

## Corrosion resistant Zn–Co alloy coatings deposited using saw-tooth current pulse

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**Abstract.** Micro/nanostructured multilayer coatings of Zn–Co alloy were developed periodically on mild steel from acid chloride bath. Composition modulated multilayer alloy (CMMA) coatings, having gradual change in composition (in each layer) were developed galvanostatically using saw-tooth pulses through single bath technique (SBT). CMMA coatings were developed under different conditions of cyclic cathode current densities (CCCDs) and number of layers, and their corrosion resistances were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) method. Optimal configuration, represented as  $(\text{Zn–Co})_{2.0/4.0/300}$  was found to exhibit ~89 times better corrosion resistance compared to monolithic  $(\text{Zn–Co})_{3.0}$  alloy deposited for same time, from same bath. The better corrosion resistance of CMMA coatings was attributed to changed interfacial dielectric properties, evidenced by dielectric spectroscopy. Improved corrosion resistance was attributed to formation of *n*-type semiconductor film at the interface, supported by the Mott–Schottky plot. Further, the formation of multilayer and corrosion mechanism was analysed using scanning electron microscopy (SEM).

**Keywords.** Composition modulated multilayer alloy; Zn–Co; saw-tooth current pulse; corrosion resistance; dielectric spectroscopy.

### 1. Introduction

Nanostructured materials are a new class of materials which can provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors including aerospace, tooling, automotive, etc. Encompassed by this class of materials are composition modulated multilayer alloys (CMMA) (Nasser Kanani 2006). These CMMA coatings consist of very thin sublayers of different metals or alloys having thickness of few nanometers with ultrafine microstructure arranged in an alternate fashion (Barrel and Maximovich 1990; Haseeb *et al* 1992, 1994; Simunovich *et al* 1994; Kalantary *et al* 1995; Yang and Cheh 1995). As a result of the layering at a near atomic dimension, the nanostructured multilayered deposits can possess remarkable and some time unique properties not attainable in normal metallurgical alloys. These properties include X-ray optical properties, magneto-optical properties, improved hardness, wear and corrosion resistance (Bull and Jones 1996; Gabe and Green 1998; Nabiyouni *et al* 2002).

There are several methods for obtaining modulated alloys. Physical vapour deposition (PVD), chemical

vapour deposition (CVD), sputtering and molecular beam epitaxy (MBE) techniques are a few among such methods. These methods have several advantages and used for specific applications. Due to some limitations such as high capital cost and high energy cost an alternative method is required. Electrolytic deposition has fulfilled this need. Its relative merits over other methods have aroused a great deal of interest among researchers. Blum (1921) first introduced the electrodeposition of multilayered alloy on Cu–Ni in 1920s. Later on, Brenner (1963) deposited Cu/Bi by varying c.d. Kalantary *et al* (1998) obtained Zn–Ni CMMA coatings with an overall thickness of 8  $\mu\text{m}$ . Chawa *et al* (1998) reported that Zn–Ni CMMA coatings had better corrosion resistance compared to that of monolithic Zn–Ni coatings of similar thickness.

Electrodeposition of CMMA can be carried out using two important techniques, viz. single bath technique (SBT) and dual bath technique (DBT) (Nasser Kanani 2006). DBT involves the deposition of constituents from two separate plating baths. In SBT, the metal ions required to form both deposit layers are contained in the single electrolyte and the alloy deposition is achieved by alternately changing the plating current/potential, possibly in combination with a modulation of the mass transport towards the cathode. Both techniques are known to have their own advantages and disadvantages. In most cases, the drawbacks of DBT have been deemed to out-

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weigh the benefits, so that the SBT approach is used instead. Liao *et al* (1998) have studied both SBT and DBT of Zn/Zn–Fe and only Zn–Fe systems. Kirilova *et al* (1998) and Kirilova and Ivanov (1999) obtained CMMA coatings of Zn–Co by means of both SBT and DBT. Though multilayer Zn–M alloy coating with improved corrosion resistance is widely reported, very little work has been done with regard to optimization of the deposition conditions using SBT. Recently, Thangaraj *et al* (2009) optimized a chloride bath for the production of Zn–Co and Zn–Fe CMMA coatings using square current pulses. They found that the CMMA coatings under optimal conditions were many times more corrosion resistant than respective monolithic alloy coatings. Though gradations in composition are possible through modulation in cathode c.d., agitation, temperature, etc, the composition can be better controlled with great degree of accuracy and reproducibility using sensitive power sources (Cohen *et al* 1983). This technique, in principle, is straightforward to design and fabricate. In SBT, cyclic multilayered alloy having gradual change in composition of coating may be developed using square, triangular and sawtooth pulses. Accordingly, it is possible to tailor the properties of coatings by proper manipulation of the coating conditions, to meet desired engineering applications.

