Effect of heat treatment on zinc whisker growth from electrodeposited coatings

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Summary

The effects of simple heat treatments on electrodeposited zinc coatings formed on mild steel substrates were examined. It was found that over a temperature range of 50-200°C for 1 and 24 h periods zinc whisker growth was evident. The additional effects of electrodeposited coating thickness and subsequent chromium-based passivation processes were also examined in terms of their effect on whisker growth. Individual whisker morphologies were investigated utilising a field emission gun scanning electron microscopy (FEGSEM) and focused ion beam field emission gun scanning electron microscopy (FIB-FEGSEM).

Introduction

Zinc coatings are widely utilized for corrosion protection on ferrous metal surfaces. In this manner carbon steels, for example, receive a wide range of zinc-based coating systems to ensure their in-service longevity. Routinely steels of this type are protected through thermally applied systems such as hot dip galvanizing and sprayed metallic zinc. For thinner coatings (typically < 15 µm) electrodeposited (electroplated) coatings are favoured.

However, although metallic zinc-based coatings are effective in terms of their corrosion protection and provide both barrier and sacrificial protection to carbon steel substrates, they are one of a limited number of metals which are susceptible to spontaneous whisker growth under certain conditions. The concept of such metallic whisker growth can be traced back to the 1940s where electrical failures had been attributed to such growths eminating from electroplated cadmium surfaces [1]. Since this initial occurrence, it has become recognised that a variety of 'eruptions' can form on the surfaces of tin, zinc and cadmium coatings. The morphology of these can vary although for convenience they are usually generically classified as 'whiskers'.

Tin whisker growth is by far the most widely studied and potentially problematic form of this phenomenon with electronics being the area where the most adverse effects of whisker growth can occur. The potential for short-circuits due to whisker growth as well as localised arcing and general reduction in signal quality are some of the more serious repurcussions of this type of problem. Further effects of tin whisker growth may become more widespread due to the removal of lead from electronics by the EU in legislation such as WEEE [2]. Zinc whisker growth is less well documented than that for tin. However, recent computer failures in the Colorado Department of State's Data Centre [3] have highlighted the problem.

The current investigations, outlined in this paper, concentrate on the occurrence of zinc whisker growth from 8 μm electrodeposited zinc coatings produced on mild steel substrates from a proprietary acid zinc electroplating bath. Whisker formation was studied after heat treatment at temperatures which are thought to be representative of values experienced by such zinc surfaces in higher temperature service environments. Zinc whisker morphologies were studied using scanning electron microscopy (SEM) and their occurrence investigated with respect to heat treatment temperature and time. A Dual Beam Focussed Ion Beam/ Field Emission Gun Scanning Electron microscope (FIB/FEG-SEM) was also utilized to observe sections of individual zinc whiskers and surrounding substrate.

Experimental Procedures

Electrodeposition

The electrodeposited zinc coatings were formed from the formulation outlined in table 1 below.

Table 1. Formulation of zinc electroplating solution

Acid Zinc Electroplating Bath	
Constituent	Concentration
Zinc	38.5 g l^{-1} (added as zinc chloride)
Chloride	147.5 g l^{-1} (added as potassium chloride)
Boric acid	27.5 g l^{-1}
Carrier	40 ml l^{-1}
Brightener	0.5 ml l^{-1}
Hydrogen peroxide	2 ml l^{-1}

The operating conditions for the electroplating process were as follows:

- pH 5.2
- Temperature 30^{o}C
- Current density 2.25 A dm^{-2}
- Nominal electrodeposit thickness 8 μm

Zinc foil was utilized as the anode material and separate anodes were positioned either side of the mild steel cathode. The latter measured 5 cm x 3.75 cm and were pretreated by pickling in concentrated hydrochloric acid for 30 s followed by thorough rinsing in deionised water. During electrodeposition, the sample and solution were periodically agitated to help even deposited metal distribution. After electroplating the samples were removed from the solution, thoroughly rinsed in deionised water and dried in a hot air stream.

Passivation

Although many of the zinc electrodeposited samples were heat treated ‘as plated’ several specimens were passivated in either trivalent of hexavalent conversion coating treatments prior to heat treatment. The passivation treatments were carried out at room temperature. The hexavalent chromium passivation solution was the “Cronak” solution, the composition of which was 200 g/l sodium dichromate, 10 ml/l sulphuric acid, pH 1.2 adjusted with nitric acid. The trivalent chromium solution was a proprietary system used for electroplated zinc surfaces.

