# SEM Investigation of Zinc Whiskers on Hot-dip Galvanized Coating and Bright Electroplated Coating.

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Whisker growth was observed on hot dip galvanised (HDG) zinc and blue chromated bright zinc plate. passivated with blue chrome passivate. For HDG, whisker growth predominated on dull areas, where grain size was small and compressive stresses were present. In electroplating, brighteners produce small crystals and shiny surfaces. SEM analysis showed the presence of chlorine and sulphur. In areas of whisker growth, the chlorine peak was stronger than that of sulphur. Small zinc crystals and surface corrosion by chlorides favour whisker growth. Sulphur is related to filament growth. Although the conditions necessary to produce whiskers are similar on HDG and plated zinc, the filaments themselves differ. On plated zinc, they are smooth and consist of pure zinc. HDG filaments are rough and contain iron and thus are brittle and prone to breakage.

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## 1. INTRODUCTION

Whisker growth on Tin is a well-known phenomenon. But whiskers grow on other metals, too. Whisker growths on Zinc, Silver, Cadmium, Indium, Aluminium, Lead and even Gold have been reported. /1/ Whisker growth on Zinc was investigated by Lindborg in 1975. In his paper Lindborg suggested that to initiate zinc whisker growth, a minimum stress must be present in the zinc coating. Any other irregularities causing micro-stresses in the coating, dislocations, interstitials or vacancies have no effect on growth. /2/ In paper published by Sugiarto et al. /3/ In 1984 the zinc whisker growth was linked to micro-stresses caused by brightener residues left in the electrodeposited coating. Films produced without brighteners showed no whisker growth. Passivation treatment slowed down whisker growth but did not prevent it. To grow whiskers, the specimens were placed in oven for 24 hours at a temperature of 170 °C. In their presentation at IPC/JEDEC Conference in 2004 Reynolds and Hilty /4/ showed that zinc whisker and the plated film had similar fine grained structure. The zinc was presumed to have diffused over long distances so no thinning of the film was observed under the whisker. Intermetallic compounds appeared to have no role in whisker growth.

It has been assumed that hot-dip galvanised (zinc) coatings (HDG) are immune to whisker growth. In their paper Brusse and Sampson /5/ mention that they had seen one report on presumed whisker growth on HDG coating. In 2005 it was reported that the computers in the Colorado Department of State's data center had began to fail on June 10, 2004. /6/ The Department turned to outside experts, who eventually diagnosed a rare condition known as "zinc whiskers" – tiny fibers of zinc barely visible to the eye, which had grown on the galvanized steel in the data center's 20-year-old floor panels. In year 2004 also other computer centers have been reported to be plagued by zinc whiskers. /7/ In December 2004 the authors received samples of both electroplated and hot-dip galvanized zinc coatings, both were growing whiskers.

In this report SEM (Scanning Electron Microscope) investigations on whisker growth of the samples (hot-dip galvanised and electroplated zinc coatings) are presented.

## 2. DESCRIPTION OF THE SPECIMENS

Two hot-dip galvanized (HDG) specimens were investigated. One was a support structure made of 25 mm U-profile. It had been used to support ventilation ducts. The second HDG specimen was a bend of pipe. Extensive whisker growth was seen on the surface of the support structure and inside the

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pipe. The surface appearance of the support structure varied from shiny spangled appearance to dull grey appearance. The surface appearance of the pipe was dull grey. The pipe had been stored on a warehouse shelf and had never been in use. The longest whiskers found on the surfaces are about 10 mm in length (figure 1).

