

# Effect of Oxalate Anions on Zinc Electrodeposition from an Acidic Sulphate Bath

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Zinc coatings were electrodeposited on steel substrate. The effect of oxalate anions as chelating agents on nucleation and growth mechanism, surface morphology, predominant texture and corrosion behaviour of zinc electrodeposits was investigated. Evaluation of nucleation mode of zinc in the presence and absence of oxalate anions showed that the instantaneous nucleation is predominant in both cases. From the AFM images, the nuclei densities for zinc deposition were  $3.5 \times 10^9$  and  $2 \times 10^9$  cm<sup>-2</sup> in the absence and presence of oxalate anions, respectively. These are one order of magnitude higher than those obtained by analysis. Electrochemical impedance spectroscopy revealed that in the bath containing oxalate anions, the growth of deposit is semi-infinite diffusion controlled. While in the absence of oxalate anions, the charge transfer control was governed. In the absence of oxalate anions, the texture components of zinc coating were mostly basal and low angle pyramidal planes, whereas in the presence of oxalate anions, the texture components of zinc surface morphology from packets of hexagonal platelets to a granular nature. In the presence of oxalate anions, the zinc coating produced had a better corrosion resistance than that deposited from bath without oxalate anions. (© 2011 The Electrochemical Society. [DOI: 10.1149/1.3575640] All rights reserved.

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Zinc coatings are widely used in order to protect steels against corrosion because zinc is anodic to steel and sacrificially protects the base metal at low cost.<sup>1</sup> It is well known that the corrosion resistance, formability and paintability of the coatings are associated with the surface morphology and predominant texture.<sup>2–5</sup> The zinc coatings can be applied using various techniques including electrodeposition. The properties of electrodeposits including the surface morphology and texture are strongly affected by various factors.<sup>6</sup> It has been shown that the temperature and pH of the bath, deposition current density, substrate surface preparation and texture intensity of substrate influence the surface morphology and texture of zinc deposits.<sup>5–9</sup> In addition, it is well known that the additives have also significant effect on the properties of electrodeposited coatings.<sup>10</sup> The presence of additives in electroplating bath is extremely important, basically due to their influence on the nucleation and growth of deposits. The adsorbed additives can cover some parts of cathode surface and influence the mechanism of zinc electrodeposition, which would decrease the nucleation rate.<sup>6</sup>

Some researchers<sup>11</sup> have investigated the influence of surfactants on the properties of zinc deposits. Their results have shown that in the presence of surfactants, uniform surface morphology and smaller grains are obtained. Alvarez et al.<sup>12</sup> have also investigated the very initial stages of zinc electrodeposition process on highly oriented pyrolytic graphite (HOPG) from a sulphate bath in the presence of gelatine. Their results indicate that the nucleation mechanism changes from instantaneous to progressive due to the formation of gelatine film on HOPG surface. Other organic additives such as thiourea and benzalaceton<sup>10</sup> and polyethylene glycol,<sup>6</sup> thiamine hydrochloride<sup>1</sup> and 1-butyl-3-methylimidazolium hydrogen sulphate-[BMIM] HSO<sub>4</sub> (Ref. 13) are also the most common additives used to improve the properties of zinc electrodeposits.

Despite of the fact that the complexing agents can play an important role in electrolytic baths, few works exist concerning their effects. Torent-Burg'es et al.<sup>14</sup> have studied the effect of tartarate anion, as a chelating agent, on the electrodeposition of zinc from a sulphate solution on vitreous carbon electrodes. Their results showed that in the presence of tartarate anions, the electrodeposition process starts at a more positive potential than in the absence of tartarate. In addition, tartarate anion allows deposits to be obtained with a more uniform composition and morphology during the electrodeposition process.<sup>15</sup>

Oxalate anion  $(C_2O_4^{2-})$  is a reducing agent as well as a chelating agent for metal cations. The oxygen atoms associated with hydrogen

in its molecular structure contributes in chelating. So far, the role of oxalate anions in zinc electrodeposition has not been fully studied. Thus, in the present work, attempts were made to investigate the effect of oxalate anion, as an additive in sulphate bath, on nucleation and growth mechanism, surface morphology, predominant texture and corrosion behaviour of zinc electrodeposits.

