The Effect of Electroplating Bath Composition on the Passivation and Subsequent Corrosion Performance of Zinc Electrodeposits

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The post-plating performance of electrodeposited zinc coatings formed from alkaline and acid electrolytes were examined using both electrochemical and surface analytical techniques. Coatings, 8 µm thick, were studied to examine surface chemistry and electrochemistry. Scanning electron microscopy (SEM) was used to examine morphology, while Auger electron microscopy (AES) was employed to study the composition of the coatings. AC impedance was used to investigate the nature of the passive films formed on zinc coatings, and scanning reference electrode technique (SRET) was used to monitor the development of corrosion in situ in a chloride environment. Exposure neutral salt fog was also employed to assess the relative corrosion resistance of these zinc coatings.

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Introduction

Zinc is one of the most important, and widely used, metallic coatings used for the corrosion protection of steel or iron components used in a variety of environments [1,2]. Zinc metal, being more electronegative than iron, corrodes preferentially to protect the functional steel component. However, in the case of electrodeposition of zinc metal, variations in the corrosion resistance provided can occur depending on the nature of the electrodeposition bath used [3]. It has also been reported that the corrosion resistance provided by zinc coatings to steel is quite dependent upon their morphology [4]. In this paper the electrochemical behaviour of zinc electrodeposited coatings, formed from both acidic and alkaline electroplating baths, have been examined using electrochemical impedance spectroscopy (EIS) and scanning reference electrode technique (SRET). Scanning electron microscopy (SEM) was also employed to assess any differences in the morphology of the electrodeposits, while salt fog exposure, according to ASTM B117 [5], was carried out to assess corrosion resistance of the materials.

The nature of the passive oxide film, formed on zinc electrodeposited coatings plated from alkaline and acidic baths, was investigated using EIS. ZnO is an n-type semiconductor with a large band gap of about 3.2 eV [6,7]. The n-type conduction results from the non-stoichiometry of the elements due to the presence of Zn^{2+} at interstitial positions in the lattice, creating shallow donor levels just below the conduction band [8]. AC impedance has been used successfully to study electronic characteristics of semiconducting passive films, such as the donor concentration (N_D) and the flat band potential (E_{FB}) in a range of non-aggressive electrolytes [9-13]. Using this type of analysis of the passive films it was hoped to assess any differences in their nature depending on whether the zinc coating had been electrodeposited under acid or alkaline conditions.

The SRET is a powerful potential scanning technique which allows real-time corrosion activity measurements to be carried out in-situ. During corrosion, anodic and cathodic reactions occur at separate sites. The potential difference between these sites is negligible due to the high conductivity of the metal. However, ionic transport in the electrolyte, due to these anodic and cathodic reactions, will produce small, but measurable, potential differences [14]. This phenomenon was exploited by Isaacs [15] in his description of the development of potential scanning techniques. The SRET measures micro-galvanic potentials existing local to the surface of the material under investigation, using a uniquely designed probe which scans across the surface. The technique is noninvasive and provides dynamic information on corrosion activity by recording ionic flux variations in the electrolyte, on a microscopic scale. This technique was used to monitor the development of corrosion on zinc electrodeposited steel during immersion in an aggressive electrolyte [16].

Experimental

Zinc coatings, nominally 8 µm thick, were electrodeposited from either an alkaline or bright acid zinc electrodeposition bath onto a mild steel substrate. Acid zinc panels were prepared from a proprietry solution, between pH 4.8 - 5.5, on a pilotplant scale. Alkaline zinc panels were prepared in industrial-scale electrodeposition baths, once more from proporietry solutions, at pH 13.4. Mild steel panels, 50 x 50 mm in area, and cylinders, 80 mm high and 94 mm in circumference, were electrodeposited with zinc. All surfaces were cleaned with acetone prior to electrochemical testing. In addition, samples were masked off with Lacomit varnish leaving an area of 1 or 2 cm² exposed for testing. For some tests samples were acid pickled as they would be prior to passivation in an industrial setting. A dilute solution of HCl was used for acid electrodeposited zinc, while 0.25% HNO3 was used for alkaline electrodeposited samples.

