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Electrodeposition of high performance multilayer coatings of Zn–Co using triangular current pulses

S. Yogesha and A. C. Hegde*

Compositionally modulated alloy (CMA) coatings of Zn–Co were electrodeposited on to mild steel from an acid chloride bath containing thiamine hydrochloride, as an additive. Electroplating was carried out galvanostatically from a single bath containing Zn^{2+} and Co^{2+} ions. Gradual change in composition in each layer was effected by triangular current pulses, cycling between two cathode current densities. Compositionally modulated alloy coatings were developed under different conditions of cyclic cathode current density and number of layers, and their corrosion resistances were evaluated by potentiodynamic polarisation and electrochemical impedance spectroscopy. The formation of multilayer and corrosion mechanism was analysed using scanning electron microscopy. The corrosion resistances of CMA and monolithic alloy coatings were compared with that of the base metal. Compositionally modulated alloy coating at optimal configuration, represented as $(Zn-Co)_{2.0/4.0/300}$, was found to exhibit ~80 times better corrosion resistance compared with monolithic $(Zn-Co)_{3.0}$ alloy, deposited for the same length of time from the same bath. Improved corrosion resistance was attributed to the formation of n-type semiconductor film at the interface, supported by Mott–Schottky plots. Decrease in corrosion resistance at high degree of layering was found, and is due to lower relaxation time for redistribution of solutes in the diffusion double layer, during plating.

Keywords: Compositionally modulated multilayer alloy, Zn–Co, Triangular pulse current, Corrosion resistance, SEM

Introduction

Nanocrystalline materials exhibit considerably different properties from conventional coarse grained polycrystalline materials. Compositionally modulated alloys (CMAs) belong to one class of such nanocrystalline materials. In CMA materials, successive layers of alloys with alternating composition are created by bringing modulation in the deposition process itself (usually by a complex pulse current sequence).¹ Because of the very fine grain sizes, CMA alloys exhibit properties not attainable in any of the metallurgically prepared alloys. These include better morphological/structural properties, higher electrical resistivity, increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, enhanced corrosion and wear resistance, superior reflectance and soft magnetic properties, in comparison with those of conventional coarse grained materials.² All these

properties can be investigated extensively for new materials with a view to exploring possible applications in a variety of areas. They are, in effect, new materials and that they are difficult to form other than by electrodeposition, promises an exciting extension to the range of surface coatings and associated applications made possible by electroplating. Such multilayers can be produced by means of two main methods, known as the dual bath technique (DBT) and single bath technique (SBT).

Codeposition of two metals requires that their individual reversible potentials are reasonably close to each other in the specific bath. This is the case when their standard potentials are close, when the concentration of one of the metals in solution is properly adjusted, or when a complexing agent that forms metal complexes with different stability constants is added.³ The term anomalous codeposition was coined by Brenner⁴ to describe an electrochemical deposition process in which the less noble metal is deposited preferentially under common plating conditions. This behaviour is typically observed in codeposition of iron group metals or in codeposition of iron group metal with Zn.^{5,6} During the alloy plating, the deposition of the two metals may be under different degrees of mass transport limitation. Thus, alloy coatings of graded or alternating composition can be produced in

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the same bath solution by changing the applied current density, commonly known as cyclic cathode current density (CCCD).⁷

The DBT involves the deposition of constituents from two separate plating baths in an alternate manner.^{8,9} Any combination of layers can be formed, provided that each can be individually deposited, and very thin metal or alloy films can easily be formed. However, the DBT has some significant drawbacks. First, it might be difficult to achieve the appropriate structure because of the periodic exposure of the substrate to potential contaminants during the transfer from one bath to another. In addition, the process might be more time consuming and difficult to automate in comparison with the alternate technique. In the SBT,^{10–12} 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. Although substantial success has been achieved with the SBT, the selection of constituents is limited because their deposition potentials must be sufficiently different to allow a separate deposition of each. Difficulties can also be encountered in the deposition of very thin layers due to the relaxation time for the redistribution of solutes in the diffusion double layer. It is also difficult to get the layers of individual metals; mostly they will be in the alloy form.

A number of investigators have examined the Zn–Ni multilayer system, Barral and Maximovitch¹³ being among the first. They developed a dual bath configuration for depositing successive layers of zinc and nickel with individual layer thicknesses of 20–500 nm using a rotating disc electrode. Kalantary *et al.*¹⁴ obtained Zn–Ni CMA coatings with an overall thickness of 8 μm by electrodepositing alternate layers of zinc and nickel from the zinc sulphate and nickel sulphate electrolytes. Chawa *et al.*⁸ reported that Zn–Ni CMA coatings from zinc sulphate and nickel sulphamate baths have better corrosion resistance compared to that of monolithic Zn–Ni coatings of similar thickness. Recently, Liao *et al.*^{15–17} have studied both SBT and DBT of Zn/Zn–Fe and only Zn–Fe systems. Kirilova *et al.*^{18–20} reported CMA coatings of Zn–Co from the SBT.

Though multilayer Zn–M alloy coating with improved corrosion resistance is widely reported, very little has been done with regard to optimisation of the deposition conditions using the SBT. Recently, Thangaraj *et al.*^{7,21} have optimised a chloride bath for the production of Zn–Co and Zn–Fe CMA coatings using square current pulses. They found that the CMA coatings under optimal conditions were many times more corrosion resistant than the respective monolithic alloy coatings. Most of the work reports the modulation in composition using square pulses of two or more current/voltages, bringing a sudden change in its composition. No work is reported with regard to the optimisation of coating configuration of coating system, having gradual change in composition using triangular current pulses. The main objective of this study is to optimise the deposition condition for development of monolithic and CMA coatings of Zn–Co alloy onto a steel substrate from a chloride bath for better corrosion resistance using thiamine hydrochloride (THC) as additive, and to compare the corrosion resistance of

CMA coating with those of monolithic alloy and mild steel.