#### **Experimental**

Zinc coatings were electrodeposited galvanostatically by applying direct current. Using a digital coulometer model BHP 2050, deposition was performed at 25°C in a cell with graphite electrode as anode and a saturated calomel electrode (SCE) as the reference. The reference electrode was set up close to the cathode surface via a Luggin capillary, filled up with bath solution. The current density was 100 mA cm<sup>-2</sup> and the plating time was set to 110 s. A plain low carbon steel sheet with 2 mm thickness was used as substrate, after punching to discs shape with 1 cm<sup>2</sup> surface area. Specimens were sealed in a stainless steel foil sack and annealed at 880°C for 3 h. After annealing, specimens were soaked in 1000 mL hydrochloric acid solution (37%) containing 20 g antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) and 50 g stannous chloride (SnCl<sub>2</sub>) as inhibitors (according to ASTM standard G1) to remove the iron oxide film formed during annealing, and then neutralized in 5% NaOH solution for 10 min. Specimens were mechanically polished to a mirror finish using a sequence of abrasive SiC papers (80–4000 grit) and then polished with 0.3  $\mu$ m alumina. Specimens were then washed with water and ethanol respectively, and finally dried quickly. Prior to electrodeposition, specimens were cleaned ultrasonically in ethanol for 20 min, activated in 10 wt% sulphuric acid at room temperature for 20 s, washed in distilled water and then immediately placed in the electroplating bath.

The electrodeposition bath contained (620 g L<sup>-1</sup>) ZnSO<sub>4</sub>·7H<sub>2</sub>O, (75 g L<sup>-1</sup>) Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte and (63 g L<sup>-1</sup>) oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) as chelating agent. All solutions were prepared by dissolving the reagents in double distilled water. The pH of the bath was adjusted to 2.0 by adding sodium hydroxide or sulphuric acid.

The electrochemical cell was connected to an EG&G (model 263A) computer–controlled potentiostat/galvanostat. An EG&G ac responser (model 1025) was coupled with the mentioned potentio-stat/galvanostat to read the ac impedance data. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). All the potential values were referred to SCE. Cyclic voltametery experiments were carried out from open circuit potentials to -1.4V with a scan rate of 40 mV s<sup>-1</sup>. The corrosion

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protection of zinc coatings was studied by exposing the samples in a salt spray chamber (ASTM B-117: NaCl 5%, 35°C).

The surface morphology of zinc electrodeposits was studied using a scanning electron microscope (SEM) (model Philips XI30). A standard Nanoscope III atomic force microscope (AFM) was employed in contact mode to observe the surface topography of the zinc electrodeposits at the initial stages. Samples were prepared galvanostatically at 100 mA cm<sup>-2</sup> for 3 s. The coating texture was examined by X-ray diffractometer (XRD) (model Philips XCpert MPD). The diffractometer was operated using Cu-K $\alpha$  at an accelerating voltage of 40 kV and a current of 40 mA.