Considerable amount of work has already been documented with evidence to support the enhanced corrosion resistance of CMMA Zn–M (where M = Fe group metals like Fe, Co and Ni) alloys, using SBT (Bahrololoom *et al* 2003; Ivanov and Kirilova 2003; Ganeshan *et al* 2007). Most of the works reported are pertaining to the sharp change in composition, using square current pulses of two or more current/voltage. But no work is reported with regard to optimization of coating configuration for better corrosion protection using saw-tooth current pulses. The aim of this work is to improve the corrosion resistance of monolithic Zn–Co alloy coatings by depositing in multilayers down to nanometer-scale, using saw-tooth current pulses. The better corrosion resistance of the nanostructured CMMA coatings is discussed in terms of changed electric properties of the coatings.

## 2. Experimental

The plating solutions were freshly prepared from distilled water and analytical grade reagents. Electroplating of mild steel plates was done at pH  $3.5 \pm 0.05$  and temperature,  $30 \pm 2^\circ\text{C}$ . The polished mild steel plates (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) had an exposed surface area of  $7.5 \text{ cm}^2$  which served as a cathode. The anode was pure Zn with the same exposed area. A rectangular PVC cell containing  $250 \text{ cm}^3$  electrolyte was used. All depositions were carried out at constant condition of stirring without purging, to maintain a steady-state of mass transport. All coatings, viz. mono-

lithic and CMMA were carried out galvanostatically using d.c. power analyser (N6705A, Agilent Technologies) for 10 min ( $\sim 15 \mu\text{m}$  thickness), for comparison purpose. While the thickness of the coating was estimated by Faraday's law, it was verified by measurements, using a digital thickness meter (Coatmeasure model M&C). The composition of the coatings was determined colorimetrically using standard method (Vogel 1951). The hardness of the deposited alloys was measured using a computer-controlled microhardness tester (CLEMEX, model: MMT-X7). All electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT<sup>3</sup>, Princeton Applied Research) in a three-electrode configuration cell. All electrochemical potentials referred in this work are indicated relative to the Ag/AgCl/KCl<sub>sat</sub> electrode. The 5% NaCl solution was used as corrosion medium. Potentiodynamic polarization study was carried out in a ramped potential of  $\pm 250 \text{ mV}$  from open circuit potential (OCP) at a scan rate of  $1 \text{ mV s}^{-1}$ . EIS study was carried out in the frequency range from 100 kHz to 10 mHz with a perturbing signal of 10 mV. The Mott–Schottky's plot was obtained by performing a potential scan in the cathodic direction at 100 Hz in the potential range from  $+0.5$  to  $-0.5 \text{ V}$  around open circuit potential. The formation of multilayers and corrosion mechanism were examined by scanning electron microscopy (SEM, Model JSM-6380 LA from JEOL, Japan).

## 3. Results and discussion

### 3.1 Development of monolithic Zn–Co alloy

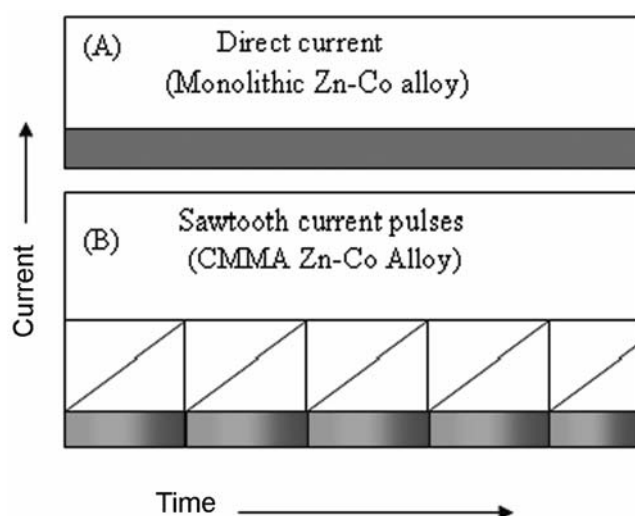
The optimization of a stable chloride bath was carried out by using a standard Hull cell method (Nasser Kanani 2006). Deposition was carried out galvanostatically at different current densities using optimized bath, consisting of 10 g/l ZnO, 30 g/l CoCl<sub>2</sub>, 200 g/l NH<sub>4</sub>Cl, 20 g/l boric acid, 10 g/l citric acid and 3 g/l THC. The effects of c.d. on wt.% Co, thickness, Vickers hardness, corrosion resistance and appearance of the coatings are reported in table 1. Zn–Co alloy at  $3.0 \text{ A/dm}^2$ , represented as (Zn–Co)<sub>3.0</sub>, was found to be more corrosion resistant ( $19.51 \times 10^{-2} \text{ mm/y}$ ), compared to all other current densities. Hence it has been taken as optimal c.d. for monolithic Zn–Co alloy deposition.