Heat Treatment

In order to investigate the effect of heat treatment on zinc whisker formation and growth, specimens were placed in normal atmosphere preheated ovens at temperatures of 50-200°C. The zinc panels were placed on aluminium foil and left for the desired period of time. After heat treatment, the samples were wrapped in soft tissue and care was taken to avoid breaking or bending the zinc whiskers on the surface of the samples. Once samples had completed their heat treatment cycle, it was imperative to conduct further testing within 48 hours to prevent any degradation of the surface.

Surface Analysis

Zinc samples were observed after heat treatment in a Leo 1530 VP FEGSEM. 1 cm^2 samples were removed from the heat treated zinc coated plates for observation of surface morphologies. In order to further examine whisker features and the underlying substrate areas, a Nova Nanolab 600 Dual Beam FIB/FEGSEM was utilized to mill highly localised cross sections away from the surface.

Results

Table 2 illustrates the whisker observations made on electroplated zinc samples that had received no passivation treatment.

Table 2 Zinc whisker observations for electroplated zinc coatings on mild steel. Effect of heat treatment temperature and duration.

Specimen	Zinc whiskers observations
Acid zinc (room temperature for 1 week)	A few small whiskers
Acid zinc (24 hours at 50 ^{o}C)	A few small whiskers
Acid zinc (1 hour at 100^{o}C)	Small nodular growths with a few small filament whiskers
Acid zinc (24 hours at 100^{o}C)	A few nodular whisker growths, small nodules, several very long filaments
Acid zinc (1 hour at 150^{o}C)	Larger nodular growths with a few small filament whiskers
Acid zinc (24 hours at 150^{o}C)	Very dense nodular whisker growth, small nodules, a few filaments, several long filaments, many different morphologies
Acid zinc (144 hours at 150^{o}C)	A few large nodular whisker growths, some long filaments
Acid zinc (1 hour at 200^{o}C)	Dense nodular growth, large tangled nodules, some short filament whiskers, several long filaments, many different morphologies
Acid zinc (24 hours at 200^{o}C)	A few large nodular whisker growths

Figures 1 and 2 show typical whisker growth highlighted in table 2. As can be seen from table 2, whiskers and associated structures (nodules and nodular growths) were evident over the temperature range studied. Although room temperature and 50°C conditions produced only a few small whiskers, increasing the treatment temperature to 100°C brought about an increase in whisker and associated structure growth activity both after 1 and 24 h heat treatment. Similarly an increase to a heat treatment temperature of 150°C brought about an even further increase. At the highest temperature tested, 200°C, there appeared to be a concurrent increase in growth activity after 1 h heat treatment, but a fall after 24 h.

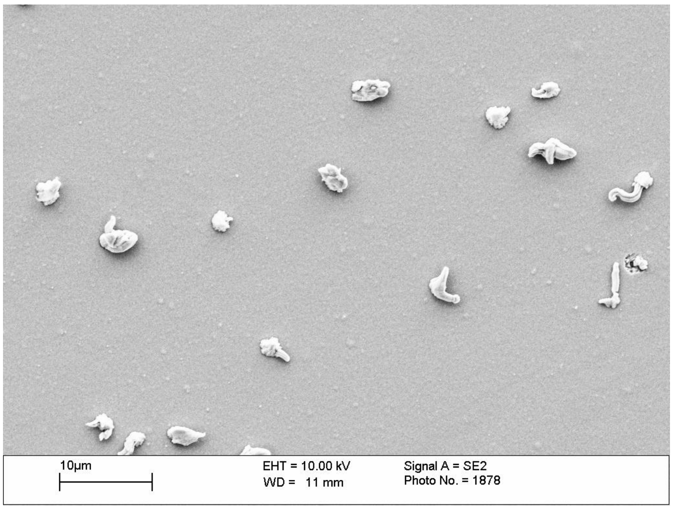

Figure 1. Micrograph of acid zinc deposit showing small nodular growths and a few short filament whiskers (heat treatment at 100°C for 1 hour)

