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The role of nodules in the growth of Zn whiskers from alkaline cyanide-free Zn electrodeposits

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Electroplated zinc finishes have been widely used in the packaging of electronic products for many years as a result of their excellent corrosion resistance and relatively low cost. However, the spontaneous formation of whiskers on zinc electroplated components, which are capable of resulting in electrical shorting or other damaging effects, can be highly problematic for the reliability of long life electrical and electronic equipment. The current work investigated whisker growth from commercial alkaline cyanide-free zinc electrodeposits on mild steel substrates. The presence of nodules on the deposit surface significantly reduced the incubation time for whisker growth in comparison with that from planar regions of the deposit. The nodules were probably formed due to the built-in residual stress within the electrodeposit during deposition. The nodules were eliminated by grinding the surface of the steel prior to Zn deposition. However, in the absence of the nodules the incubation time for whisker growth was reduced compared with that from the as-received surface.

Introduction

Metallic whiskers are spontaneous growths that most often develop from metal surfaces such as tin, zinc and cadmium, particularly when they are used in the form of electroplated coatings [1]. The growth of metallic whiskers is capable of inducing localised short circuiting and is problematic for the reliability of long life electrical and electronic components. The most widely reported problem related to zinc whisker growth is their formation on the bottom surface of zinc-electroplated raised floor tiles used in computer rooms or data centres. Filament whiskers are prone to break off and be drawn into computer equipment by cooling fans, resulting in equipment failure [2]. During the last two decades, a number of computer equipment failures have been attributed to problems induced by zinc whisker growth [3,4]. However, the majority of research effort has been focused on tin whiskers and today whisker growth on tin is a well-documented phenomenon; in comparison much less attention has been paid to the investigation of zinc whiskers.

A few mechanisms to explain zinc whisker growth have been proposed. However, none of them are widely accepted and some are in conflict with each other; for example, Baated et al. proposed that Fe-Zn intermetallic compounds (IMCs) were present at the Fe/Zn interface and responsible for zinc whisker growth [5,6]; whilst other investigators have reported that no intermetallics, or only a very thin layer of Fe-Zn IMCs, were

present at the interface [7,8]. The current work was carried out to observe whisker growth from zinc electrodeposits and to understand the growth mechanism. Techniques that include scanning electron microscopy (SEM), dual beam focused ion beam scanning electron microscopy (FIBSEM) and electron backscatter diffraction (EBSD), have been used to support the investigation.

Experimental

As-received mild steel substrates, with dimensions $2\text{cm} \times 4\text{cm} \times 1\text{mm}$, were used, as the cathode with an electroplated area of 2×2 cm. Pure zinc was electrodeposited onto the steel substrate from a proprietary bright alkaline cyanide-free zinc bath provide by MacDermid Ltd. The anode material was $a \ge 99.9\%$ zinc metal foil (0.3 mm thickness). Prior to deposition, the substrates were first washed using detergent, degreased using acetone, pickled in a 32 wt. % solution of (SG 1.16) hydrochloric acid for 1 minute to remove surface oxides, rinsed with deionised water and finally dried using hot air. The anode material underwent a similar pre-treatment, except that in the pickling stage it was immersed in a 20 vol. % solution of (SG 1.83) sulphuric acid for 30 seconds. All the electrodeposition was carried out at a cathode current density of 25 mA/cm² for 10 minutes and the resultant deposits exhibited an average thickness of approximately 6 µm. No agitation was applied during electrodeposition. After deposition, all the samples were stored at room temperature (20 $^{\circ}$ C). To evaluate the influence of surface finish on whisker growth, mild steel substrates were ground, using silicon carbide paper, prior to electrodeposition. Each sample was gradually ground from P240 to P400, P800 and finally P1200. After grinding, the samples were rinsed using deionised water and then dried using hot air.

Whisker growth from the zinc electrodeposits was investigated using a Carl Zeis (Leo) 1530VP field emission gun scanning electron microscope (FEMSEM). Initially, samples were monitored every week until the first whiskers were observed, after which they were observed at monthly intervals. The cross-sectional microstructure of the zinc electrodeposits and the whiskers growing from them were investigated using a FEI Nova 600 Nanolab dual beam focused ion beam (FIB). The ion beam energy used for both imaging and milling was 30 kV. Initially, a layer of platinum (~ 1 μ m thick) was deposited on the area of interest for protection from ion milling. In order to observe the cross-section, a rectangular trench of approximately 40 μ m in length, 25 μ m in width and 10 μ m in depth was ion milled using a current of 20 nA. After this, the area of interest went through two cleaning cross-section surface finish. The current used for ion beam imaging of the resultant cross-section was 30 pA.