### **Results and discussion**

Voltammetric study.—Figure 1 shows cyclic voltametery plots of zinc electrodeposit in two sulphate baths, with and without oxalate anions. As it is noted, there is a wide peak for each cathodic scan at potentials within -700 and -1020 mV. This peak disappears just before the redox potential of zinc deposition (around -1020 mV). The existence of such a wide peak indicates an irreversible process, which represents hydrogen reduction on the steel surface.<sup>16</sup> According to Casanova et al.,<sup>16</sup> this peak arises due to the hydrogen evolution and formation of an adsorbed zinc monolayer just before the zinc crystallization. Zinc reduction occurs at potentials lower than its redox potential which can be seen as a tail on each plot. The large peak in the anodic range corresponds to dissolution of zinc. The redox potential is exactly the potential at which the current density is brought to zero, (i.e., -1020 mV), and is almost the same in both baths. This means that the complexion of some zinc ions by the oxalate anions had no changes on redox potential of zinc, but, it affects electrodeposition overpotential. The readings indicate that the zinc electrodeposition overvoltage is higher in the presence of oxalate ions than that in the absence of oxalate ions. This can be easily seen by comparing the tail of cathodic scans below -1020 mV. The shift of the zinc reduction potential to a more negative value can be related to the complexion of zinc ions by the oxalate anions.<sup>12</sup> In addition, the intensity of anodic peak, which corresponds to the zinc dissolution, decreases for the coating deposited in the presence of oxalate anions. Therefore, it can be concluded that the oxalate anions would decrease the mass of zinc electrodeposited. This is in coincidence with above discussion.

*Nucleation of zinc.*—*Nucleation mode.*—In order to determine the nucleation mode, Scharifker's model<sup>17</sup> was applied. Two forms of nucleation which can be observed during the electrode-position process are instantaneous and progressive. In instantane-



Figure 1. Cyclic voltametery plots in sulphate bath with oxalic acid (curve a) and without oxalic acid (curve b), scan rate = 40 mV s<sup>-1</sup>, vertex pot =-1.4 V.

ous nucleation, all the nuclei form in the beginning of process. So, the number of nuclei would be constant during the deposition process and all nuclei have similar age and size.<sup>17</sup> In progressive nucleation, the number of nuclei increases during the process. Thus, the age of nuclei will be different.<sup>7</sup> Figures 2a and 2b show a typical family of potentiostatic current-time transients for zinc deposition in the presence and absence of oxalate anions, respectively. The transients have the characteristic shape of diffusion controlled three-dimensional nucleation.<sup>18</sup> It is known that in the first stages of nucleation, the nuclei grow independently and the growth is controlled by hemispherical diffusion. As the time passes, the diffusional fields around nuclei overlap each other and the nucleation process terminates with a large proportion of the surface remained un-nucleated.<sup>7,17</sup> Finally, the growth of nuclei is controlled by extension of linear diffusion to the area of electrode surface.<sup>7,17</sup>

As proposed by Scharifker, the nucleation mode can be determined by comparing the non-dimensional plots of  $(i/i_m)^2$  versus  $(t/t_m)$  according to Eq. 1a for instantaneous nucleation and Eq. 1b for progressive nucleation<sup>17,19,20</sup>

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.9542}{(t/t_m)} \left\{1 - \exp[-1.2564(t/t_m)]\right\}^2$$
[1a]

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{(t/t_m)} \left\{1 - \exp[-2.3367(t/t_m)^2]\right\}^2$$
[1b]

The curves are obtained from potentiostatic current-time transient plots, where the time  $(t_m)$  can be determined from the maximum current density  $(i_m)$ .<sup>17</sup>

The calculated dimensionless  $(i/i_m)^2$  versus  $(t/t_m)$  curves for instantaneous and progressive plots have been shown in Figs. 3a and 3b. In these figures, the thick and thin lines correspond to extreme



Figure 2. Family of potentiostatic current-time transient plots obtained during the electrodeposition of Zinc onto steel (a) with oxalate anions (b) without oxalate anions.



**Figure 3.** Dimensionless curves  $(i/i_m)^2 vs(t/t_m)$  at 25°C and *p*H 2. Key: ( $\blacktriangle$ ) – 1.25 V, ( $\blacklozenge$ ) – 1.3 V, ( $\square$ ) – 1.35 V, (\*) – 1.4 V. (thick line) instantaneous nucleation mode, and (thin line) progressive nucleation mode; (a) with oxalate anions (b) without oxalate anions.