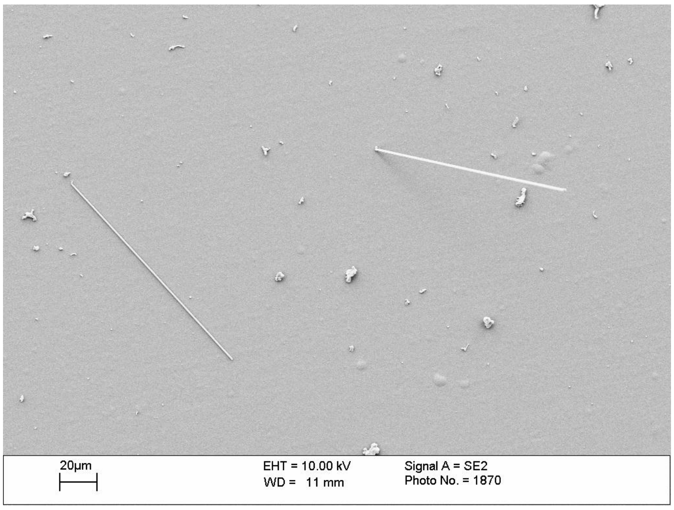

Figure 2 . Micrograph of acid zinc deposit showing two very long filament whiskers along with small nodules (heat treatment at 100°C for 24 hours)

Table 3 illustrates whisker growth for electrodeposited zinc coated mild steel samples after further changes to process parameters.

Table 3 Zinc whisker observations for specimens with different coating thickness and different brightener/carrier electroplating bath contents. Treatment temperature of 150°C for 24 h.

Specimen	Zinc whisker observations
Acid zinc (24 hour at 150^{o}C) 5 ml brightener	A few nodular whisker growths, some tangled nodules, some very long filaments
Acid zinc (24 hours at 150^{o}C) no brightener	Dense nodular whisker growth, small nodules, a few filaments
Acid zinc (24 hours at 150^{o}C) no brightener, no carrier	A rough surface but no whisker growth
Acid zinc (24 hours at 150^{o}C) 4 μm coating thickness	A few nodular whisker growths, small nodules, a few filaments
Acid zinc (24 hours at 150^{o}C) 16 μm coating thickness	Very dense nodular whisker growth, many tangled filaments, several very long filaments

The effects of carrier and brightener bath contents can be seen. 5 ml of brightener (10x recommended level) seemed to produce a reduction in whisker activity, whereas no brightener (but still with the correct amount of carrier) produced an increase in whisker growth. No brightener and no carrier produced a rough zinc electrodeposit which had no evidence of any zinc whisker activity. The effects of electrodeposited zinc coating thickness was also examined. In essence the coatings of 8 and 16 μm thickness produced the most whisker growth.

Table 4 illustrates the effects imparted by trivalent and hexavalent passivation treatments onto subsequent zinc whisker growth following heat treatment at 150°C.

The two conversion coating treatments seemed to have little effect on actually diminishing whisker activity. Both passive surfaces were not able to preclude the whisker growth. Figures 3 and 4 illustrate zinc whiskers breaking through the cracked passive film imparted by the hexavalent chromium-based treatment.

Trivalent chromium treatments, in comparison, lacked the extensive microcracked morphology associate with the hexavalent treatments. Instead of the whiskers appearing to eminate from the cracks, individual whisker growths seemed to break through the uncracked passive film in a more random fashion as evidenced in figures 5 and 6.

Table 4 Zinc whisker observations for trivalent and hexavalent chromium passivated zinc electroplated surfaces following heat treatment at 150°C

Specimen	Zinc whisker observations
Acid zinc (1 hour at 150^{o}C) passivated with trivalent chromium	Some large nodules, a few small filaments
Acid zinc (24 hours at 150^{o}C) passivated with trivalent chromium	Some large nodules, some cracks, a few long filaments
Acid zinc (1 hour at 150^{o}C) passivated with hexavalent chromium	Dense cracks, a few long filaments
Acid zinc (24 hours at 150^{o}C) passivated with hexavalent chromium	Very dense cracks, dense large nodules, some very long filament

The two conversion coating treatments seemed to have little effect on actually diminishing whisker activity. Both passive surfaces were not able to preclude the whisker growth. Figures 3 and 4 illustrate zinc whiskers breaking through the cracked passive film imparted by the hexavalent chromium-based treatment.