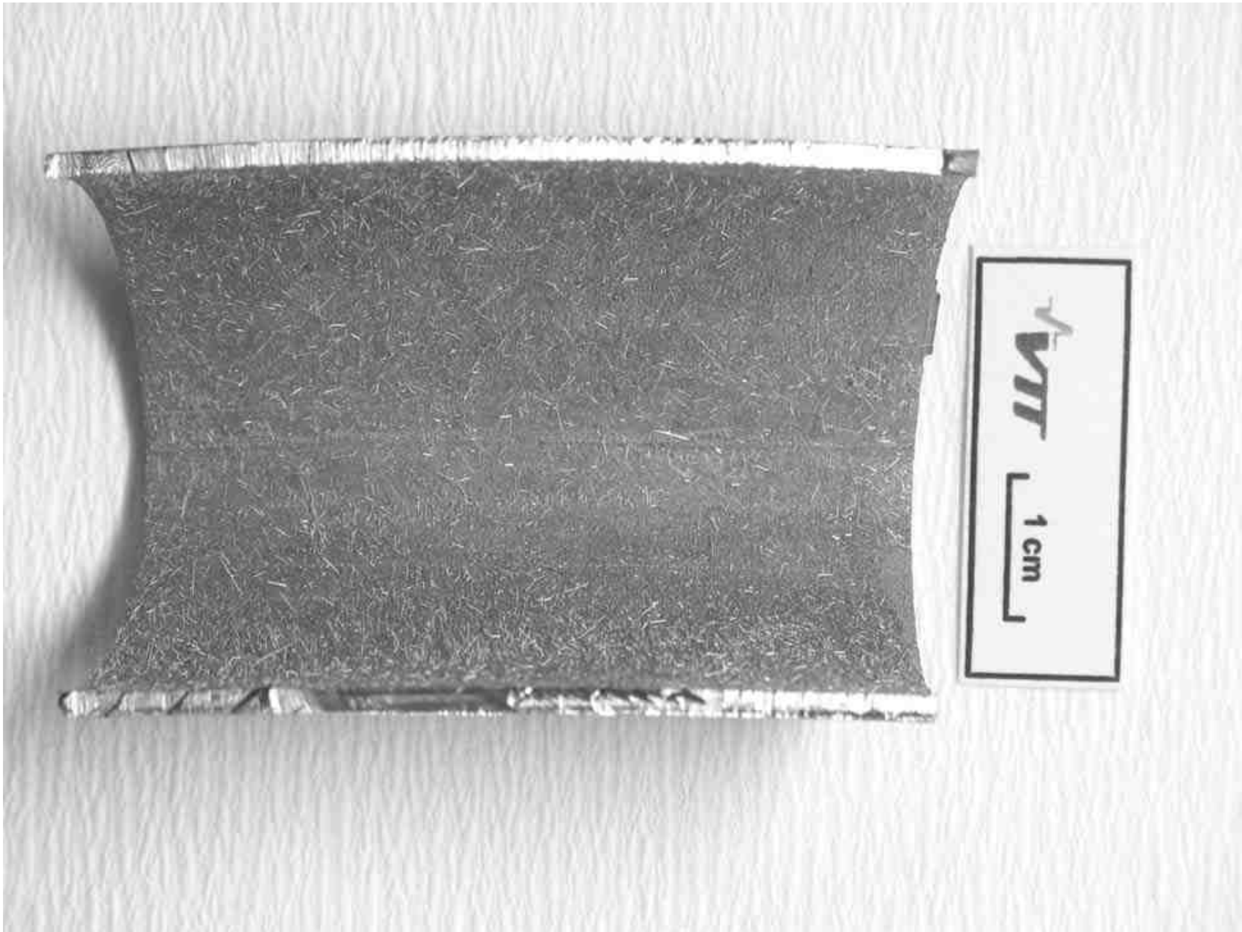

*FIG.1. Heavy whisker growth on HDG surface (pipe sample).*

The electroplated specimen was a frame structure that is made of carbon steel, electroplated with bright zinc and passivated with blue (colourless) chrome passivate. The appearance was still bright, but the surface feel was rough and grainy.

All the specimens had been in use or stored about twenty years in a power plant situated by sea.

## 3. INVESTIGATIONS

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Pieces were cut from the samples to be photographed and analysed with a SEM equipped with an x-ray microprobe (EDS). Metallurgical cross sections were made for determination of the coating microstructure. An additional TEM analysis of a single whisker was made to find out the crystal structure of the filament.

## 4. RESULTS OF THE INVESTIGATIONS

### *4.1 Whisker appearance on electroplated coating*

Figure 2 shows typical whisker filament found on the electroplated coating. There were nodular whiskers and filament like whiskers on the surface. All filament whiskers had a nodular base. The overall appearance was similar to that published in reference 3. There is a pit at the filament root. The pit is formed through the action of chlorides on the passive chromate layer. Similar pits were found by all filament roots on the investigated electroplate coating. The filament itself has smooth surface and is made of pure zinc.