Results and Discussion

Observation of whisker growth

SEM analysis showed that a few small (< 1 μ m in length) whiskers (shown in Figure 1) had started to grow from the deposit surface 4 weeks after deposition. After 4 months storage, an increased number of whiskers, the majority of which were in the form of large

irregular eruptions, were observed on the deposit surface (shown in Figure 2a). A few filament-type whiskers were also observed, some of which were greater than 100 μ m in length (shown in Figure 2b). Importantly, it was found that, up to 4 months after deposition, all the whiskers were associated with raised hemispherical features. These features are henceforth referred to as "nodules". The nodules should not be confused with the eruption-type whiskers, since they did not exhibit any typical whisker characteristics, such as striations, and were comprised of the same surface morphology as the remainder of the deposit. The nodules varied in size and some of the larger nodules were more than 20 μ m in diameter. SEM analysis immediately after deposition showed that the nodules were formed during electroplating rather than developing afterwards. This assumption is further supported by SEM analysis of the nodules after 6 months storage, which showed that the size and the shape of the nodules remained unchanged.



Figure 1 (a) and (b) SEM images showing incipient whisker growth present on the deposit surface 4 weeks after deposition



Figure 2 SEM images showing large whisker growth present on the deposit surface 4 months after deposition: a) a large irregular eruption-type whisker and b) a long filament-type whisker

5 months after deposition, a few small whiskers had started to grow from a planar region of the deposit (shown in Figure 3a), and 10 months after deposition, an increased number of longer whiskers growing from the planar regions of the deposit were observed (shown in Figure 3b). These results suggest that the formation of the nodules is not a prerequisite for zinc whisker growth, but significantly promotes whisker growth by shortening the incubation time. The incubation time for whisker growth associated with

the nodules was approximately 4 weeks, whilst that for whisker growth from the planar deposit surface was markedly increased to 5 months. Thus, the nodules must have some unique characteristics that are favourable for whisker formation. It is not known, however, whether the presence of the nodules has an effect on whisker growth rate.



Figure 3 SEM images showing whiskers growing from the planar regions of the deposit surface: a) a small whisker present 5 months after deposition and b) a longer filament whisker present 10 months after deposition

The relationship between nodules and whisker growth

Another important observation is that, for zinc whisker growth from the nodules, a series of parallel lines were always associated with whisker growth (shown in Figure 4). These lines have the appearance of a "staircase" and are henceforth termed "staircase structures". It was found that numerous staircase structures were present on the surface of the nodules approximately 1 month after deposition. Staircase structures were not evident on the planar regions of the deposit. Once a staircase structure appeared, subsequent whisker growth would typically follow. It was noted that whiskers only grew from the staircase structures rather than other regions on the nodules, i.e. it appears that a whisker was "extruded" from one or more steps of the staircase structures. These results suggest that the staircase structures are pre-cursors to the growth of zinc whisker growth. A more detailed discussion of the relationship between nodules, staircase structures and whisker growth will be published at a later date.

The nature of the nodules is clearly very important for understanding zinc whisker growth. To more fully investigate the structure of the nodules, a focused ion beam (FIB) technique was utilised to characterise the cross-sectional microstructure of the nodules. Two nodules, one with a whisker growing from it and one without whisker growth were FIB cross-sectioned (shown in Figure 5). In both cases, a cavity was present beneath the nodule. To date, a cavity has been observed beneath every cross-sectioned nodule (more than 20 nodules have been cross-sectioned), irrespective of whether a whisker is growing from it or not. Also, FIB analysis, immediately after deposition, of nodules on freshly electroplated samples showed that the cavities were already present; i.e. both the nodules and the cavities were formed during deposition rather than developing afterwards.



Figure 4 SEM images showing whisker growth associated with staircase structures on nodules: a) whisker growth associated with the staircase structures and b) a high magnification image showing a whisker "extrusion" from the staircase structures



Figure 5 FIB images showing the cross-sectional microstructure of nodules: a) with whisker growth and b) without whisker growth

To understand the mechanism for the formation of the nodules and cavities, short time duration depositions were carried out to monitor their initial development using different deposition times of 30, 60, 90, 120, 150, 180, 210 and 240 seconds. Figure 6a shows the morphology of the deposit surface after only 30 seconds deposition. It was found that some regions of the deposit were fractured and had peeled away from the underlying substrate. As the deposition time was increased, the size of the fractured regions was reduced and the lifted regions of the deposit increased in thickness. When the deposition time was increased to 150 seconds, the lifted regions of the deposit typically merged together to form a complete layer (shown in Figure 5e). This is probably the preliminary stage in the development of the nodules. When the deposition time reached 180 seconds, some incomplete nodules were observed on the deposit surface (shown in Figure 5f). As the deposition time was increased to 240 seconds, no discrete lifted regions were present and the deposit surface was similar to that observed after 10 minutes. These observations suggest that the formation of the nodules and cavities is closely associated with the fractured and lifted regions of the deposit observed at short deposition times. The mechanism responsible for the formation of the nodules could be stresses developed