### 3.2 Development of Zn–Co CMMA coatings

CMMA coatings were developed by making the cathodic current to change gradually from one c.d. to another by proper setting up of the power source. Multilayer coatings having alternate layers of alloys with different compositions were developed using saw-tooth current pulses (gradual change in composition is effected by gradual change in c.d.). The power pattern generated for CMMA

**Table 1.** Effect of c.d. on deposit characters of monolithic Zn-Co alloy.

c.d. (A/dm <sup>2</sup> )	wt.% Co	Thickness ( $\mu\text{m}$ )	Vicker's hardness ( $V_{100}$ )	$E_{\text{corr}}/V$ vs Ag, AgCl/KCl <sub>sat</sub>	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	CR ( $\times 10^{-2}$ mm/y)	Nature of deposit
1.0	17.0	6.2	138	-1.125	20.33	30.16	Blackish
2.0	1.77	6.8	151	-1.187	13.63	20.22	Bright
3.0	1.69	11.1	154	-1.158	13.15	19.51	Bright
4.0	2.10	12.1	168	-1.102	14.98	22.22	Bright
5.0	2.21	14.9	179	-1.055	16.49	24.47	Bright
6.0	2.24	16.3	195	-1.049	18.47	27.41	Bright
7.0	1.93	17	201	-1.051	20.84	30.52	Semi bright

**Figure 1.** Schematic representation of constant cathode current pulses for deposition of monolithic Zn-Co alloy (A), and sawtooth current pulses for deposition of CMMA coatings with gradually changing composition (B).

coating is shown schematically in figure 1. In the present study, CMMA coating systems are represented as:  $(\text{Zn-Co})_{1/2/n}$ , where 1 and 2 represent cathode current densities between which the cathode current cycles,  $n$ , represents the number of layers formed during total plating time.

**3.2a Optimization of CCCDs:** In the case of alloys of Zn-M, it is well known that, even a small change in the concentration of the latter may result in significant properties change due to change in the phase structure. Thus, by precise control of the cathode current densities (CCCDs), it is possible to develop alternate layers of alloys with different compositions and consequently, different properties. Table 2 demonstrates effect of CCCDs on the corrosion behaviour of the coatings. To begin with, multilayer coatings having 10 layers were developed at different sets of CCCDs to increase their corrosion resistance. Among the various sets tried, the less corrosion rate was measured in the coatings produced at difference of 2.0 A/dm<sup>2</sup> and 4.0 A/dm<sup>2</sup> between

CCCDs as shown in table 2. These coatings were found to be bright and uniform. This combination of CCCDs has been selected for studying the effect of layering, as described in the following subsection and in table 3.

**3.2b Optimization of overall number of layers:** The physico-mechanical properties of CMMA coatings, including their corrosion resistance, may often be increased substantially by increasing the number of layers (usually, up to an optimal limit), without sacrificing the demarcation between each layers. Therefore, few sets of CCCDs such as 2.0/4.0 and 2.0/6.0 A/dm<sup>2</sup> have been selected for layering. Zn-Co coatings with 20, 60, 120 and 300 layers were developed and their corrosion rates were measured. The corrosion rate (CR) of coatings were found to decrease with number of layers in each set of CCCDs as shown in table 3. However, at 2.0/4.0 A/dm<sup>2</sup>, the coating with 300 layers showed minimum CR of  $0.22 \times 10^{-2}$  mm/y relative to  $19.51 \times 10^{-2}$  mm/y for monolithic Zn-Co alloy coatings (shown in table 1). Though there is a substantial decrease of CR with layering at other set of CCCDs also (i.e. at 2.0/6.0 A/dm<sup>2</sup> with 300 layers as shown in table 3), the result pertaining to 2.0/4.0 A/dm<sup>2</sup> is more encouraging due to better homogeneity and brightness of the deposit. However, an effort of increasing the corrosion resistance by further increasing number of layers in each set of CCCDs has resulted in increase of corrosion rate, which may be due to less relaxation time for redistribution of solutes in the diffusion double layer, during plating. Hence,  $(\text{Zn-Co})_{2.0/4.0/300}$  has been proposed as the optimal configuration of coating from the proposed bath for peak performance against corrosion.

### 3.3 Corrosion study

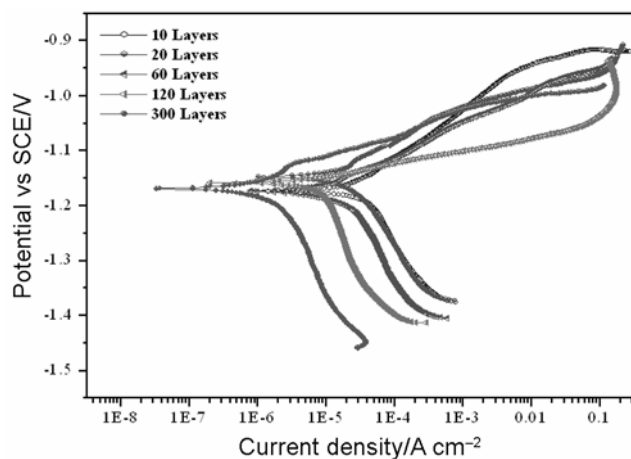
**3.3a Tafel's polarization study:** The polarization behaviour of  $(\text{Zn-Co})_{2.0/4.0}$  coatings with different degrees of layering is shown in figure 2. The corrosion rates of coatings were evaluated by Tafel's extrapolation method, and the results are reported in table 3. It may be observed that in each coating, the corrosion current ( $i_{\text{corr}}$ ) values