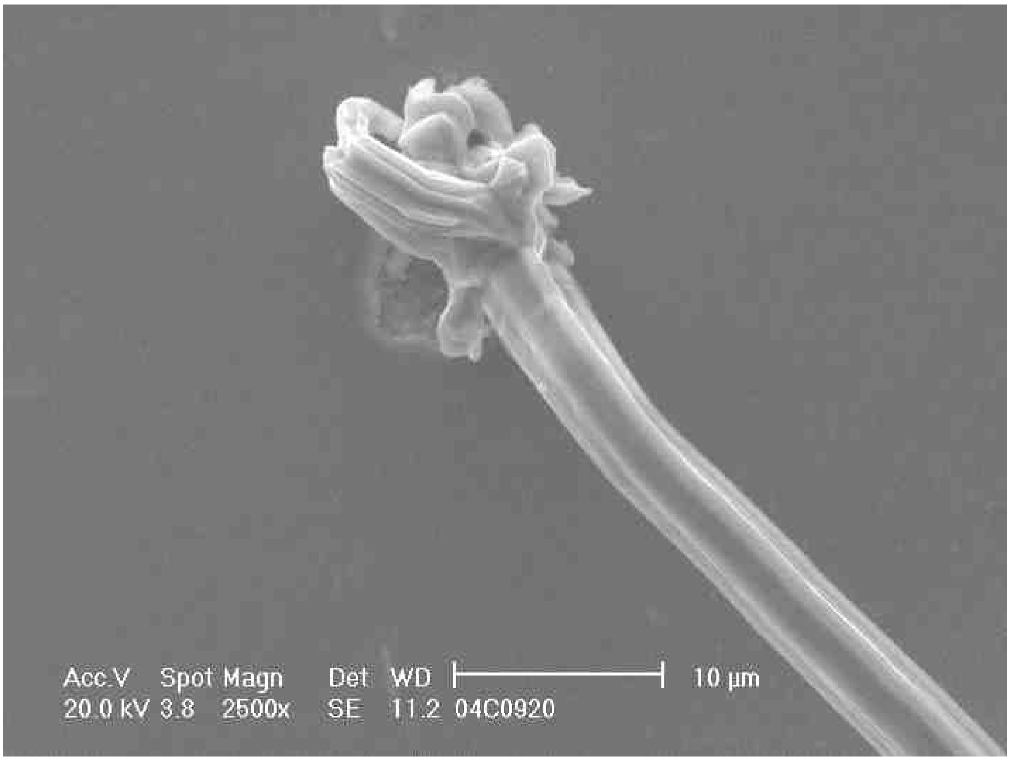


*FIG. 2. A typical whisker on the electroplated surface. There is a nodule and a chloride pit by the root of the whisker filament.*

### *4.2 Whisker appearance on hot-dip galvanised coating*

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In Figure 3 is a SEM photograph of whiskers that just have started to grow on the (HDG) support structure. These kinds of whiskers were found in the boundary area between the shiny and the dull surface. The whiskers have a "hat" which is the original surface of the zinc coating.