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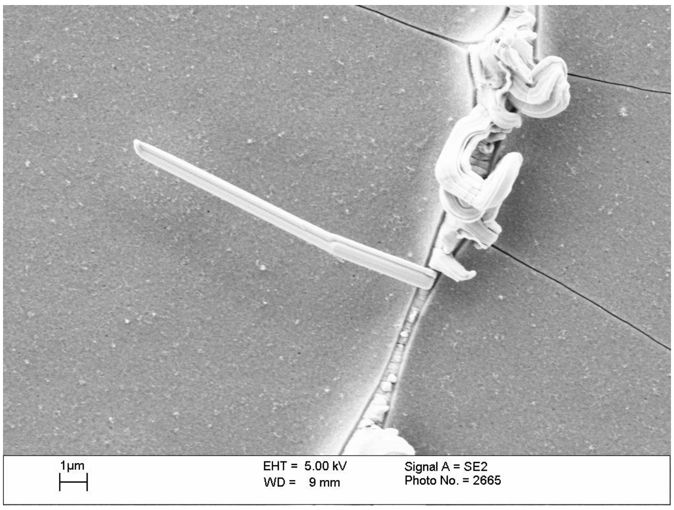


Figure 3 Micrograph of Acid zinc deposit with hexavalent chromium passivation showing a long filament (heat treatment at 150^{o}C for 1 hour)

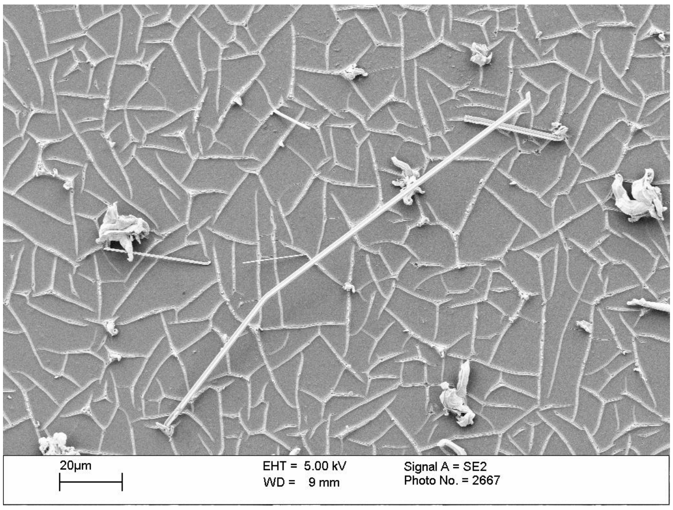


Figure 4. Micrograph of zinc deposit with hexavalent chromium passivation showing a very long filament whisker (heat treatment at 150^{o}C for 24 hours)

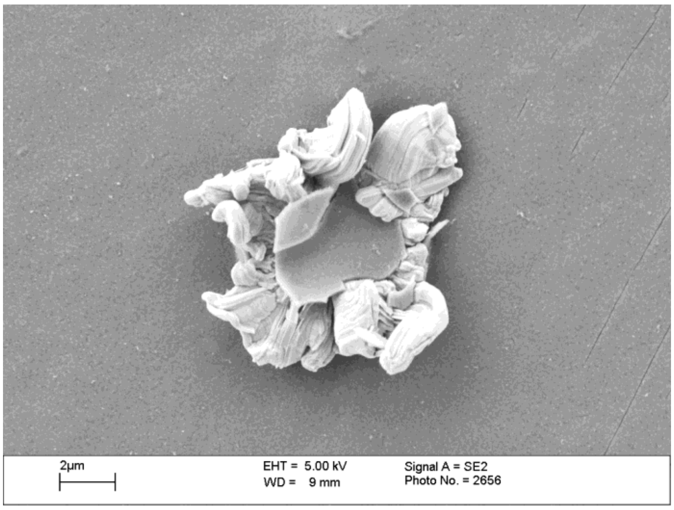


Figure 5. Micrograph of zinc deposit with trivalent chromium passivation film And ‘sunflower’ type whisker feature (heat treatment at 150^{o}C for 1 hour)