instantaneous and progressive nucleation, respectively. According to Scharifker, at the beginning of each transient, the current density increases due to an increase in the electro-active area. In this stage, the nuclei grow in size and/or number.<sup>7,17</sup> During this stage, expansion of diffusion zones around each nucleus occurs. The decrease in current density after the maximum current density would be due to overlapping the diffusional fields around these nuclei.<sup>21</sup> In addition, hydrogen evolution reaction can disperse zinc ions from the cathode surface and cause decay after the maximum.<sup>22</sup> Some of the discrepancies that are observed could possibly be due to non-uniform coverage of the substrate surface by diffusional zones, which could be due to non-uniform distribution of active sites for nucleation on the steel substrate.<sup>23</sup> Non-uniform distribution of active sites for nucleation on steel substrate is generally expected because of heterogeneity and defects, which usually exist on a commercial steel surface. It has been claimed that the experimental results obtained on a carbon substrate show better correspondence.<sup>24</sup> As can be seen, in both cases (with and without oxalate additions), the experimental data lie near the theorical instantaneous curves. Thus, the instantaneous nucleation would be predominant.

*AFM observation.*—Figure 4 shows the AFM image of mechanically polished steel surface used as the substrate. The AFM image of steel substrate was scanned over a  $1 \times 1 \mu m$  of surface area. The average roughness value (Ra) of the surface was about 10 nm. AFM images of the initial stages of zinc electrodepositon from both baths at -1350 mV after 3 s are shown in Figs. 5 and 6. Figure 5a shows the isolated islands developed on all areas of the steel substrate. The average roughness value (Ra) of the islands



**Figure 4.** AFM micrograph of mechanically polished surface, (a) 3D view, (b) top view and (c) section analysis diagram.

obtained in oxalate-free bath is about 12.07 nm (Fig. 5c), while the Ra of those obtained from oxalate-containing bath (Fig. 6c) is about 14.20 nm.

Compared with bath with oxalate anions (Fig. 6a), in the bath with no oxalate anions the zinc deposit obtained at the early stages of electrodeposition creates more isolated islands (Fig. 5a). This means that in the latter case more nucleation occurs. Nuclei measurement showed that the average nuclei



**Figure 5.** AFM micrograph of zinc electrodeposited galvanostatically at 100 mA cm<sup>-2</sup> for 3 s in the absence of oxalate ions, (a) 3D view, (b) top view and (c) section analysis diagram.



**Figure 6.** AFM micrograph of zinc electrodeposited galvanostatically at 100 mA cm<sup>-2</sup> for 3 s in the presence of oxalate ions, (a) 3D view, (b) top view and (c) section analysis diagram.

density (N) for zinc deposition is  $3.5 \times 10^9$  cm<sup>-2</sup> and  $2 \times 10^9$  cm<sup>-2</sup> in the absence and presence of oxalate anions, respectively. These values are estimated by direct counting the nuclei (i.e., obvious isolated islands) observed on AFM top view images in Figs. 5b and 6b. The nuclei density values for zinc deposition reported by some authors using AFM or SEM observations are in the range of  $10^9-10^{10}$  cm<sup>-2</sup>.<sup>14</sup>

The analysis of current transients obtained requires that the proton reduction (PR) reaction is taken into account in addition to the nucleation process. The current density ( $i_{PR}$ ) associated with the proton reduction reaction is given by<sup>18</sup>

$$i_{PR}(t) = P_1 S(t)$$
<sup>[2]</sup>

with  $P_1 = z_{PR}F k_{PR}$ , where  $z_{PR}F$  is the molar charge transferred during the proton reduction process,  $k_{PR}$  is the rate constant of the proton reduction reaction and

$$S(t) = \left(\frac{2CM}{\pi\rho}\right)^{1/2} \times \left\{1 - \exp\left\{-P_2\left[t - \frac{1 - \exp(-P_3 t)}{P_3}\right]\right\}\right\}$$
[3]

where C is the bulk concentration of metal ion, M is the molar mass of the deposit,  $\rho$  is the density of the deposited material,  $P_2 = N\pi D (8\pi C/\rho)^{1/2}$  and  $P_3 = A$ , with N and A being the nuclei density and the nucleation rate constant, respectively.<sup>18</sup>