**Table 2.** Corrosion rate (CR) of CMMA Zn–Co coatings at different sets of CCCDs (with 10 layers).

CCCDs (A/dm <sup>2</sup> )	$E_{\text{corr}}$ (V vs Ag, AgCl/KCl <sub>sat</sub> )	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	CR ( $\times 10^{-2}$ mm/y)
CMMA Zn–Co coatings developed at difference of 2.0 A/dm <sup>2</sup> between CCCDs			
(Zn–Co) <sub>2.0/4.0/10</sub>	–1.172	9.027	13.39
CMMA Zn–Co coatings developed at difference of 4.0 A/dm <sup>2</sup> between CCCDs			
(Zn–Co) <sub>2.0/6.0/10</sub>	–1.3058	9.676	14.35

**Table 3.** Decrease of corrosion rate (CR) of CMMA Zn–Co coatings with increase of layers.

Current density (A/dm <sup>2</sup> ) and no. of layers	$E_{\text{corr}}$ (V vs Ag, AgCl/KCl <sub>sat</sub> )	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	CR ( $\times 10^{-2}$ mm/y)
Optimization of layer thickness at CCCDs of 2.0–4.0 A/dm <sup>2</sup>					
(Zn–Co) <sub>2.0/4.0/10</sub>	–1.172	23.42	24.80	9.02	13.39
(Zn–Co) <sub>2.0/4.0/20</sub>	–1.147	31.88	25.23	7.35	10.91
(Zn–Co) <sub>2.0/4.0/60</sub>	–1.173	20.00	31.12	4.27	6.34
(Zn–Co) <sub>2.0/4.0/120</sub>	–1.158	8.859	14.09	1.38	2.05
(Zn–Co) <sub>2.0/4.0/300</sub>	–1.169	13.112	11.77	0.15	0.22
Optimization of layer thickness at CCCDs 2.0–6.0 A/dm <sup>2</sup>					
(Zn–Co) <sub>2.0/6.0/10</sub>	–1.305	24.81	24.44	9.67	14.35
(Zn–Co) <sub>2.0/6.0/20</sub>	–1.264	17.70	22.93	7.26	10.77
(Zn–Co) <sub>2.0/6.0/60</sub>	–1.260	17.52	19.12	5.45	8.08
(Zn–Co) <sub>2.0/6.0/120</sub>	–1.256	20.03	19.47	3.55	5.27
(Zn–Co) <sub>2.0/6.0/300</sub>	–1.315	11.83	15.25	2.14	3.18

**Figure 2.** Potentiodynamic polarization curves of CMMA (Zn–Co)<sub>2.0/4.0</sub> coatings with different number of layers.

decreased with increase in number of layers. The progressive decrease of  $i_{\text{corr}}$  with number of layers indicated that improved corrosion resistances are due to layering of alloys, having distinct properties. The slight variation of  $E_{\text{corr}}$  value with number of layers (table 3) showed that the coatings provide sacrificial protection to the substrate. Polarization curve shown in figure 2 indicates that coating with (Zn–Co)<sub>2.0/4.0/300</sub> configuration is the most corrosion resistant. The Tafel's slopes shown in table 3 reveal

that both anodic and cathodic slopes are very sensitive to the degree of layering, i.e. the Tafel's slopes found to decrease progressively with number of layers. It indicates that protection efficacy of CMMA coatings is due to both barrier effect and sacrificial protection of coatings, in alternate layers. Potentiodynamic polarization behaviours of monolithic and CMMA coatings (both under optimal conditions) in comparison with that of mild steel is shown in figure 3. It may also be noted that both  $i_{\text{corr}}$  and  $E_{\text{corr}}$  value of electroplates have changed considerably from that of base metal.

**3.3b Electrochemical impedance spectroscopy (EIS) study:** Electrochemical impedance spectroscopy, generally known as EIS technique, is one of the most powerful tool for studying the electrochemical behaviour of the materials. In this technique, impedance behaviour is being studied by the application of an a.c. signal (sinusoidal wave) (Yuan *et al* 2010). The current–voltage relationship form of the impedance in an electrochemical system can also be expressed as

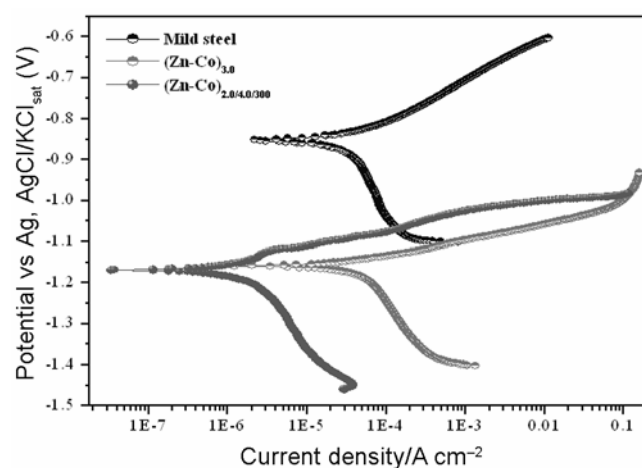
$$Z(\omega) = V(t)/I(t), \quad (1)$$

where  $V(t)$  and  $I(t)$  are the measurements of voltage and current in an a.c. system.