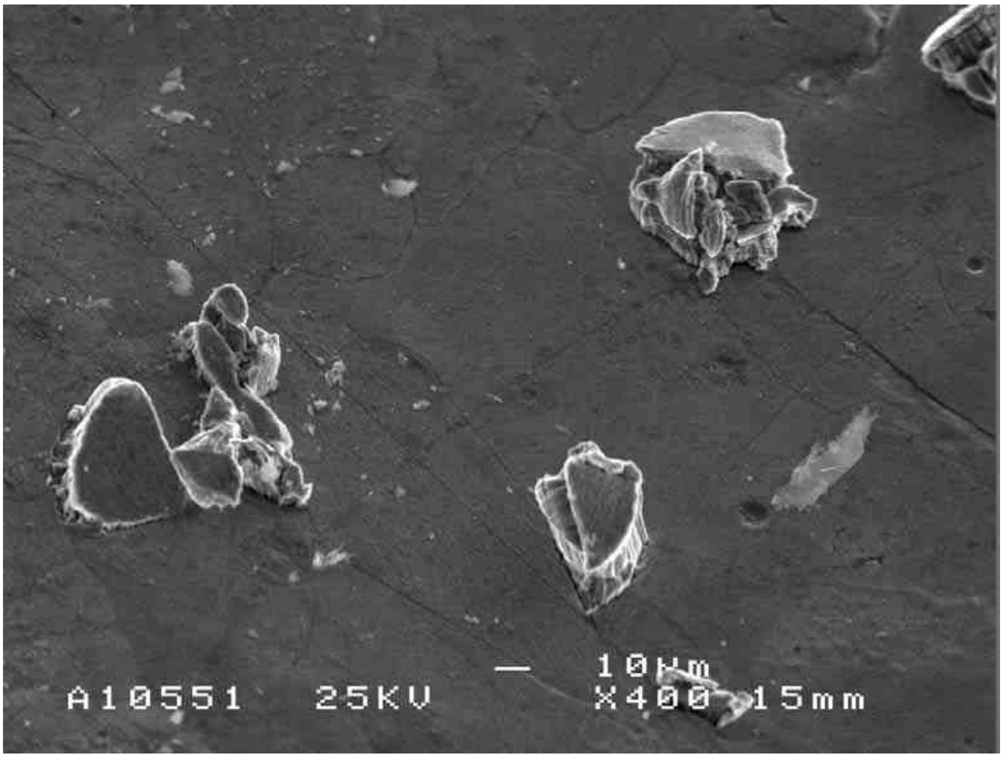


*FIG.3. Whisker nodules found on the boundary between dull and shiny HDG surface.*

A SEM photograph of long whisker on HDG coating is shown in figure 4. The filament is quite different from those found on the electroplate coating. The surface is rough and grooved. At the root a small nodule formation is seen. A shallow pit at the root is also seen.

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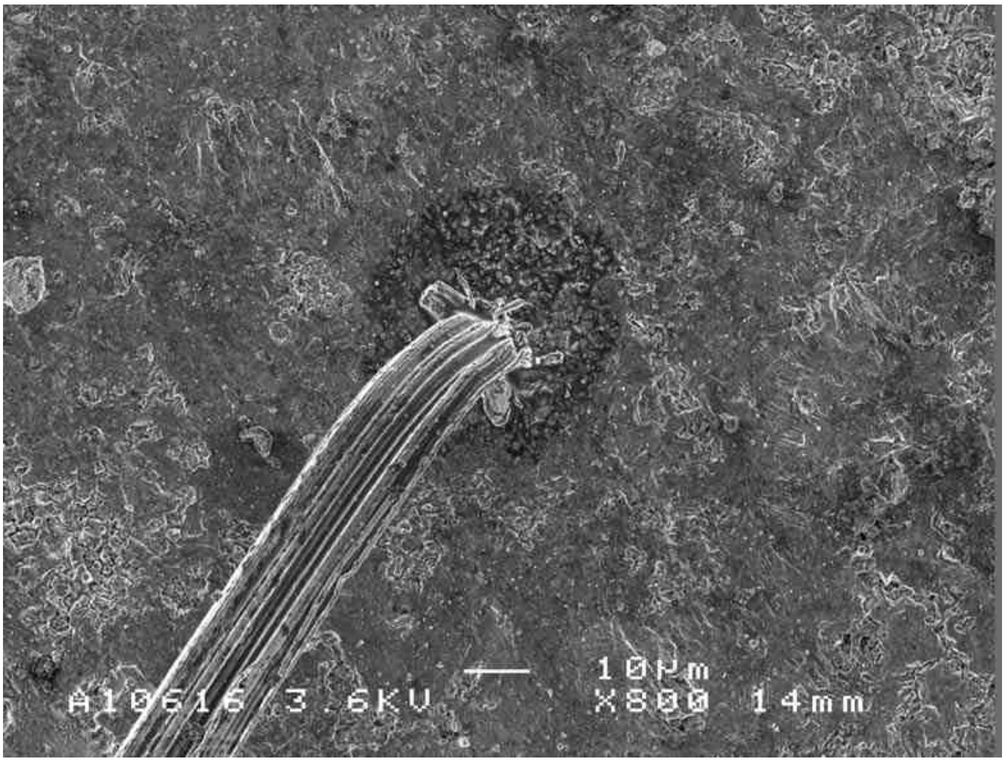

*FIG. 4. Whisker filament on the dull HDG surface.*

*4.2.1 Additional TEM-Analysis of single whiskers from hot-dip galvanised coating*

Single whiskers were taken from the pipe sample and analysed with TEM (Transmission Electron Microscope). A TEM photograph of a single whisker is seen in figure 5. The whisker contains Iron (Fe) approximately the same amount as is present in the η-phase of HDG coating as seen in table 1. /8/ Whisker is a single crystal formation elongated along c-axis. A bend in the filament marks a crystal boundary. The whisker is covered with a thin oxide layer.

