electrical and electronic equipment. As the spacing of components decreases in new equipment, whiskers become an even greater hazard. Hence, the whisker phenomenon has stimulated research efforts at many laboratories including the Bell Telephone Laboratories. The work at Bell Telephone Laboratories has included preparation and observation of an extensive series of plated specimens representing a large variety of plating conditions, substrate-finish combinations and exposure environments. The observed whisker growth patterns on these samples has led both to the development of empirical rules concerning whisker growth[2] and to methods of repressing the formation of whiskers in components[4]. However, a detailed mechanism for the growth of these crystals still is not available although some general mechanisms have been proposed[5].

One of the problems in experimental studies of whiskers has been the difficulty in observing individual whiskers and in resolving the morphology of the whisker crystals. Such observations could lead to an improved understanding of the mechanism of growth. The few morphological observations that have been reported have been made by patient use of either optical microscopy or replication and electron microscopy[3]. However, neither replication nor optical microscopy can be used to examine the overall structure of a whisker crystal attached to a plating. The scanning electron microscope, with its large depth of focus, is ideally suited to making such an examination. This paper summarizes observations of the surface morphology of whisker crystals of tin, zinc, and cadmium using a scanning electron microscope. Whiskers representing a variety of plating conditions, substrate-finish combinations and exposure environments have been examined. These variables included plating conditions such as the effect of organic brightening agents and variations in current density, and substrates of zinc, copper, copper alloys, and steel. Also the strong whisker inhibiting effect of lead co-plated with tin to produce a solder finish[4] has been confirmed. Whiskers grown on both laboratory specimens, including some specimens that have been in test since 1964, and on actual components were examined. Some comments on the implications of these observations for possible growth mechanisms are also discussed.

II. OBSERVATIONS

Typical whiskers on tin, zinc, and cadmium finishes are shown in Figs. 1-3. The whiskers of the various metals appear very similar and are seen to be cylindrical and either straight or with a small number of sharp kinks joining straight segments. The length of whiskers observed varied significantly from 0.03mm to 10mm. The diameter of the whiskers was 2-5µm and did not show the same variations between whiskers that whisker length did. Thus, the diameter was apparently independent of crystal length. In addition, the diameter of the whisker is uniform along the length of the crystal without appreciable change at either the tip or the base of the whisker. Previous investigations[6] have determined that these crystals are normally single crystals of the finish metal and that the whiskers have favored crystallographic growth directions.

The detailed description of a whisker crystal can be conveniently divided into descriptions of the base structure where the whisker emerges from the finish, of the shaft of the whisker, and of the tip of the whisker. Two different forms for the base of the whiskers has been observed. Figure 4 shows the first structure which is a discrete, nodular growth from which the whisker emerges. On a sample with nodular growths, all whiskers appear to emerge only from such growths. However, there are also nodules without whisker growth indicating that the nodules are a necessary but not a sufficient precursor of whisker growth on these samples. These nodular growths are sometimes smooth as in Fig. 4a and sometimes exhibit considerable structure as in Fig. 4b. The nature of this nodule and its mechanism of formation is not known at the present time. This base form of the whisker has been observed with tin, zinc, and cadmium whiskers. A second base form is really no structure at all as illustrated in Fig. 5. The whisker appears to emerge directly from the electroplate. This second base form has been observed only with tin whiskers but would probably also be observed with zinc and cadmium if additional specimens were examined. In general, the type of base structure was unique on a given specimen. However, in the case of both types of base structure, it is significant that no depression or other evidence of thinning of the electroplated finish was observed around the base. Even in the case of several whiskers growing in close proximity (Fig. 6), there were no depressions and no apparent interference in growth between whiskers.

The shaft of a whisker was either smooth (Fig. 4a) or longitudinally striated (Fig. 3b). These striations generally extend over the entire length of the whisker from tip to base with little change in pattern or depth on an individual whisker. The depth of the striations varied from zero up to an estimated ten percent of the whisker diameter and it also varied among the whiskers on a given sample. One mechanism for the formation of the especially deep stria is illustrated in Fig. 7. This figure shows the end of a whisker which was broken off by directing a stream of air ($4 \times 10^5 N/m^2$) onto the sample. It appears that this whisker was actually two crystals growing alongside each other and the deep striation represents the boundary between the two crystals. No evidence has been seen for a similar origin of the shallower stria and no other mechanism for the formation of the stria can be proposed now. However, these stria do not appear to have crystallographic significance as the specific striation pattern varies from whisker to whisker. In addition, no evidence of any other surface structure with crystallographic significance such as faceting has been observed on any whisker crystal. These observations on stria apply to whisker crystals of tin, zinc, and cadmium.