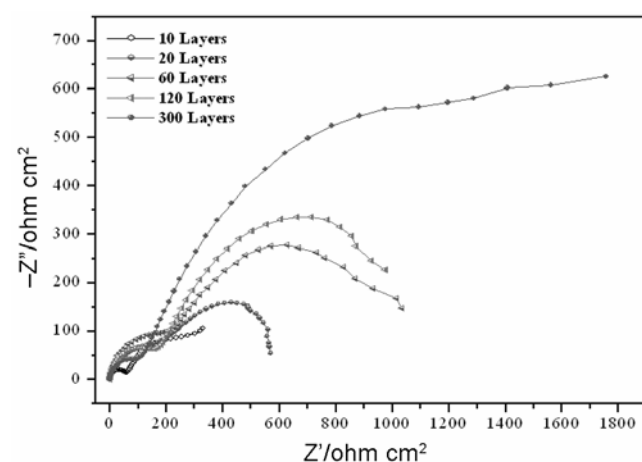
Generally, the impedance spectrum of an electrochemical system can be presented in Nyquist and Bode plots, which are representations of the impedance as a function

of frequency. A Nyquist plot is displayed for the experimental data set  $Z(Z_{re,i}, Z_{im,i}, \omega_i)$ , ( $i = 1, 2, \dots, n$ ) of  $n$  points measured at different frequencies, with each point representing the real and imaginary parts of the impedance ( $Z_{re,i}, Z_{im,i}$ ) at a particular frequency  $\omega_i$ . A Bode plot is an alternative representation of the impedance. In a plot of phase angle,  $\theta$  vs  $\log \omega$ , describes the frequency dependencies of the phase angle. Both plots usually start at a high frequency and end at a low frequency, which enables the initial resistor to be found more quickly.

Nyquist response of  $(\text{Zn-Co})_{2.0/4.0}$  with different number of layers is shown in figure 4. At high frequency limit, all electroplates exhibited  $R_{real} = 0$ , indicating that the solution resistance,  $R_s$ , is same for all analysis. Two semicircles observed in each impedance spectrum shows that two capacitors are operative in the electrochemical cell. At



**Figure 3.** Comparison of potentiodynamic polarization curves of monolithic  $(\text{Zn-Co})_{3,0}$ , CMMA  $(\text{Zn-Co})_{2,0/4,0/300}$  coatings (of same thickness) and mild steel.



**Figure 4.** Real vs imaginary resistance values of CMMA  $(\text{Zn-Co})_{2,0/4,0}$  coatings with different number of layers measured as a function of frequency.

low frequency limit, the radius of semicircle was found to increase with the number of layers, indicating that polarization resistance, ( $R_p$ ) increases with layering. The highest corrosion resistance with optimal number of layers, i.e. 300 layers, is evidenced by bigger incomplete semicircle, with large capacitive reactance. Nyquist plots with incomplete semicircles indicated that the corrosion behaviour of the coatings is not controlled only by electrical double layer capacitor,  $C_{dl}$  and charge transfer resistance,  $R_{ct}$ , but also by other constant phase elements (CPE).

**3.3c Mott–Schottky behaviour of passive film:** The marked increase in corrosion resistance of all coatings is attributed to the semiconductor behaviour of passive film at metal-medium interface during corrosion. In general, passive films are always semiconductors (Bianchi *et al* 1972; Wilson 1977). The semiconductor property of passive film, i.e. the relationship between space charge capacitance ( $C$ ) and applied potential ( $E$ ) can be described by using Mott–Schottky equations (2) and (3) (Morison 1980; Hakiki and Da Cunha Belo 1996)

$$n\text{-type: } \frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left( E - E_{fb} - \frac{kT}{e} \right), \quad (2)$$

$$p\text{-type: } \frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} \left( E - E_{fb} - \frac{kT}{e} \right), \quad (3)$$

where  $e$  is the elementary charge ( $+e$  for electrons and  $-e$  for holes),  $\epsilon$  the dielectric constant of the passive film,  $\epsilon_0$  the permittivity in vacuum ( $8.854 \times 10^{-12}$  F/m),  $N_D$  and  $N_A$  stand for the donor and acceptor electron density, and  $E_{fb}$ , the flat band potential,  $k$  the Boltzmann constant,  $T$  the absolute temperature. The donor or acceptor concentrations can be estimated from the slopes of the straight lines obtained.

When adopted (2) and (3) to describe the electronic property of metal surface passivation film, the key point is to determine the capacitance of the space charge layer, and the space charge amount of the passivation film, and is related to the capacitance measured from experiment. Therefore, when the range of the given potential is changed widely, the space charge amount of the passivation film may change largely. It is clear that by plotting  $C^{-2}$  vs  $E$ , a straight line should result. A positive slope of the straight line reveals a passive film with  $n$ -type semiconductor behaviour and a negative slope of the straight line reveals a passive film with  $p$ -type behaviour. The type of semiconductor can be determined from the  $C^{-2}$  vs  $E$  plot. Figure 5 shows the  $C^{-2}$  vs  $E$  profile for optimal configuration  $(\text{Zn-Co})_{2,0/4,0/300}$  coating system, deposited at optimized processing parameter. The linear plot with positive slope, indicated that protection efficacy of coatings are due to formation of  $n$ -type semiconductor film at the interface during corrosion.