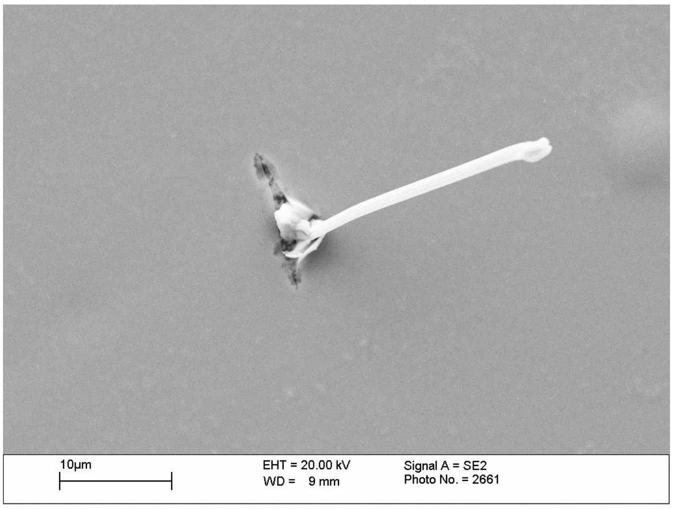
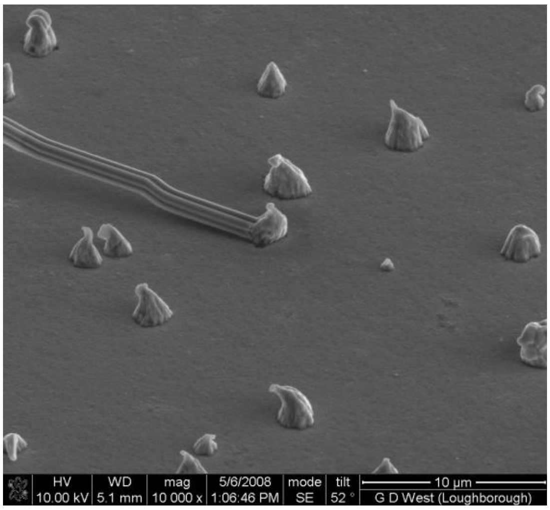


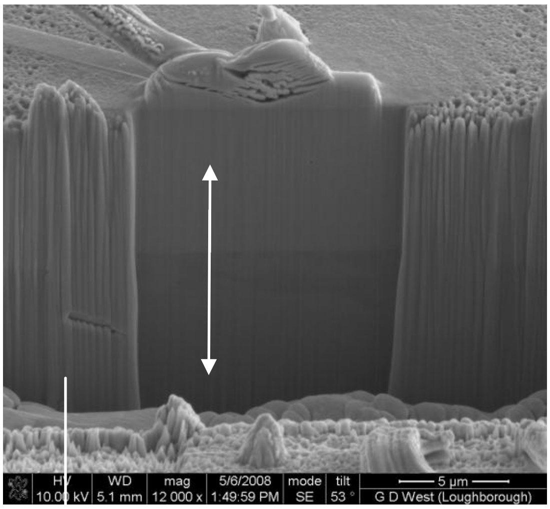
Figure 6 . Micrograph of zinc deposit with trivalent chromium passivation film Showing a filament whisker breaking through the film (heat treatment at 150^{o}C for 24 hours)

Focused Ion Beam Investigations

The purpose of the FIB analysis was to take a cross section of the zinc whisker at its root in order to examine how the zinc microstructure was effected by its growth from the surface of the zinc coating. Figures 7(a) and 7(b) illustrates a typical whisker and its FIB image. In general it was found that the zinc electrodeposit had a columnar structure which gave way to a much finer grain pattern in the interior of the whisker and nodule. It was also noted that there appeared to a distinct level of porosity associated with the interior of the initial nodular base of the whisker. It could almost be construed that the material appeared folded.



(a)



(b)

Figure 7. (a) FIB image of a whisker on the zinc deposit (b) FIB image of the cross section of the whisker (heat treatment at 150^{o}C for 24 hours)

Discussion

The aim of the present investigations was to examine the factors and driving forces for zinc whisker growth. In the experiments, zinc whisker growth was observed through variation of the temperature and time of heat treatment, the coating thickness and the concentrations of the brightener and carrier in the zinc electroplating solution. The examination of post electrodeposition passivation treatments was also undertaken.