The current associated with the zinc reduction process is given by<sup>18</sup>

$$i_{3D-dc}(t) = P_4 t^{-1/2} \times \left\{ 1 - \exp\left\{ -P_2 \left[ t - \frac{1 - \exp(-P_3 t)}{P_3} \right] \right\} \right\}$$
[4]

where,  $P_4 = \frac{2FD^{1/2}C}{\pi^{1/2}}$  and the total current due to overall process (i<sub>total</sub>) is given by:

$$\dot{t}_{total}(t) = \left(P_1^* + P_4 t^{-1/2}\right) \\ \times \left\{1 - \exp\left\{-P_2\left[t - \frac{1 - \exp(-P_3 t)}{P_3}\right]\right\}\right\}$$
[5]

where

$$P_1^* = P_1 \left(\frac{2CM}{\pi\rho}\right)^{1/2}$$
[6]

Fitting the experimental current-time transients by non-linear relationship of Eq. 5,  $P_1^*$ ,  $P_2$ ,  $P_3$ , and  $P_4$  parameters are obtained. From these parameters, electrodeposition processing parameters such as N, A and  $k_{PR}$  could be obtained. Table I shows the above mentioned parameters obtained at -1350 mV. From  $P_1^*$ , the  $k_{PR}$  is calculated in the order of  $10^{-8}$  mol cm<sup>-2</sup> s<sup>-1</sup>. Other authors have also found the value of  $k_{PR}$  in the same order for nickel and cobalt electrodeposition. <sup>18,25</sup> The value of N, in order of  $10^8$  cm<sup>-2</sup>, is obtained from fitting i-t transients. The N values are  $31 \times 10^7$  cm<sup>-2</sup> in the absence and  $22 \times 10^7$  cm<sup>-2</sup> in the presence of oxalate anions, which are at least one order of magnitude less than those obtained by AFM (i.e.,  $3.5 \times 10^9$  cm<sup>-2</sup> and  $2 \times 10^9$  cm<sup>-2</sup> in the absence and presence of oxalate anions). The disagreement between values of N obtained from the chronoamperometric analysis and those obtained by observations has also been pointed out in literature. <sup>14</sup> Using SEM, Torent-Burg'es et al. <sup>14</sup> have found nuclei density in order of  $10^9$  cm<sup>-2</sup>, 2 orders of magnitude higher than those obtained by chronoamperometric analysis.

It has been reported that the values of A for zinc electrodeposition are within  $1-100 \text{ s}^{-1}$ .<sup>14</sup> The A values obtained by fitting i-t transient curves (Table I) are in agreement with above results.

*Nucleation rate constant.*—As seen in Fig. 2, the current transients obtained in the bath containing oxalate anions is qualitatively similar to that obtained in the bath with no oxalate anions. The main difference observed is the lower current density obtained in the bath with oxalate anions, which means that a lower current density is associated with nucleation and growth of zinc deposit in this case. This is in a good agreement with the previous results obtained by cyclic voltametery and AFM observations. Consequently, a lower nucleation rate is expected in the presence of oxalate anions.

Considering the nucleation rate constant (A) and nuclei density (N) at -1350 mV, the term A × N can be calculated from Eq. 7, where ZF is the moles of charge transfers during electrodeposition, C is the bulk concentration of metal ion, M is the molar mass of the deposit, and  $\rho$  is the density of the deposited material<sup>15</sup>

$$A \times N = 0.2898 \left(\frac{\rho}{8\pi M}\right)^{1/2} C^{3/2} \frac{Z^2 F^2}{i_{\rm m}^2 t_{\rm m}^3}$$
[7]

For zinc coatings, M is 65.37 g mol<sup>-1</sup> and  $\rho$  is 7.14 g cm<sup>-3</sup>. By substituting these values in Eq. 7 and considering the values of N

Table I. Best-fit parameters and kinetic data resulting from analysis of the experimental current-time transient in Fig. 2 at -1350 mV according to the model described by Eq. (5).