The ends of the whiskers observed on tin, zinc, and cadmium finishes were usually smooth and rounded without striations or other significant structural features (Fig. 8) although occasionally the tip appears to be bent sharply as in Figures 2a and 8. In summary, whisker crystals of tin, zinc, and cadmium appear morphologically similar. Whiskers were observed on finishes applied to a wide variety of substrates as shown in Table I and no effect of the substrate was observed on the whisker form. In addition, the whiskers observed in this evaluation were formed in a variety of exposure environments from actual component operating conditions to laboratory conditions such as aging at 60°C. It did not appear that the principal structural features such as shape, size or striations depended upon such environmental factors. Additional studies in which the exposure conditions are closely controlled are planned to confirm this observation. The possible influence of environment on nodule growth will be given special attention.

TABLE I
Substrate-Finish Combinations On Which Whiskers Were Observed

Substrate	Finish
Copper	Sn
Brass	Sn
Beryllium-Copper	Sn
Steel	Sn, Zn, Cd
Zinc	Cd
Phosphor Bronze	Sn

Observations have also been made on some other aspects of whiskers on electroplated finishes. For example, Fig. 9 shows a whisker on a tin finish to which a brightening agent had been added to produce a bright tin finish. This sample had been in test for 48 months when examined. There has been some controversy over the possible whisker inhibiting effects of such brighteners but, in this case at least, the brightener obviously did not prevent whisker growth. In contrast, the effectiveness of lead additions to tin in reducing whisker growth[4] was confirmed by this examination. Samples of several tin-lead alloy finishes (Sn-0.5, 5, 20, 40Pb) were examined that had been in test for up to 56 months. No whiskers were observed on the 20 and 40 percent lead samples. On the 0.5 and 5 percent lead finishes some nodule-like structures were observed and, on one sample of the 5 percent lead finish, a few short whiskers (about 10μm long maximum) were observed. The longest such whisker is shown in Fig. 10b while the nodule-like structures are shown in Fig. 10a. This whisker, similar to others on this sample, is curved rather than straight and appears more like an extended nodular growth than like the whiskers seen on finishes of a pure metal. It appears that the whisker forming tendency of the finish has been significantly reduced by the addition of lead to the finish.

Recently, a technique has been reported to accelerate the growth of whiskers[7]. Specifically, by adding special organic agents to the plating bath, plating at high current densities ($10 A/dm^2$) and annealing the specimens at a temperature of 60°C, whiskers could be observed in days rather than the usual months. Such a technique has obvious advantages for experimental studies of whisker growth and the procedure has been tried at Bell Telephone Laboratories. Figure 11 shows a whisker grown overnight by this procedure. Although it is short (about 10μm), it is similar in structure to the whiskers grown normally. Thus, the accelerated growth technique may prove useful for future studies of whisker growth.

A recent paper has proposed that whiskers be removed by blowing them off the component with high pressure air[8]. Figure 12 shows the result of such a removal scheme on a tin finish which had grown whiskers. The air blast has bent or broken off the whiskers but has not removed them entirely. Since the mechanism of growth is not understood, one cannot say if these whisker remnants will regrow. One must conclude that such a repair procedure, while extending the useful life of the component, may not permanently prevent reoccurrence of whisker induced electrical problems with the component. Figure 13 shows the result of another suggested whisker removal procedure, etching in dilute acid (1 percent HCl in ethyl alcohol). Although the whiskers exhibit evidence of attack by the acid, they are clearly not removed. Both of these examinations of whisker removal schemes show that the whiskers are very well attached to the finish and are not completely removed by the procedures used. More severe treatments might be used but they would probably also damage the component.

III. DISCUSSION

This study of the surface morphology of whisker crystals is the first part of a re-examination of the whisker growth phenomenon. The principal result of this evaluation has been to present a more detailed description of the whisker crystals which subsequent theoretical or experimental programs must explain. For example, the absence of local depressions around whiskers and the lack of growth interference between whiskers (Fig. 6) suggest that whiskers are able to effectively drain large regions of the plating rather than only local, neighboring ones. Because of their great length relative to the plating thickness, the volume of a whisker represents a significant volume of the plating around a whisker. For example, consider a whisker 0.5cm long by 2µm in diameter on a plating 5µm thick. An area of the plating 65µm in diameter would be required to supply the metal atoms for this whisker. However, the whiskers in Fig. 6 are only about 10µm apart. Alternately, the whiskers on a typical sample may represent as much as 15-20 percent of the volume of the plated finish. This should produce a measurable reduction in average plating thickness.