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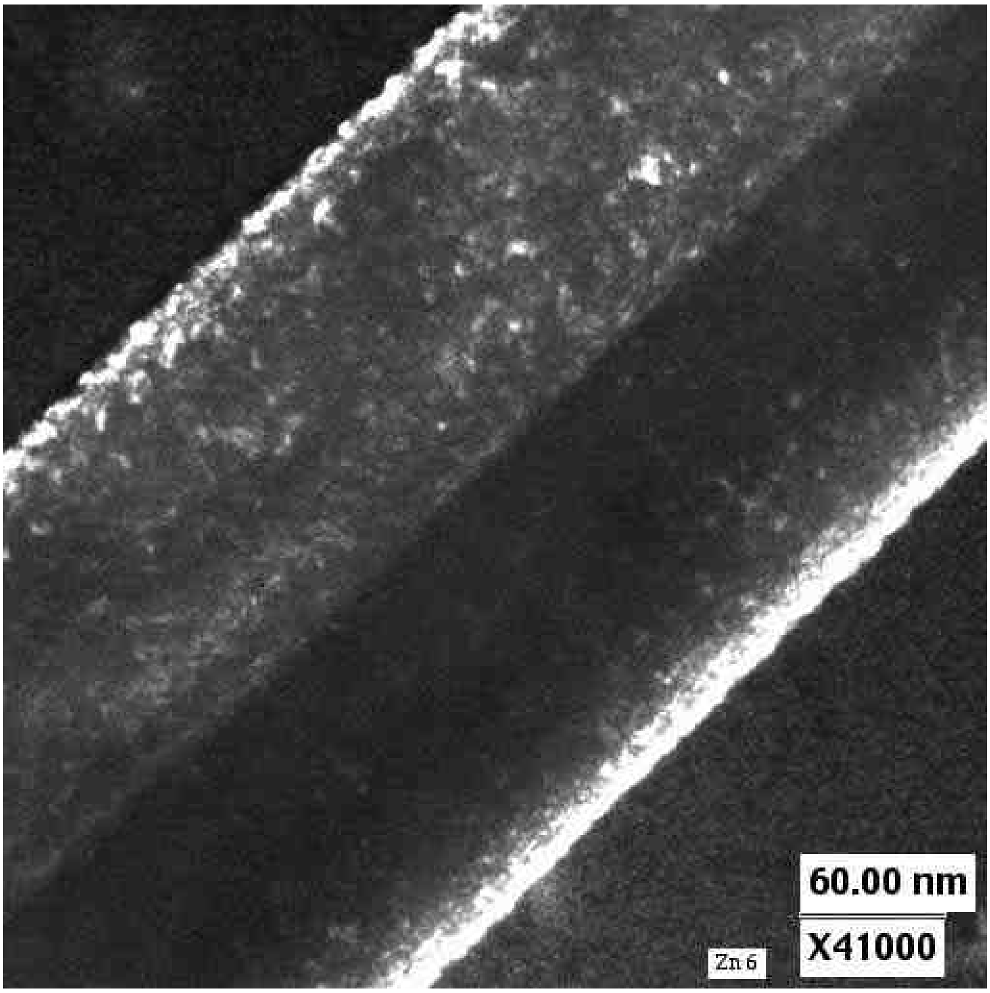


*FIG. 5. A TEM photograph of a single whisker from HDG-coating.*

**Table 1. TEM analysis of two single whiskers**

| **Whisker #1** | **Fe** | **Zn** | **Wt % Err.** |
|---|---|---|---|
| Weight % | 0.43 | 99.57 | ± 0.06 |
| Atom % | 0.50 | 99.50 | ± 0.66 |
| **Whisker #2** | **Fe** | **Zn** | **Wt % Err.** |
| Weight % | 0.29 | 99.71 | ± 0.09 |
| Atom % | 0.34 | 99.66 | ± 0.96 |

*Fe content of different phases of hot-dip galvanised Zinc coating /8/*
*Pure Zinc (0% Fe)*
*η-phase 0.3 % Fe*
*ζ-phase 5.8 – 6.7 % Fe*
*δ-phase 7 – 11 % Fe*
*γ-phase 21- 28 % Fe*
*Steel base (0% Zn)*

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*4.3 SEM/EDS investigations of the surfaces*

In the EDS analyses of the surfaces of both electroplate and HDG coatings Chlorine and Sulphur were detected. In the area near whisker root and in areas where heavy whisker growth was observed, the chlorine peak was higher than the sulphur peak. In areas where whisker growth is not as extensive, or completely lacking, the chlorine peak was much lower than the sulphur peak.