3.4 Dielectric barrier of CMMA coatings

The relative permittivity,  $\epsilon_r$ , of the coatings were calculated from film thickness,  $\delta$ , area,  $A$  and coating capacitance,  $C$ , using (4):

$$\epsilon_r = \frac{C_c \delta}{A \epsilon_0}, \tag{4}$$

where  $\epsilon_0$  is permittivity of the vacuum. Improved corrosion resistance of CMMA coatings can be explained in terms of the effect of time dependent electric field (i.e. frequency response). Figure 6 shows the variation of relative permittivity vs frequency, of the coatings having different number of layers. It was observed that the value of  $\epsilon_r$  for all coatings is high at low frequency which are diminished as the frequency is increased. At low frequency side, the decrease of  $\epsilon_r$  with increase of number of layers

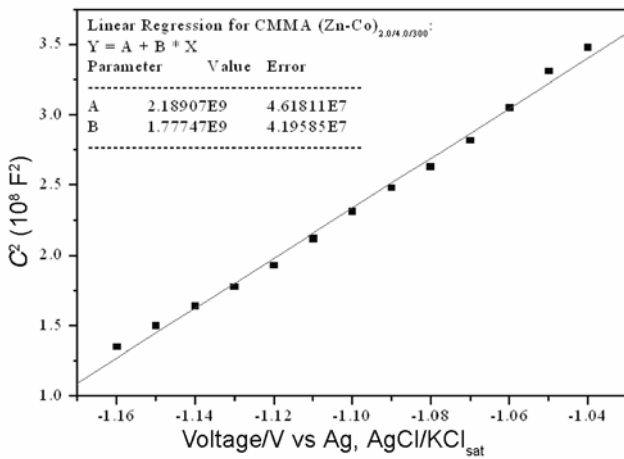


Figure 5. Mott-Schottky plot of CMMA coating under optimal condition, having configuration, represented by CMMA (Zn-Co)<sub>2.0/4.0/300</sub>.

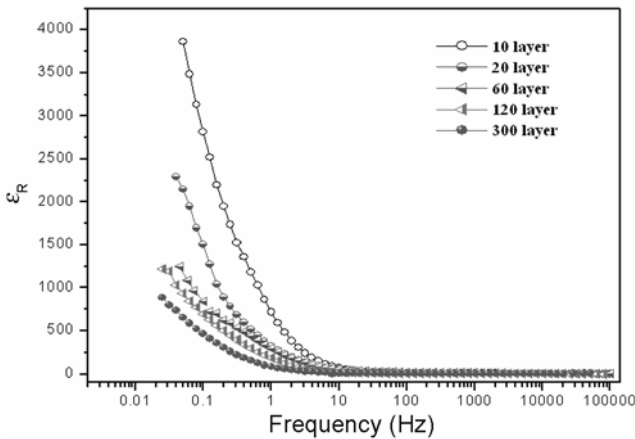


Figure 6. Relative permittivity of CMMA (Zn-Co)<sub>2.0/4.0</sub> coatings with varying number of layers as a function of frequency.

indicates that the dielectric barrier of coatings has increased with layering. This attributes to the increased interfacial polarization effect, caused by the heterogeneous media consisting of phases with different dielectric permittivities (Kouloumbi *et al* 1996). There are many causes for heterogeneity in materials, but concerning the CMMA coatings in the present work, it is related to interfaces created by electron charge density. Thus the peak corrosion resistance of CMMA (Zn-Co)<sub>2.0/4.0/300</sub> coating is due to the decreased permittivity of the coating.

3.5 Comparison between monolithic and CMMA Zn-Co coatings

The corrosion rates of coating systems having (Zn-Co)<sub>2.0/4.0/300</sub> and (Zn-Co)<sub>3.0</sub> configuration (both optimized) in comparison with mild steel are given in table 4. It was found that corrosion protection of coatings with (Zn-Co)<sub>2.0/4.0/300</sub> configuration is ~ 89 times better ( $0.22 \times 10^{-2}$  mm/y) than that of monolithic (Zn-Co)<sub>3.0</sub> alloy ( $19.51 \times 10^{-2}$  mm/y) obtained from the same bath, during the same time. High corrosion rate ( $50.67 \times 10^{-2}$  mm/y) observed in case of mild steel, shows that both monolithic and multilayer coatings offer better protection to base metal against corrosion. Relative impedance response of mild steel in comparison with that of monolithic (Zn-Co)<sub>3.0</sub> alloy and (Zn-Co)<sub>2.0/4.0/300</sub> coating systems, respectively are given in figure 7. The protection efficacy of the CMMA (Zn-Co)<sub>2.0/4.0/300</sub> coatings was related to the barrier effect of the alloys having alternate alloy configuration (i.e. (Zn-Co)<sub>2.0/4.0</sub> and (Zn-Co)<sub>4.0/2.0</sub>). Impedance signals showed that substantial decrease of corrosion rate is due to increased polarization resistance, evidenced by the shape of the Nyquist plots shown in figure 7.