Other aspects of whisker crystals seen in this study and that must be explained are the development of two types of base structure and the formation of longitudinal striations. This study has shown that these features apparently do not depend upon either the nature of the metal finish or its crystal structure or upon the specific substrate or plating parameters. This does not mean that these variables do not have significance for the mechanism of whisker growth, but only that they do not control the surface morphology of the crystals. It is probable that they strongly influence whisker growth rate, however. In this regard, it is interesting to note that whiskers have been reported principally on tin, zinc, and cadmium finishes and that these finishes are usually deposited with a high intrinsic compressive stress whereas most other common finishes have either a tensile stress or very low stresses[9]. Recent investigations have also shown that substrate characteristics and plating conditions may strongly affect growth rates of whiskers[7].

IV. CONCLUSIONS

The principal conclusions of this work are:

1) Whisker crystals of tin, zinc, and cadmium spontaneously formed on electroplated finishes of these metals are morphologically similar.

2) The surface morphology of these crystals does not seem to depend upon plating conditions or substrate.

3) The longitudinal striations on whisker crystals do not appear to have crystallographic significance. Some of the deeper striations may be a boundary between two whiskers growing together.

4) The base of whisker crystals shows no evidence of local thinning of the electroplate indicating the atom transport mechanism in whisker growth is long range.

5) Two types of base structure for whisker crystals have been observed; the nodular growth form and the direct emergence form.

6) Whiskers form on tin finishes with brightening agents but are significantly reduced on tin-lead finishes.

V. ACKNOWLEDGMENTS

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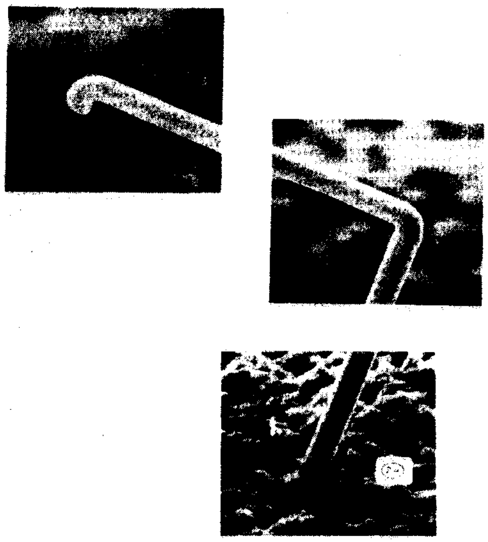
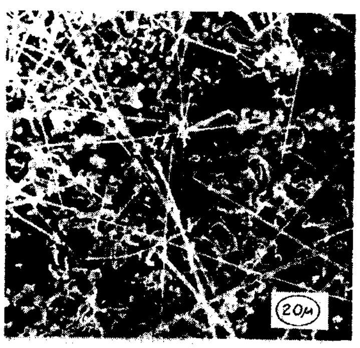


Fig. 1 Composite Micrograph of a Typical Tin Whisker. Finish is 5μm tin on a copper substrate.

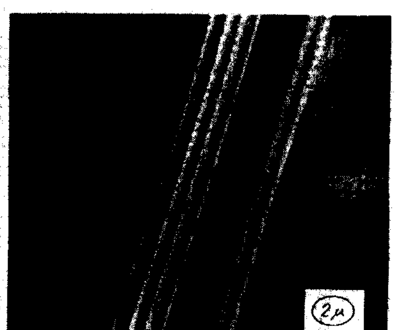
(a) Overall View of Whisker.

(b) Surface Structure.

Fig. 2 Structure of a Typical Zinc Whisker. Finish is passivated zinc on a steel substrate.

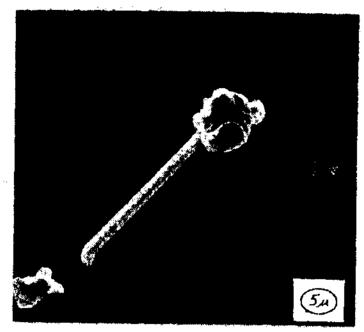


(a) Overall View of Whisker.



(b) Surface Structure.

Fig. 3 Structure of Typical Cadmium Whiskers. Substrate is steel.



(a) Smooth Nodule on a Tin Finish.

(b) Irregular Nodule on a Zinc Finish.

Fig. 4 Nodular Base Form for Whiskers. Substrate for both finishes is steel.

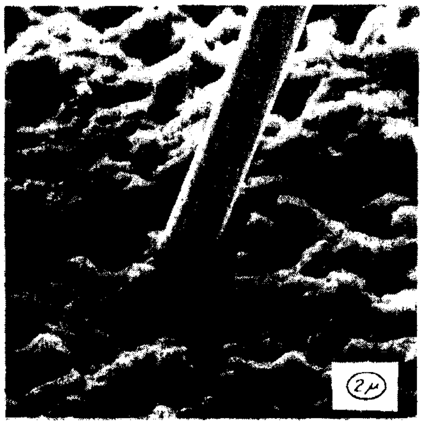


Fig. 5 Typical Whisker Emerging from Finish without Nodular Base Form.
Finish is 5μm tin on a copper substrate.