$\begin{array}{c} D(\times10^8) \\ (cm^2s^{-1}) \end{array}$	$\begin{array}{c} N(\times10^{-7}) \\ (cm^{-2}) \end{array}$	$\mathop{A}\limits_{(s^{-1})}$	$K_{pr}(\times 10^8)$ (mol cm <sup>-2</sup> s <sup>-1</sup> )	$P_4$ (mA cm <sup>-2</sup> s <sup>1/2</sup> )	$\underset{\left(s^{-1}\right)}{P_{3}}$	$\underset{\left(s^{-1}\right)}{\overset{P_{2}}{}}$	$\stackrel{P_1^*}{(\text{mA cm}^{-2})}$	Bath
0.42	31	12	7.2	15.3	12	0.335	0.78	Sulphate bath without oxalic acid
0.30	22	5.8	11.7	12.9	5.84	0.18	1.26	Sulphate bath with oxalic acid



Figure 7. (Color online) Nyquist plots drawn at -1350 mV in the bath (a) without oxalate anions, (b) with oxalate anions

estimated from AFM observations, the term A can be calculated which is about  $0.04 \text{ s}^{-1}$  in the presence and  $0.1 \text{ s}^{-1}$  in the absence of oxalate anions, respectively. These values are about 2 orders of magnitude lower than those obtained by i-t transient analysis (Table I). Anyway, the value of A in the absence of oxalate anions is twice of that in the presence of oxalate anions. This means that the number of nuclei created on the steel substrate decreases to about half magnitude in the electrodeposition bath containing oxalate anions. This denotes on the inhibitive effect of oxalate anions on nucleation of zinc.

Growth of zinc deposits.—Electrochemical impedance spectroscopy.—In order to study the effect of oxalate anions on zinc electrodeposition mechanism, EIS measurements were performed in the frequency range of 100 kHz–10 mHz, at –1350 mV. Figure 7 shows the Nyquist plots of experimental and simulated impedance spectra for zinc deposition from baths without (Fig. 7a) and with (Fig. 7b) oxalate anions, respectively. As seen, the correlation between experimental and simulated data is recognized to be acceptable. According to Fig. 7a, the impedance plot shows two loops including a capacitive at high frequencies which arises due to the double layer construction and charge transferring and an inductive developed at low frequencies. The induction is associated with an adsorption process of electrochemical active specie such as zinc hydroxides.<sup>7,26</sup>

From Fig. 7b, it can be seen that the capacitive loop at high frequencies is very similar to what is observed in Fig. 7a. However, in the low frequency region, a different behaviour is observed. As is evident from Fig. 7b, a low-frequency straight line with an angle near  $45^{\circ}$  against the real axis is appeared, indicating Warburg behaviour. Generally, the Warburg behaviour arises due to the presence of diffusion barriers in electrochemical systems. The chelating agents may produce a surface film layer during the electrodeposition, which provides a diffusion barrier against  $Zn^{+2}$  ion movements across the metal/solution interface. The Warburg impedance ( $Z_w$ ) is observed whenever the reaction is under partial or complete mass transport control by diffusion.<sup>27</sup> The term is reserved for the special case of semi-infinite linear diffusion. In the condition of semi-infinite linear diffusion,  $Z_w$  for a system at equilibrium can be expressed by<sup>27</sup>

$$Z_{\rm w} = \sigma_{\rm \omega} \omega^{-0.5} - j \sigma_{\rm \omega} \omega^{-0.5}$$
<sup>[8]</sup>

where  $\sigma_{\omega}$  is the Warburg constant,  $\omega$  is the ac angular frequency,  $Z_w$  can be considered as a series combination of Warburg capacitance ( $C_w$ ) and a psudoresistance ( $R_w$ ), which are given by the following equations<sup>27</sup>

$$C_{\rm w} = \sigma_{\rm \omega}^{-1} \omega^{-0.5} \tag{9}$$

$$R_{\rm w} = \sigma_{\omega} \omega^{-0.5}$$
 [10]