In the dense whisker area of the HDG coating small amounts of Potassium were detected at the root of a long whisker.

In X-ray analysis of some of the whisker nodules of the electroplate coating a carbon rich layer was detected. The carbon is probably a residue from brightener used in the plating bath.

*4.3.1 Coating microstructure*

In HDG coating the microstructure differed in the shiny, spangled area and the dull grey area. Figures 6 and 7 show the difference in cross sections between the shiny and the dull surface. Some large crystals were seen on the cross section of the shiny area. In the dull area there were none as distinguishable features.

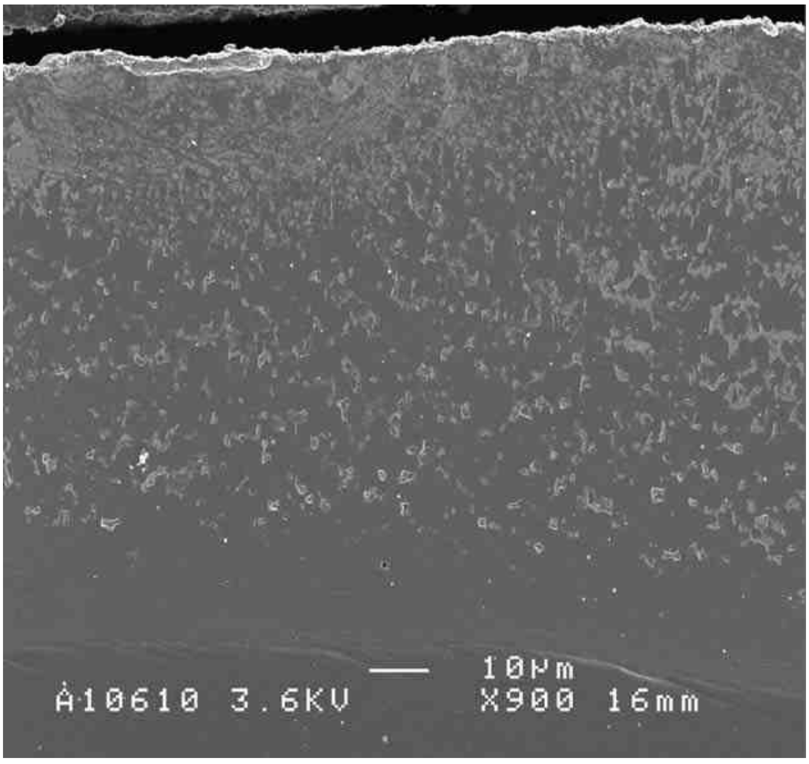


*FIG. 6. Cross-section of the shiny HDG surface.*

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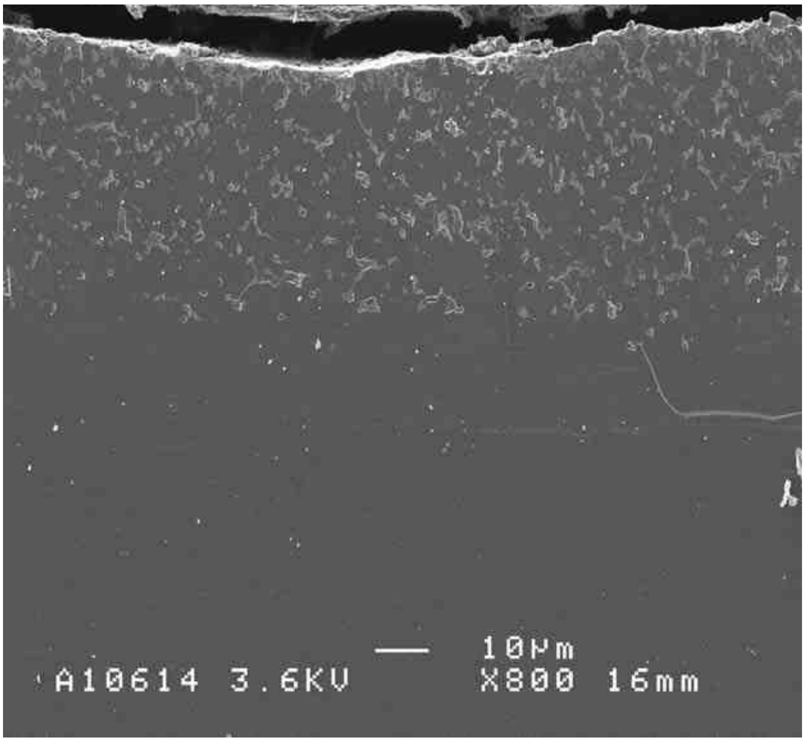