Zinc whiskers were observed in detail using the FEGSEM. For the unpassivated zinc electroplated samples, observation of heat treatment variables suggested there was a clear change in the surface after heating, and the abnormal whisker features were found indicating that temperature was a fundamental factor. Through the comparison of the three samples treated at 100^{o}C, 150 ^{o}C, 200 ^{o}C for 1h, the area density of nodular whiskers increased with increase in temperature. Due to the shorter heat treatment time, there were few short filament whiskers on the surface of the 100^{o}C and 150^{o}C heat treated specimens. However, at 200 ^{o}C it was observed that some filament whiskers, some of which were longer than 20 μm, were present which provided evidence to suggest that increasing temperature was a principle inducing factor for advanced whisker growth and increased formation. Moreover, there appeared to be an increase in the size of nodular whiskers at increased temperature, which also suggests that temperature accelerated nodular whisker growth. The mean size of the nodular whiskers at 150 ^{o}C was smaller than that at 100 ^{o}C. However, at a heat treatment time of 24 hours, the area density of the nodular whiskers reached its maximum at 150 ^{o}C and then reduced as the temperature increased. It can be suggested that the ability to form nodular whiskers increased with temperature and reached a maximum. Though the area density of the nodular whiskers was lower at 200^{o}C, the mean size of the nodules was much larger. It also confirms the suggestion that temperature accelerated the nodular whisker growth. Only a few small nodular whiskers were found on the surface of the samples treated at 50 ^{o}C and those maintained at room temperature.

Only a few short filaments were observed on the surface of the samples treated at 150 ^oC for 24 hours while some very long filaments were observed on the surface of the samples retained at 100 ^oC for 24 hours though the temperature was lower. However, the density of the whiskers at the 150 ^oC variable was higher than that of 100 ^oC. It can be suggested that the zinc coatings took energy from the raised temperature level for the formation of new nodular whiskers or the filaments protruding out from the nodular bases. At a lower temperature filament growth may tend to predominate. There appeared to be no significant difference in the size and density of the nodular whiskers of the samples treated at 100 ^oC for 1 hour and 24 hours. However, very long filament whiskers, some reaching up to 150 μm (Figure 2), were observed protruding out from their nodular bases at 24 hours whilst at 1 hour only a few small filaments, shorter than 5 μm (Figure 1), were evident. The samples showed differences in the size and density of the nodular whiskers at 150 ^oC for 1 hour, 24 hours and 144 hours. An increase in the mean size and the density of the nodular whiskers was observed at 150 ^oC for 1 hour and 24 hours, which suggests that heat treatment exposure time induced the growth and formation of the nodular whiskers. However, there was a difference in the size but not in the density of the nodules at 150 ^oC for 24 hours and 144 hours. This suggested a difference in the influence of heat treatment exposure time on whisker formation and growth. A longer exposure time could result in more time for stress relaxation. To some extent, stress relaxation could mitigate nodule formation. It is therefore suggested that heat treatment exposure time had more effects on whisker growth rather than their formation.

Since micro stresses have been suggested by Fisher et al [4] as a possible cause of tin whisker formation, it was necessary to investigate different variables that may introduce these stresses into the zinc coating. Brightener content in zinc electroplating baths has been suggested by several previous studies to have a stress inducing effect on the electrodeposited coating [5] and was thus investigated. It was found that nodule formation increased with increase in brightener concentration but the ability was limited and appeared to reach a maximum. There were still some whiskers observed on the surface of the sample without brightener (but which still had its organic carrier additive present in solution). Moreover, the growth of the nodular and filament whiskers was also influenced by the amount of the brightener. The size of nodules increased with the amount of brightener present. There were few short filaments observed on the surface of the standard brightener variable while some very long filaments were evident on the surface of the sample electrodeposited from a solution with increased brightener content. The stresses accelerating the growth of nodular and filament whiskers were not only induced by the brightener but also by the carrier. The dense whisker growth was observed on the surface of the sample with no brightener but with the carrier present while no whisker features were observed on the surface of the sample with no brightener and no carrier. The surface of the latter sample was rough due to the absence of both deposit modifying agents. No brightener and no carrier additives suggested little stress induced by co-deposited impurities and changes in the crystal growth habit of the zinc electrodeposit, which mitigated the whisker formation.

Glazunova and Kudryavtsev [6] reported that there were critical thicknesses for tin electroplating above and below which whisker formation may not be supported. An interesting trend was also observed with the zinc electrodeposits in this investigation. Observing a coating thickness of 16μm, there was no significant difference in nodular whisker density from the standard thickness (8μm). However, much longer filaments were observed on the double thickness variable than on the standard thickness. This suggests that a greater thickness induced growth of the whiskers rather than further development and growth of nodules, which suggests that increased material in the coating can generate more stress and coupled with a high temperature, there were more opportunities for the long filament whiskers to form. Observing a coating thickness of 4 μm (half the standard thickness), the density of the nodular whiskers was much less than the standard thickness. This provides evidence to support that increasing the coating thickness induced the formation of the nodular whiskers. However, in the comparison of double thickness and the standard thickness, there was no significant difference in the density of the nodular whiskers. Hence, it can be assumed that there was a limit to the density of nodular whiskers at a constant temperature. Increased thickness was shown to induce the growth and formation of the zinc whiskers, so there may be reasons to suggest that increased thickness caused more stress concentrations zones and provided more material for forming whiskers.