The appearance of Warburg impedance means that the growth process of deposit is intensively under semi-infinite diffusion control. Therefore, it seems that the presence of oxalate anions, via bouncing the diffusion of Zn (II) ions across the metal/solution interface, leads to a retardation of the zinc electrodeposition kinetics. Consequently, zinc growth can proceed through a semi-infinite length of diffusion pathway.

The electrical equivalent circuits (ECs) are determined by applying the Zview software and are inserted in Figs. 7a and 7b. In the ECs,  $R_{ct}$  is the charge transfer resistance,  $R_1$  and  $L_1$  are elements of inductive loop,  $L_1$  is the inductor referred to the adsorption of electrochemical active specie and  $R_1$  is the resistance of the inductor.  $R_S$  is the uncompensated solution resistance,  $W_1$  is the Warburg resistance,  $R_p$  is polarization resistance and CPE is the constant phase element. When the Nyquist plot contains a "depressed" semicircle with the centre under the real axis, the parallel network charge transfer resistance. The depression is related to roughness and in homogeneities of the solid surface<sup>28</sup> and is a characteristic for solid electrodes. For improving the fitness, CPE is used. The impedance of CPE is expressed by the following equation

$$Z_{\rm Q} = [Y_0(j\omega)^n]^{-1}$$
 [11]

where  $Z_Q$  is the CPE impedance ( $\Omega \text{ cm}^{-2}$ ),  $Y_0$  is the CPE admittance ( $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ ). The parameter n is a constant, which shows the degree of deviation from ideal capacitive behaviour.<sup>29</sup>

In Table II, the calculated values of circuit elements are summarised. The results show that the oxalate containing bath possesses a larger value of  $R_p$ . The  $R_p$  may be proportional to the surface

Table II. Parameters extracted from Nyquist plots in Fig. 7.							
$Rp~(\Omega~cm^2)$	$W_1(cm^{-2}\Omega^{-1}s^{-0.5})$	$R_1(\Omegacm^2)$	$L_{1}\left( H ight)$	$R_{ct}(\Omegacm^2)$	${\rm CPE}~(\mu{\rm F~cm^{-2}})$	$R_{s}(\Omegacm^{2})$	Bath
3.0 5.2	7.3	17.55	0.0011	3.85 3.0	28 15	7.3 8.6	Sulphate bath without oxalic acid Sulphate bath with oxalic acid



**Figure 8.** Morphology of zinc electrodeposited on mechanically polished steel substrate at 100 mA  $\text{cm}^{-2}$  after 110 s, (a) in the absence of oxalate anions, (b) in the presence of oxalate anions.

diffusion of zinc adions on substrate surface.<sup>5</sup> Thus, a larger value of  $R_p$  denotes on retarded growth of deposit.

SEM observation.—Figure 8a shows the SEM images of zinc coating deposited from the bath with no oxalate anions. The zinc deposits were galvanostatically grown at 100 mA cm<sup>-2</sup> on steel substrate for 110 s. It can be seen that the zinc coatings consist of thin platelets of hexagonal crystals, packed on the steel substrate. The packets of hexagonal platelets with various orientations are stacked on each other, all over the substrate surface. As seen, the coatings exhibit a uniform and compact appearance. This result is in a good agreement with the result obtained previously.<sup>5</sup>

In the presence of oxalate anions, a zinc coating with dull appearance was obtained. Some researchers<sup>30</sup> believe that the crystallographic orientation is related to the surface crystal appearance. The dull surface appearance is due to the pyramidal (10.2 or 10.1) or prismatic (10.0) grain orientations.<sup>31</sup> As seen from Fig. 8b, the presence of oxalate anions in the bath changes the surface morphology of the zinc coating markedly. Surface morphology of zinc coating is changed from packets of hexagonal to granular nature, most probably due to the diffusion controlled condition governed by the presence of oxalate anions.