Fig. 8 Tip of a Typical Whisker.
Finish is 5μm tin on a copper substrate.

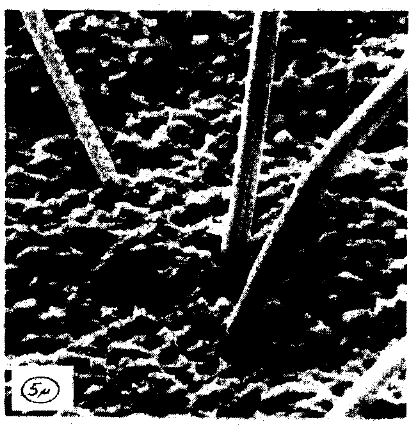
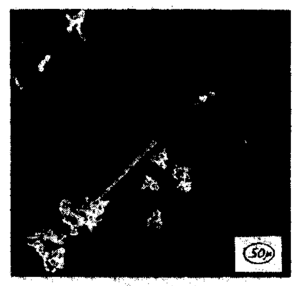
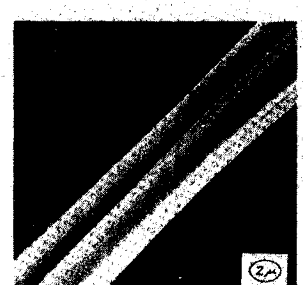


Fig. 6 An Array of Closely Spaced Tin Whiskers.
Finish is 5μm of tin on a copper substrate.



(a) Overall View of Whiskers and Nodules.



(b) Structure of an Individual Whisker.

Fig. 9 Whiskers on a Bright Tin Finish. Finish is 2.5μm bright tin on a brass substrate. Examination after about 48 months.

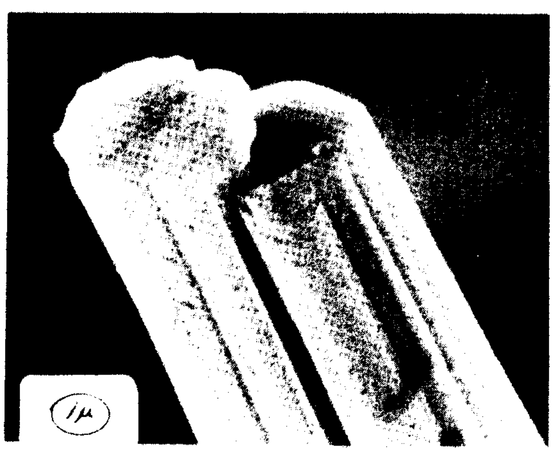
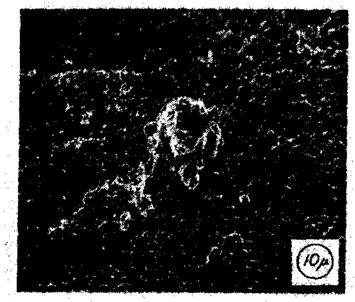


Fig. 7 Broken End of a Tin Whisker Revealing Nature of Deep Striation as a Boundary Between Adjacent Whiskers.
Finish is tin on a phosphor bronze substrate.



(a) Nodular Growths.

(b) Largest Observed Whisker.

Fig. 10 Nodular Growths and Small Whisker Observed on Lead-Tin Finish. Finish is 2.5μm thick, 5 percent lead-tin on a brass substrate. Examination after about 56 months.

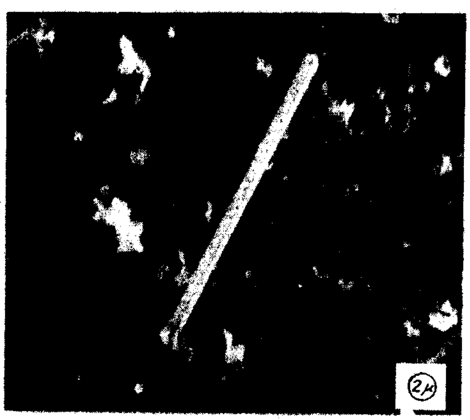


Fig. 11 Accelerated Whisker Growth. Whisker formed overnight on tin finish using procedure of Politycki and Kehren. Substrate is copper.

Fig. 12 Whiskers Remaining on Surface After Attempted Removal with Air Blast ($4x10^5$ N/m^2). Finish is tin on a phosphor bronze substrate.

Fig. 13 Whiskers Remaining on Tin Finish After Attempted Removal by Etching. Sample etched for 2 seconds in 1 percent HCl in ethyl alcohol. Substrate is phosphor bronze.