Electrochemical impedance spectroscopy was carried out on EG&G model 273A potentiostat with 5210 Lock-in amplifier. EIS was controlled via a PC using EG&G m398 impedance software. A three electrode configuration was employed with the zinc coated sample as working electrode, a standard calomel electrode (SCE) as reference and a platinum sheet as counter electrode. For impedance measurements the reference electrode was coupled to Pt probe through a 10 µF capacitor. The electrolyte employed in these studies was 0.15 M Na₂B₄O₇ with 0.3 M H₃BO₃ at pH 8.4. Samples were pre-polarised, at 1 mV s⁻¹, from open circuit potential (OCP) to 1.2 V (vs. SCE). They were then pre-anodised at this high potential for 2 h. The potential was then stepped down, at 0.15V intervals, towards lower potentials within the passive region. At each potential interval, impedance measurements were recorded, in the high frequency region. In addition, the behaviour of acid and alkaline electrodeposited zinc samples in this borate solution at pH 8.4 was carried out at 0.3V (vs. SCE) over a wide frequency range following prepolarisation at 1.2V (vs. SCE) for 2 hours. Linear polarisation resistance (LPR) measurements were carried out using an ACM Autotafel operated via computer control. 3.5% NaCl was used as electrolyte with a three electrode configuration as described above. Sample areas were kept at 2 cm^2 for these studies.

For SRET studies the specimens were rotated in solution using a stepper motor, allowing variable rotation speeds between 1-250 rpm. A rotation speed of 100 rpm was employed during these studies. With a knowledge of specimen diameter and the use of an optical trigger, the horizontal displacement along the circumference of the specimen can be determined. Measurement of corrosion activity was made via a differential probe and differential head amplifier. The probe moves vertically, in 0.5 μ m resolution steps, whilst monitoring micro galvanic activity over the circumference of the specimen, allowing 2-D area potential map scans to be produced for any region of interest. These maps are produced with a user-defined colour palette, allowing contours of corrosion activity to be displayed, in real-time. In these studies the electrolyte employed was 0.35% (w/v) NaCl and area potential maps were recorded at OCP. An approximate working distance from the probe tip of 150 µm was used throughout these studies.

Scanning electron microscopy (SEM) was carried out on an Leica Cambridge Stereoscan S360 system. Auger electron spectroscopy (AES) was carried out using a Varian AES Spectrometer, with a primary electron beam approximately 100-200 μ m in diameter, an energy of 3 x 10³ eV and a current of 0.7 μ A. Depth profiling was carried out by a sequential Ar⁺ ion bombardment, using a primary energy beam of 0.75 μ A cm⁻². An etch rate of 1 nm s⁻¹ was assumed. Salt fog exposure tests were carried out, according to ASTM B117 [5], in a C+W Specialist Equipment model SF450 Salt Fog Cabinet. Any changes in the appearance of the samples were noted on, at least, a daily basis.

Results and Discussion

In Figure 1 & 2 SEM micrographs of as received acid and alkaline electrodeposited zinc are presented. From these images it is evident that alkaline zinc electrodeposits, used in these studies, have a more granular morphology than the acid zinc electrodeposited samples. AES was used to examine the differences in composition. Depth profiles of the oxide film of, as received, acid and alkaline electrodeposited zinc, obtained using AES, are presented in Table 1. It would appear that the oxide for acid zinc has lower levels of impurities, especially sulphur and carbon, than alkaline electrodeposited samples.