within the coating. The electroplating bath used was an alkaline cyanide-free zinc solution, for which the cathode current efficiency is comparatively low (~40%). Strong hydrogen evolution occurs during deposition and a large amount of gas is generated on the cathode surface, which may be absorbed by the steel and result in a highly stressed electrodeposit [9]. Also, it was observed that only part of the coating was fractured and lifted. These particular regions are potentially related to the areas where the zinc coating is poorly adhered to the steel surface. In the early stages of deposition, when the deposit is very thin, these regions with poor adherence are likely to be more prone to delamination and susceptible to fracture due to the stresses developed in the electrodeposit. This contributes to the large number of fractured and lifted regions of the deposit observed at short deposition times. The poor adherence between the coating and the substrate may be attributed to the presence of oxides and/or contaminants on the steel surface. Therefore, the stresses developed in the electrodeposit and the poor adherence between the zinc and the steel may be responsible for the development of the fractured and lifted regions of the deposit in the early stages of deposition and the subsequent formation of the nodules. Since the nodules were actually up-lifted regions of the deposit, a cavity is always present beneath them.





Figure 6 SEM images showing the initial development of the nodules as a function of deposition time: a) 30 seconds, b) 60 seconds, c) 90 seconds, d) 120 seconds, e) 150 seconds, f) 180 seconds, g) 210 seconds and h) 240 seconds

On the basis of the previous results, it was determined that the presence of the nodules on the deposit surface promoted whisker growth by significantly shortening the incubation time. Hence, stopping the development of the nodules was thought a potential way to hinder whisker growth. It was observed from other trials carried out as part of this study that nodules were not evident on the surface of electrodeposited Hull cell samples produced from the same alkaline cyanide-free zinc electroplating bath. The main difference between the as-received mild steel substrate and the Hull cell panels is that the latter has a much better surface cleanness, i.e. much fewer oxides and/or contaminants are present on the surface of the Hull cell panels. Hence, the surface cleanness of substrate material could play a role in the formation of the nodules. It is thought that, on the asreceived mild steel, some surface oxides and/or organic contaminants may be embedded in the steel surface in depth during rolling process and were difficult to remove by chemical pickling. In this case, in order to achieve a clean surface, the as-received mild steel substrates were ground to a P1200 grit finish using silicon carbide paper prior to electrodeposition. Grinding was able to remove the oxides and contaminants by abrading away a thicker steel layer, and thus eliminating a favourable source for delamination of the coating and subsequent nodule formation. Figure 7 shows the surface morphology of the mild steel before and after grinding.



Figure 7 (a) SEM image showing the surface morphology of the as-received mild steel and (b) SEM image showing the surface morphology of the same steel after grinding to 1200 grit

In terms of nodules formation, it was found that no nodules were observed on the electrodeposits produced on the ground samples. In other words, the development of the nodules was completely prevented by grinding the surface of the as-received mild steel substrate. In terms of whisker growth, SEM analysis 18 days after deposition showed that a large number of whiskers were observed on each of the electrodeposits produced on the ground samples and all the whiskers were growing from planar regions of the deposit (shown in Figure 8). The majority of the whiskers were curved eruptions with a diameter of $\sim 2 \,\mu m$ and a few filament-type whiskers, longer than 100 μm in length, were also present, which means that these whiskers had started to grow within 18 days of deposition. Thus, elimination of the nodules did not reduce whisker growth; instead it markedly shortened the incubation time for whisker growth from planar regions of the deposit from ~5 months to less than 18 days. At present, it is not fully understood why whisker growth initiated much earlier on the electrodeposits on the ground samples than that on the as-received samples, even though the nodules, a favourable site for whisker growth, were eliminated. It is thought that the development of the nodules may serve to relieve some stress within the deposit. In other words, the zinc electroplated ground samples, with no nodule formation, were potentially more highly stressed, which resulted in accelerated whisker growth. Further investigations are ongoing to fully determine the cause of the much shorter incubation time for whisker growth on the ground samples.



Figure 8 SEM images showing a high density of whiskers growing from the planar regions of the deposit on the ground samples electrodeposited at $25 \text{ mA/cm}^2 18$ days after deposition

Conclusions

Zinc electrodeposits on mild steel substrates prepared from a commercial alkaline cyanide-free zinc electroplating bath were prone to develop whiskers at room temperature. Whiskers growing from nodules were observed 4 weeks after deposition and those from planar regions of the deposit were present 5 months after deposition. The presence of the nodules promoted zinc whisker growth by shortening the incubation time. A cavity was observed beneath every FIB cross-sectioned nodule. The mechanism of nodule formation was associated with the built-in residual stress within the electrodeposit. The nodules were eliminated by mechanically grinding the surface of the mild steel substrates. However, this resulted in a significantly reduced incubation time for whisker growth compared with deposits electroplated onto the as-received substrate.

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