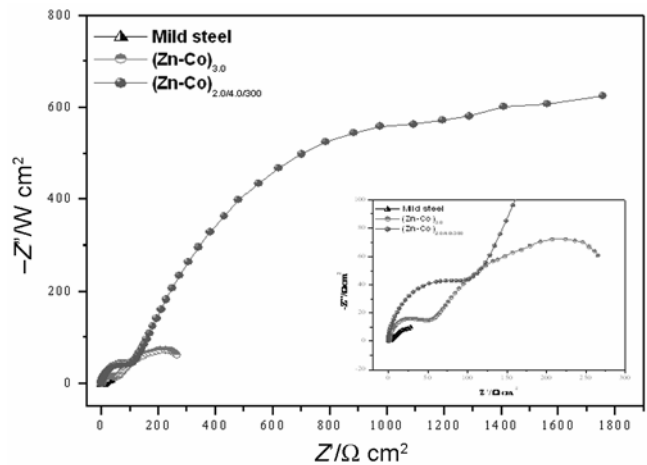
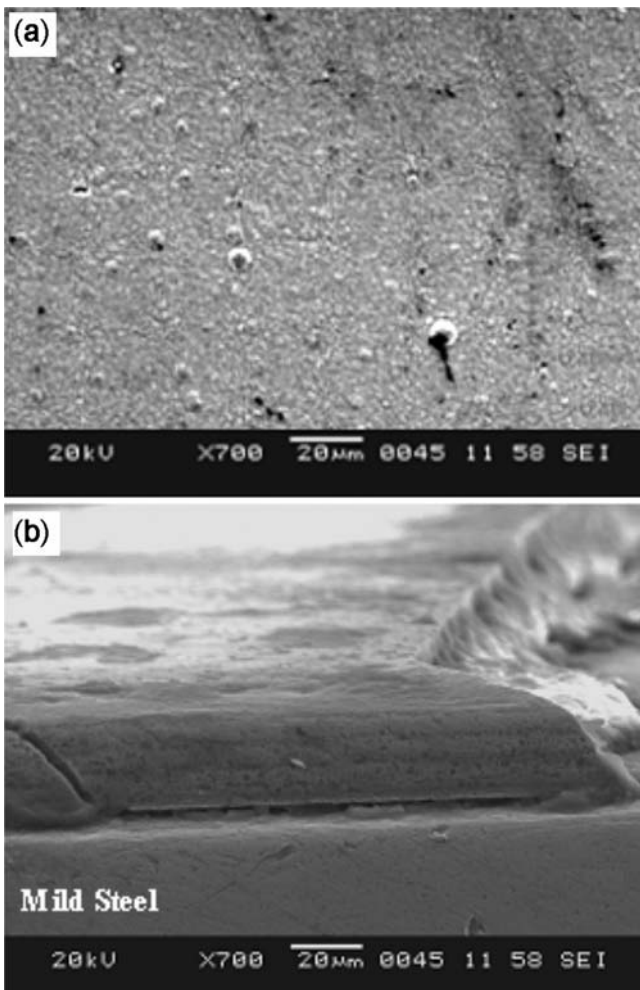


Figure 7. Comparison of Nyquist response of monolithic (Zn-Co)<sub>3.0</sub>, CMMA (Zn-Co)<sub>2.0/4.0/300</sub> coatings (of same thickness) and mild steel (inset shows part in high frequency limit).