| Acid electrodeposited zinc | | | | | | | |
|--------------------------------|----------------------|------|-----|-----|------|-----|-----|
| Depth | Composition (atom %) | | | | | | |
| (nm) | 0 | Zn | S | Cl | С | Ν | Ca |
| 0 | 43.3 | 40.0 | 0.2 | 1.0 | 14.8 | 1.0 | 0.0 |
| 4 | 46.2 | 51.7 | 0.0 | 0.0 | 1.7 | 0.0 | 0.4 |
| 10 | 42.0 | 57.2 | 0.0 | 0.0 | 0.7 | 0.0 | 0.0 |
| 20 | 40.9 | 59.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 30 | 36.8 | 63.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 40 | 32.2 | 67.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 50 | 27.1 | 72.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 70 | 15.7 | 84.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Alkaline electrodeposited zinc | | | | | | | |
| 0 | 40.6 | 30.7 | 3.7 | 0.8 | 22.4 | 0.7 | 1.1 |
| 4 | 46.1 | 41.6 | 3.3 | 0.3 | 5.8 | 0.0 | 2.9 |
| 10 | 46.6 | 45.4 | 2.3 | 0.0 | 2.9 | 0.0 | 2.9 |
| 16 | 47.0 | 46.6 | 1.6 | 0.0 | 2.2 | 0.0 | 2.5 |
| 26 | 46.5 | 49.6 | 1.0 | 0.0 | 1.0 | 0.0 | 1.8 |
| 36 | 44.8 | 52.5 | 0.6 | 0.0 | 0.0 | 0.0 | 2.0 |
| 50 | 42.9 | 55.3 | 0.6 | 0.0 | 0.0 | 0.0 | 1.2 |
| 70 | 37.6 | 61.3 | 0.3 | 0.0 | 0.0 | 0.0 | 0.8 |
| 90 | 29.4 | 69.8 | 0.4 | 0.0 | 0.0 | 0.0 | 0.5 |
| 110 | 15.8 | 83.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 150 | 8.9 | 91.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

Table 1 - Depth profile for acid and alkaline electrodeposited zinc, as received.



Figure 1 – SEM micrograph of acid electrodeposited zinc, as received (x 4000).



Figure 2 – SEM micrograph of alkaline electrodeposited zinc, as received (x4000)

In Tables 2 & 3 the depth profiles obtained for acid and alkaline zinc following acid pickling, in dilute HCl and 0.25% HNO3 respectively, are displayed. Acid pickling for acid zinc samples appeared to be a more effective procedure for acid electrodeposited zinc samples resulting in the removal of a good deal of carbon and the elimination of nitrogen and calcium (Table 2). However, as would be expected after immersion in HCl, a large increase in chlorine concentration has occurred, throughout the depth of the passive film. Acid pickling for alkaline electrodeposited zinc appears to have a lesser effect on surface composition (Table 3). The sulphur concentration was observed to decrease throughout the entire depth of the oxide film. A slight reduction in calcium and nitrogen concentration was also apparent, while little or no effect could be observed on the either the carbon or the chlorine concentration in comparison with an unpickled surface (Table 1).

Table 2 - Depth profile of acid electrodepositedzinc following pickling in dilute HCl.

| Depth | Composition (atom %) | | | | | |
|-------|-----------------------------|------|-----|-----|--|--|
| (nm) | 0 | Zn | Cl | С | | |
| 0 | 47.2 | 45.4 | 1.0 | 6.4 | | |
| 8 | 47.4 | 52.6 | 0.0 | 0.0 | | |
| 12 | 42.1 | 57.9 | 0.0 | 0.0 | | |
| 17 | 38.7 | 61.3 | 0.0 | 0.0 | | |
| 23 | 40.4 | 59.6 | 0.0 | 0.0 | | |
| 30 | 37.6 | 62.4 | 0.0 | 0.0 | | |
| 40 | 37.9 | 62.1 | 0.0 | 0.0 | | |
| 50 | 36.0 | 64.0 | 0.0 | 0.0 | | |
| 70 | 33.5 | 66.5 | 0.0 | 0.0 | | |
| 90 | 29.4 | 70.6 | 0.0 | 0.0 | | |
| 110 | 15.4 | 84.6 | 0.0 | 0.0 | | |
| 130 | 7.9 | 92.1 | 0.0 | 0.0 | | |

Table 3 - Depth profile for alkalineelectrodeposited zinc following pickling in 0.25%HNO3.