*X-ray analysis.*—Figure 9 shows XRD spectra of zinc coatings obtained in both baths (i.e. with and without oxalate anions). The relative texture coefficients (RTC) of deposits were determined using Eq. 12 (Ref. 31) and are shown in Fig. 10

$$\operatorname{RTC} = \frac{I_{T(hkl)}/I_{R(hkl)}}{\left(\sum_{l=1}^{n} I_{T(hkl)}/I_{R(hkl)}\right) \times 1/n}$$
[12]

where n is the number of planes selected from X-ray diffraction pattern,  $I_{T(hkl)}$  is the peak intensity of hkl plane in X-ray diffraction pat-



Figure 9. X-ray diffraction patterns of zinc coatings deposited on mechanically polished steel substrate at 100 mA cm<sup>-2</sup> after 110 s (a) with oxalic anions and (b) without oxalate anions.



Figure 10. RTCs of zinc coating electrodeposited in the bath (a) with oxalic anions and (b) without oxalate anions.

tern and  $I_{R(hkl)}$  refers to the intensity of hkl plane in standard zinc powder which is compared with the standard compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), with included card #04-0831.<sup>32</sup>

In the absence of oxalate anions, in addition to basal (00.2) plane, low angle pyramidal {10.3} and {10.4} planes can be considered as the texture components. It is important to notice that if the relative texture coefficient (RTC) value is more than 1, the corresponding texture is preferred.<sup>33</sup> By adding oxalate anions, high angle pyramidal {10.1}, prism {10.0} and {11.0} planes are appeared as the texture components (Fig. 10). Such differences in texture can be explained in terms of the diffusion controlled condition built up by the presence of oxalate anions in the electrodeposition bath, which has been discussed before. The granular surface morphology obtained from the bath containing oxalate anions (Fig. 8b) is developed due to the presence of high angle pyramidal and prism texture components. From the above discussion, it can be concluded that the oxalate anions evidently play an important role on development of high angle pyramidal and prism texture components in the zinc electrodeposit coating.

*Salt-spray results.*—The sustainability of coated specimens to chloride corrosion attack can be assessed by salt-spray tests. In these tests, the more corrosion resistance of coatings, the longer is the time for corrosion products to be appeared on the coating surface. In the case of steel substrates, appearance of red rust on the coating surface is the sign of substrate corrosion. The results obtained (time for red rust observations) for the coatings produced in baths with and without oxalate anions are shown in Table III. The results show that the time of red rusting is longer for zinc coating produced in oxalate-free bath (i.e., 40 h). This indicates that the zinc coating produced in the presence of oxalate anions has a more corrosion protective property.

Table III. Salt spray tests results.

64 h	40 h	Spray time
_	Emerging of ed rust spots	Zinc coating in the absence of oxalate anions
Emerging of red	Rustless	Zinc coating in the
rust spots		presence of oxalate anions

## Conclusions

1. The nucleation mode of zinc coatings on steel substrate is instantaneous and no change is observed by the presence of oxalate anions in bath. However, a less number of nuclei are formed on steel substrate in the presence of oxalate anions.

2. In the presence of oxalate anions, different impedance behaviour is observed in low frequency domain. In the bath containing oxalate anions, the growth of deposit is controlled by semi-infinite diffusion, which differs from charge transfer control condition observed in the absence of oxalate anions.

3. The presence of oxalate anions in the bath can change the surface morphology of the zinc coating from packets of hexagonal platelets to granular morphology. In oxalate-containing bath, higher percentages of high angle pyramidal and prism planes develop at the expense of basal plane.

4. The zinc coatings produced in the presence of oxalate anions showed better substrate corrosion protectivity, as compared with zinc coatings obtained in the bath without oxalate anions.

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