*FIG. 7. Cross-section of the dull HDG surface.*

In our investigations we found a pit on root of each long whisker filament of the electroplated coating. The pit exposes a similar grainy structure as reported by Reynolds and Hilty. It is a typical crystal structure of bright zinc electroplate.

## 5. DISCUSSION

*5.1 On the factors affecting whisker growth*

*5.1.1 Coefficient of thermal expansion.*

In table 2 are coefficients of thermal expansion of Zinc single crystal as published by International Zinc Association. /9/ The figures show that thermal expansion along c-axis is about four times that of a-axis. This means that temperature fluctuations create four times more stress along c-axis than along a-axis.

**Table 2. Coefficients of thermal expansion for Zinc /9/**

| | |
|---|---|
| Single crystal along a-axis 0-100 °C | 15 $\mu$m/m K |
| Single crystal along c-axis 0-100 °C | 61 $\mu$m/m K |
| Polycrystalline 20-250 C | 39.7 $\mu$m/m K |
| Volume CTE 20-400 °C | $0.89 \times 10^{-6}$ / K |

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*5.1.2 Coating microstructure - Electroplated coating*

The microstructure of electroplate coating consists of small crystals. The anisotropic CTE can in these circumstances create local stresses between crystals. Small temperature fluctuations may not be enough to cause whiskers to grow, but any additional stress may then exceed the strength of the material and push it out to build a nodule. The electroplating process itself leaves residual stresses in the coating. Reference source /10/ gives values for compressive stresses in electroplated zinc coating between 6.9 – 13.8 MPa depending on the used plating process. The compressive stresses are caused by impurities (metal hydroxides, brightener residues, foreign cations, etc.) that co-deposit into the coating.

*5.1.3 Coating microstructure - HDG coating*

The support structure had a surface where there were (bright) large zinc crystals and (dull) small zinc crystals. The dull areas grow long whiskers but the bright areas do not. In the pipe sample the coating is made altogether from (dull) small crystals.

The thermal stresses caused by fluctuation of temperature in the dense environment of small crystals have no room for relaxation and the probability for whisker growth is much greater. The anisotropic CTE of zinc crystal have in the dull areas the possibility to create large pressures between individual crystals.

The HDG coatings contained small amounts of Aluminium as alloying element as seen in the EDS spectrum in figure 8. Aluminium decreases the crystal size. In the past hot-dip galvanisers used a layer of molten Lead in the tank bottom and the zinc was saturated with lead. Lead increases the crystal size. From the past to the present the average crystal size of HDG Zinc coatings have decreased and HDG Zinc coatings have started to grow long whiskers.