| Depth | Composition (atom %) | | | | | | |
|-------|-----------------------------|------|-----|-----|-----|-----|-----|
| (nm) | 0 | Zn | S | Cl | С | N | Ca |
| 0 | 39.3 | 34.3 | 1.9 | 0.8 | 22 | 0.7 | 1.0 |
| 4 | 45.1 | 44.2 | 1.9 | 0.5 | 5.8 | 0.4 | 2.0 |
| 10 | 48.9 | 44.4 | 1.0 | 0.2 | 3.4 | 0.0 | 2.0 |
| 20 | 48.2 | 51.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 30 | 46.9 | 53.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 40 | 43.9 | 56.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 50 | 38.5 | 61.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 70 | 33.1 | 66.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 100 | 22.0 | 78.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 130 | 13.7 | 86.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

Variations in the corrosion resistance of acid and alkaline electrodeposited steel were observed during electrochemical investigations and exposure to neutral salt fog according to ASTM B117 [5]. In Figure 3(a) and (b) the variation in polarisation resistance and corrosion rate with immersion time in 3.5% NaCl for acid and alkaline electrodeposited zinc are presented. In Table 4 a summary of the observations made during salt fog exposure are displayed. In the initial stages of immersion in chloride solution alkaline electrodeposited (Figure 3(b)) zinc appears more active with lower R_p values and a higher corrosion rate than was observed for acid electrodeposited zinc (Figure 3(a)). During exposure to neutral salt fog it was observed that alkaline electrodeposited zinc had 5% area coverage in red rust at consistently shorter times than acid electrodeposited samples. These variations in the corrosion resistance of zinc coatings deposited from electroplating baths with either acid or alkaline electrolytes has been observed by other authors [3,12].



(b)

Figure 3 – R_p and Corrosion rate vs. immersion time in 3.5% NaCl for (a) acid and (b) alkaline electrodeposited zinc.

Table 1 - Summary of observations during salt fog exposure of acid & alkaline electrodeposited zinc, according to ASTM B117 [5].

| Substrate | Exposure Time (hours) | | | |
|-----------|-----------------------|-------------|--|--|
| | 5% White Rust | 5% Red Rust | | |
| Acid Zinc | 4 | 96-144 | | |
| Alkaline | 4 | 48-72 | | |
| Zinc | | | | |



Figure 4 – SRET potential maps for (a) acid and (b) alkaline electrodeposited zinc in 0.35% NaCl at OCP for 30 minutes.

In Figure 4(a) and (b) the SRET potential maps recorded for acid and alkaline electrodeposited zinc, after approximately 30 minutes immersion in 0.35% NaCl at OCP, are presented. From these maps the development of isolated anodic (dark grey) and cathodic (light grey/white) sites can be observed. It would seem that dark grey areas correspond to more than one anodic site, situated in close proximity to each other, causing a smearing effect on the ionic flux in the electrolyte. For alkaline electrodeposited zinc (Figure. 4(b)) the anodic sites appear to develop in a line, while on acid electrodeposited zinc (Figure 4(a)) these sites are distributed over the entire surface area. In addition, cathodic activity, represented by light grey/white areas on the SRET potential maps, is evident adjacent to anodic sites of activity.

In Figure 5 the equivalent circuit, used to model the AC impedance behaviour of anodically formed passive films, for both acid and alkaline electrodeposited zinc in 0.15 M Na₂B₄O₇ with 0.3 M H₃BO₃ at pH 8.4, is presented. The circuit used is based upon the transfer function [9]:

$$Z(s) = R_{\Omega} + R_{H}(1 + sR_{H}C_{H})^{-1} + R_{sc}(1 + sR_{sc}C_{sc})^{-1}$$
(1)

where $s = j\omega$ is the complex variable for a sinusoidal perturbation with $\omega = 2\pi f$. R_{sc}-C_{sc} refer to the resistance and capacitance of the space charge region and R_H-C_H refer to the resistance and capacitance of the Helmhotlz double layer of the interphase between the electrode and the electrolyte, and R_{Ω} refers to the ohmic resistance. This equivalent circuit has been found to adequately describe the electrochemical system at the electrode/electrolyte interface [9-13]. However, the two RC-time constants of the transfer function (1) do not differ significantly, thus, making it difficult to determine all the parameters of the transfer function. Therefore, capacitance was determined from high frequency data where equation (1) can be approximated by;

$$\lim_{s \to \infty} Z(s) = R_{\Omega} + (sC_{H})^{-1} + (sC_{sc})^{-1} = R_{\Omega} + (sC)^{-1}$$
(2)
s \to \infty