Sugiarto [5] suggested that passivation treatments slowed down whisker growth but did not prevent it. The effect of chromium-based passivation treatments on zinc whisker formation and growth were also investigated in the project. Though the comparison of the unpassivated sample and the passivated sample, it is shown that the density of the nodular whiskers of the passivated sample was lower than that of the unpassivated sample but the size of the nodular whiskers on the former sample was much larger. It is suggested that passivation treatments slowed down whisker formation but not whisker growth. In figures 3-6, it can be seen that the whiskers formed from the zinc coating beneath the passivation film and forced themselves up through the film and spilled out onto the surface. The growth in turn peeled away the passivation film from the zinc deposit. The sunflower shape of the whisker (figure 5) seemed to be peculiar to the passivated samples. The centre of the sunflower was the passivation film fragment peeled by the formation of the whiskers and the whiskers spilled out onto the surface. In figures 3 and 4, with the hexavalent chromium passivation treatment, it is observed that the whiskers formatted along the cracks in the passivated surface. Trivalent chromium films did not produce such a significant crack structure. When no other whiskers formatted around the initial eruption, the whisker grew to long filament lengths as figures 5 and 6 show.

Using FIB analysis, it was possible to produce a fine cross section of both nodular and filament whiskers. Zinc whiskers grow from the coating, which must cause changes in density and structure of the electrodeposited zinc. In figure 7 (b), porosity was observed in the cross section of the whisker nodule structure. The root of some nodular whiskers showed considerable changes in grain structure. The root grains appeared more irregular and non-equiaxed when compared to the regular columnar grains seen elsewhere in the coating. The grains become extremely fine and polycrystalline in nature when moving up into the nodule. The whiskers grew from the centre of the nodule and the grains become refined towards the whisker tip. Figure 7 (b) also indicates that there were some bulk porosity similar to folded material in the nodule.

Conclusions

From the study conducted, the primary findings relating to the factors and driving forces behind zinc whisker formation and growth have been examined. It has been found that heat treatment temperature and time, effects induced by brighteners/carriers, coating thickness, passivation treatment, and changes in grain structure appear to be fundamental factors in the formation and growth of these abnormal surface features.

Through the comparison of the samples treated at identical temperatures for the two different treatment times, it can be suggested that increasing the temperature was a principle inducing factor for whisker growth and formation. The temperature also accelerated nodular whisker growth. However, the increasing ability for the formation of nodular whiskers with temperature was limited and it reached a maximum. The difference in the levels of nodular and filament whiskers suggests that zinc coatings took energy from the heat treatment for the formation of the new nodular whiskers and the filaments protruding out from the nodular bases. At lower temperatures, acceleration may be confined to filament whisker growth with nodule formation more evident at a higher temperature.

The results for the samples treated at different temperatures for the same time suggest that heat treatment exposure time induced growth and formation of nodular whiskers. However, the heat exposure time had a greater effect on whisker growth rather than whisker formation.

The amount of brightener did not appear to influence the formation of nodules, however, it did influence their growth and that of the filament whiskers. The size of nodules increased with the amount of brightener. That no whiskers were observed on the surface of the sample without the brightener and the carrier shows that possible stresses accelerating the growth of nodular and filament whiskers were not only induced by the brightener but also by the carrier.

The effect of the zinc coating thickness was also shown in this study. A greater coating thickness induced growth of the whiskers, which suggests that increased material in the coating can perhaps generate more stress and coupled with a high temperature, there were more opportunities for long filament whiskers to form. However, there was a limit to the density of the nodular whiskers at a constant temperature. The increased thickness may have caused more stress concentration zones and provided more material for forming the whiskers.

The observations for the passivated samples suggests that the treatments slowed down whisker formation but not whisker growth.

From FIB analysis the grains making up the whiskers became extremely fine and polycrystalline in nature as moving up from the substrate into the nodule. The whiskers grew from the centre of the nodule and the grains became refined as the structure advanced towards the tip. The significant change in structure from the bulk of the coating to the whisker suggests this change in grain structure may be a requirement for whisker growth to occur.

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