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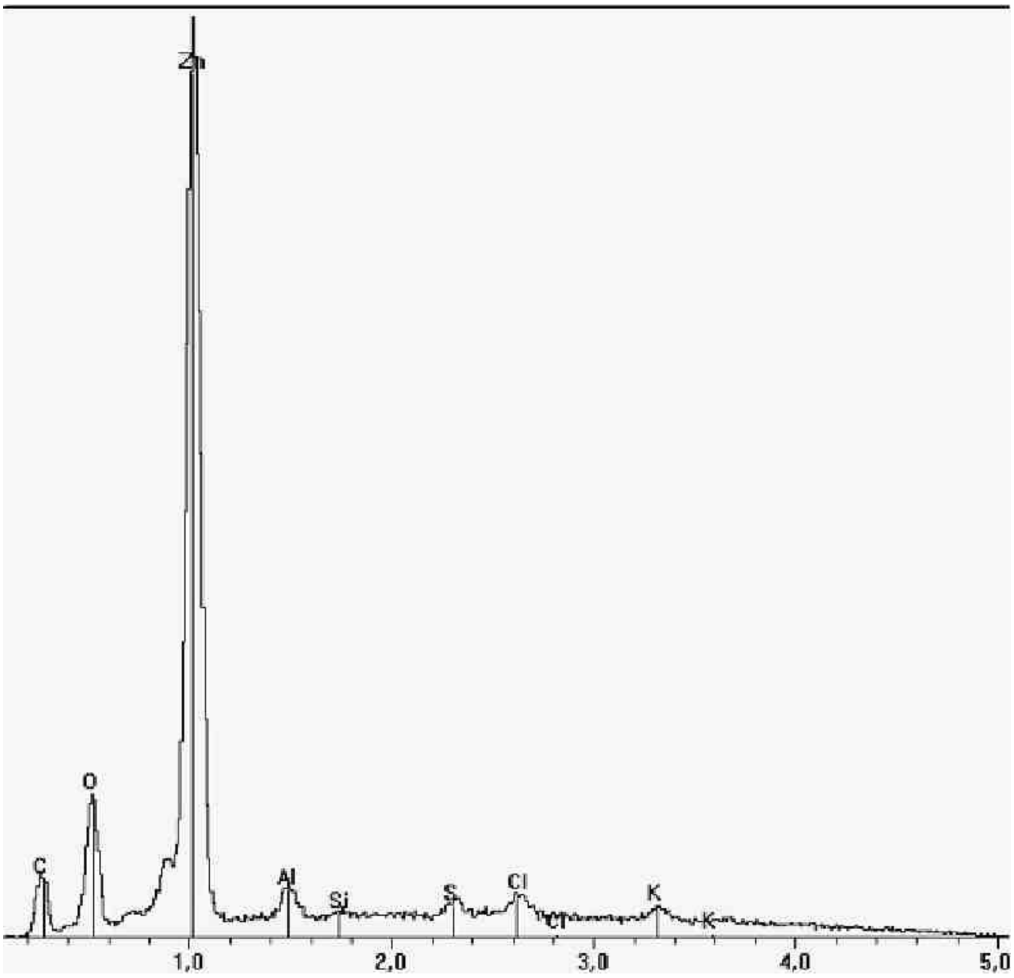

*FIG. 8. EDS spectrum from the pit area of the whisker in figure 4.*

### *5.1.4 Corrosion of zinc coatings*

Corrosion of zinc coating creates two kinds of effects. Chlorides destroy the top passive layer of the coating exposing the underlying crystalline zinc. In our investigation this is seen as a pit formation. Secondly corrosion products that are formed on grain boundaries create additional stress in the coating. In some SEM photographs chloride formations indeed seemed to be growing in the zinc film.

### *5.2 Suggested mechanism for whisker growth*

Based on our investigations there are common requirements for whisker filament to grow on both electroplated and hot-dip galvanised zinc coating.

* First; compressive stresses must be created in the zinc film. These are created either during the coating process as in electroplated coatings or are caused by corrosion on the top layer.
* Second; the top passive layer (chromate/oxide layer) is destroyed exposing crystalline zinc. A chloride pit and a nodule are formed on the surface.
* Third; zinc sulphide is formed in the chloride pit. The platy zinc sulphide may serve as a suitable crystal plane for filament growth.

The nodule like whisker is probably formed because local impurities, that cause compressive stresses in the film, become partly incorporated in the zinc crystal lattice twisting the growth. Once all the impurities are consumed and there is a suitable crystal plane available, the whisker filament can start to grow.

## 6 SUMMARY

In our investigations the following preconditions, for the growth of zinc whiskers were found.

The prime precondition is that compressive stresses are build up in the zinc film. This is the result of several factors.

* Small crystal size, an inherent property of bright electroplated coating and corresponding to dull HDG surface.

* Chlorides form corrosion products partly embedded in the zinc film. Chloride corrosion then finally destroys the top (passive) layer of the coating exposing the crystalline zinc.

* Anisotropic coefficient of thermal expansion of zinc crystal combined with small crystal size and thermal fluctuations are the final cause that forces zinc to form a whisker nodule.

To start the filament growth zinc sulphide is formed in the chloride pit. Platy zinc sulphide serves as a suitable crystal plane for filament growth.

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