The overall capacitance, C, of the passive Zn electrode, at a given applied potential, was estimated from the imaginary component $\text{Im}\{Z(s)\} = (sC)^{-1}$ of the experimental impedance data in the range 1 kHz $\leq f \leq 10$ kHz using equation (2). Total capacitance, C_{tot} , at a given applied potential, was determined form extrapolation of C vs. f^{-1} at $f \rightarrow \infty$ [9]. In Figure 6 the variation in capacitance, with applied potential, of these anodically formed passive layers is presented. It is evident that the capacitance is higher at lower potentials and decreases with increasing applied potential becoming approximately constant at potentials higher than 0.5 V (vs. SCE). This is in agreement with the findings of Pech-Canul *et al* [12]. In addition, it is evident that C_{tot} for alkaline

electrodeposited zinc is somewhat higher than that obtained for acid electrodeposited samples.



Figure 5 – Equivalent circuit used to model the impedance data for acid and alkaline electrodeposited zinc in 0.15 M $Na_2B_4O_7$ with 0.3 M H_3BO_3 at pH 8.4 according to the transfer function (1).



Figure 6- Total capacitance vs. applied potential for anodically formed passive layers on acid and alkaline electrodeposited zinc in 0.15M Na₂B₄O₇ with 0.3M H₃BO₃ at pH 8.4.

Assuming that correction for C_H would lead to values for the space charge capacitance that follow similar behaviour to that observed in Figure 6, it can be concluded that the anodically formed passive films, on both acid and alkaline electrodeposited zinc, behave as n-type semiconductors. If C_H has a value in the region of 30-50 μ F cm⁻², and a typical dielectric constant (ϵ) of 8.5 the Mott-Schottky equation [17,18]

can be used to determine the donor density N_D of the space charge region of the interphase between the electrode and the electrolyte. It was found that the N_D for alkaline zinc was, on average, of the order of 10^{21} cm⁻³, while that for acid zinc was an order of magnitude lower, on average. From the literature N_D for ZnO single crystal electrodes are of the order of 10^{16} cm⁻³ [9]. It is clear that the electrodeposition of zinc coatings results in the incorporation of a large number of impurities into the oxide film (Table 1), resulting in an increase in N_D for these materials. In addition, N_D for alkaline electrodeposited zinc tested during these investigations was higher than that for acid electrodeposited samples. This may be related to the lower corrosion resistance observed for alkaline electrodeposited samples both during both salt fog exposure (Table 4) and LPR (Figure 3). The variations in impurity levels for these zinc coatings may also be related to the differences observed in their morphology. It has been noted by other authors that morphology has an effect on the corrosion resistance provided by zinc coatings [4].

Conclusions

From SEM analysis of the morphology of acid and alkaline electrodeposited zinc coatings on steel it is evident that alkaline zinc electrodeposits (Figure 2) possess a much more granular morphology than acid zinc coatings (Figure 1). Depth profiling, carried out using AES, demonstrated that prior to acid pickling alkaline zinc has higher impurity levels in its oxide film (Table 1). In addition, acid pickling, which is routinely carried out prior to chromate passivation of these surfaces, appears to have a more profound effect on the elemental composition of acid electrodeposited zinc (Table 2) than on that of alkaline zinc coatings (Table 3). During both salt fog exposure tests (Table 4) and LPR (Figure 3) it was observed that alkaline zinc coatings tended to provide inferior corrosion resistance in comparison with acid electrodeposited zinc samples. In addition, from SRET potential maps it appears that anodic activity

on alkaline zinc surfaces was concentrated in one area (Figure 4(b)) while that of acid zinc coated samples (Figure 4(a)) was more evenly distributed over the surface in the initial stages of immersion in 0.35% NaCl at OCP. From EIS studies it was determined that anodically formed oxide films on alkaline zinc tended to have a higher donor density in the space charge region of the interphase between the electrode and the electrolyte. This may be related to the higher corrosion rate observed for these panels in comparison with acid zinc coatings. The variations in impurity levels for these zinc coatings may also be related to the differences observed in their morphology.

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