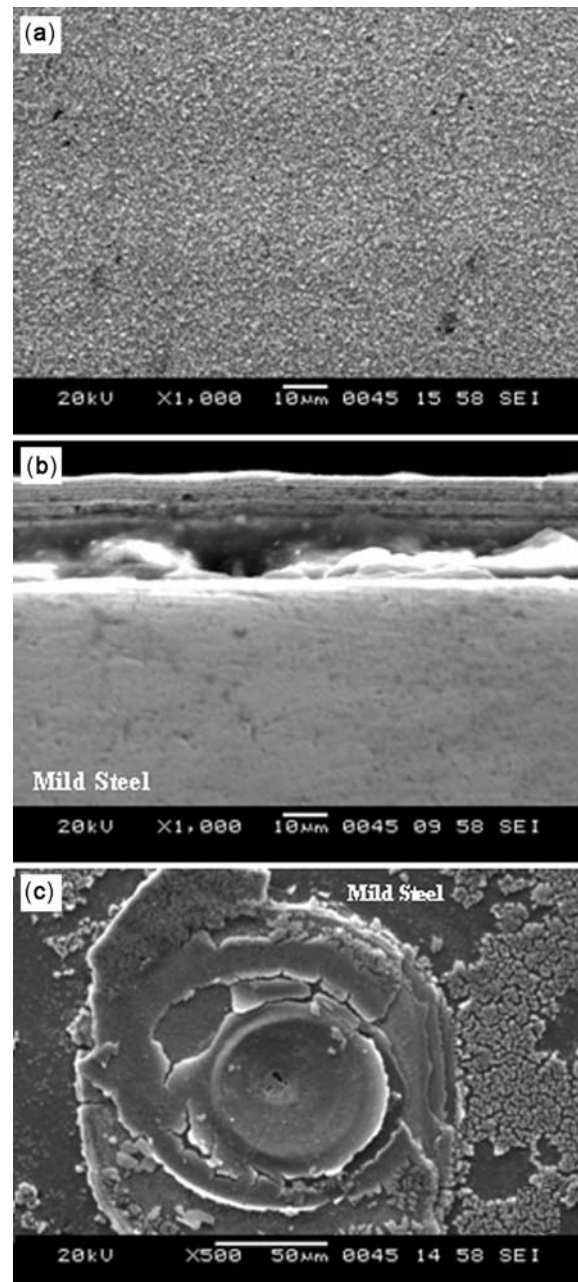
### 3.6 SEM study

Surface morphology and cross-sectional view of monolithic  $(\text{Zn-Co})_{3.0}$  alloy is shown in figures 8(a) and (b), respectively. Figure 8(b) shows that there is no formation of multilayers. Surface morphology of  $(\text{Zn-Co})_{2.0/4.0/16}$  coating without corrosion marked as figure 9(a), displayed a smooth, uniform and crack-free morphology. Cross-sectional view of  $(\text{Zn-Co})_{2.0/4.0/16}$  is shown in figure 9(b). The poor contrast in multilayer may be due to marginal difference in chemical composition of each layer. Inspection of the microscopic appearance of the surface after corrosion tests was used to understand the reason for the improved corrosion resistance of CMMA coatings. The coatings with  $(\text{Zn-Co})_{2.0/4.0/5}$  configuration is subjected to anodic polarization at +250 mV vs OCP in 5% NaCl solution. The corroded specimens were washed with distilled water and examined under SEM. Figure 9(c) shows a sample with CMMA  $(\text{Zn-Co})_{2.0/4.0/5}$  configuration, after corrosion test. The image in figure 9(c)



**Figure 8.** SEM images of monolithic  $(\text{Zn-Co})$  coatings: surface morphology of monolithic  $(\text{Zn-Co})_{3.0}$  coating (a), cross-sectional view of monolithic  $(\text{Zn-Co})_{3.0}$  coatings without layers (b).

exposes the alternate layers formed during the process of deposition. It is evident that the layers with lower concentration of Co were preferentially dissolved, although eventually the steel substrate was exposed. Thus it may be inferred that with the development of Zn-Co alloy up to 300 layers (i.e. Zn-Co films with individual layer thicknesses of about 50 nm) under optimal condition showing better corrosion resistance is due to individual alloy layer thickness reaching nanometric scale. Short *et al* (1984) reported that an improved barrier layer was



**Figure 9.** SEM images of CMMA  $(\text{Zn-Co})$  coatings: surface morphology of  $(\text{Zn-Co})_{2.0/4.0/16}$  coatings (a), cross-sectional view of alloy having 16 layers (b) and CMMA  $(\text{Zn-Co})_{2.0/4.0/5}$  after corrosion test (c).

**Table 4.** Comparison of corrosion rates of (Zn–Co)<sub>3,0</sub> (monolithic) and CMMA (Zn–Co)<sub>2,0/4,0/300</sub> coatings of same thickness with mild steel.

Coating configuration	$E_{\text{corr}}$ (V vs Ag, AgCl/KCl <sub>sat</sub> )	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	CR ( $\times 10^{-2}$ mm/y)
Mild steel	–0.851	77.249	342.42	43.08	50.67
(Zn–Co) <sub>3,0</sub> (monolithic)	–1.158	25.239	35.20	13.15	19.51
CMMA (Zn–Co) <sub>2,0/4,0/300</sub>	–1.1691	13.19	11.77	0.158	0.22

formed on Zn–Co deposits under anodic control due to dezincification, thus reducing the rate of anodic dissolution properties of CMMA coatings, evidenced by its impedance spectroscopy.

#### 4. Conclusions

The corrosion resistance of CMMA coatings produced by the single bath technique was shown to be ~89 times higher than that of the monolithic (Zn–Co)<sub>3,0</sub> coatings with the same thickness. (Zn–Co)<sub>2,0/4,0/300</sub> has been proposed as the optimal configuration of CMMA deposit (with individual layer thickness, ~50 nm), from the proposed bath for peak performance against corrosion. The corrosion resistance of CMMA coating increased as the number of layers was increased. An effort to increase the corrosion resistance beyond 300 layers has resulted in increase of corrosion rate. Decrease of corrosion rate at high degree of layering is due to less relaxation time for redistribution of solutes in the diffusion double layer, during plating. Substantial improvement in the corrosion resistance of CMMA coatings is due to alternate layers of Zn–Co alloy, having gradually changing Co content (due to gradually changing cathodic current during deposition). The electrochemical stability of CMMA coatings was explained in terms of changed intrinsic electrical property, evidenced by Mott–Schottky plot and EIS spectroscopy. The decrease of  $\epsilon_r$  with increase in number of layers, evidenced by dielectric spectroscopy indicated that the improved corrosion resistance is due to decreased dielectric properties of the coatings. Surface and cross-section microstructures of the coatings before and after corrosion tests have evidenced the formation of composition modulated multi-layers and the mechanism of corrosion.

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