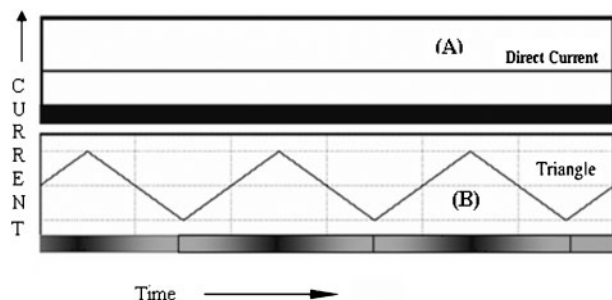
Experimental

The plating solutions were freshly prepared from distilled water and analytical grade reagents. Electroplating of mild steel plates was carried out in a bath consisting of 10 g L⁻¹ ZnO, 30 g L⁻¹ CoCl₂, 200 g L⁻¹ NH₄Cl, 20 g L⁻¹ boric acid, 10 g L⁻¹ citric acid and 3 g L⁻¹ THC at pH 3.5 \pm 0.05 and temperature 30 \pm 2°C. The polished mild steel plates (0.063C–0.23Mn–0.03S–0.011P–99.6Fe) had an exposed surface area of 7.5 cm² serving as the cathode. The anode was pure Zn with the same exposed area. A rectangular PVC cell containing 250 cm³ electrolyte was used. All depositions were carried out under constant condition of stirring without purging to maintain a steady state of mass transport. All coatings, namely, monolithic and CMA, were carried out galvanostatically using a sophisticated power source (N6705A; Agilent Technologies, Santa Clara, CA, USA) for 10 min (\sim 12 μm thickness), for comparison purpose. While the thickness of the coating was estimated by Faraday's law, it was also verified by measurement, using a digital thickness meter (Coatmeasure model M & C). The composition of the coatings was determined colorimetrically using a standard method.²² The hardness of the deposited alloys was measured using a computer controlled microhardness tester (CLEMEX, model: MMT-X7). All electrochemical studies have been carried out using a potentiostat/galvanostat (VersaSTAT,³ Princeton Applied Research, Oak Ridge, TN, USA) in a three-electrode configuration cell. All electrochemical potentials referred to in this work are relative to the Ag/AgCl/KCl_{sat} electrode. A 5% NaCl solution was used as corrosion medium. Potentiodynamic polarisation studies were carried out at a ramped potential of \pm 250 mV from open circuit potential (OCP) at a scan rate of 1 mV s⁻¹. Electrochemical impedance spectroscopy studies were carried out in the frequency range from 100 kHz to 10 mHz with perturbing signal of 10 mV. The Mott–Schottky plots were obtained by performing a potential scan in the cathodic direction at 100 Hz in the potential range from +0.5 to –0.5 V around OCP. The formation and morphology of multilayers, and corrosion mechanism were examined by scanning electron microscopy (SEM, Model JSM-6380 LA from JEOL, Tokyo, Japan).

Results and discussion

Development of monolithic Zn–Co alloy coating

The optimisation of a standard chloride bath was carried out by the normal Hull cell method.¹ Deposition was carried out galvanostatically at different current densities (CDs) using the optimised bath, consisting of 10 g L⁻¹ ZnO, 30 g L⁻¹ CoCl₂, 200 g L⁻¹ NH₄Cl, 20 g L⁻¹ boric acid, 10 g L⁻¹ citric acid and 3 g L⁻¹ THC. The effects of CD on weight percentage of Co, thickness, Vickers hardness, corrosion resistance and appearance of the coatings are reported in Table 1. Zn–Co alloy at 3.0 A dm⁻², represented as (Zn–Co)_{3.0}, was found to be the most corrosion resistant (19.51 \times 10⁻² mm/year loss in thickness), compared with deposits at other CDs. Hence, this has been taken as the optimal CD for monolithic Zn–Co alloy deposition.



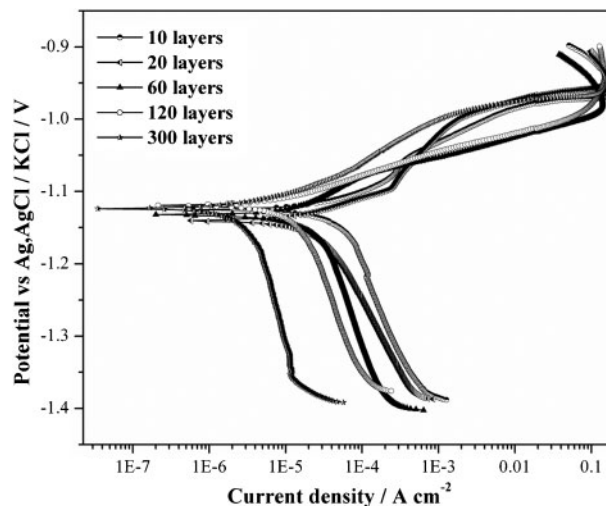
1 Schematic representation of (A) constant cathode current pulses for deposition of monolithic Zn-Co alloy and (B) triangular current pulses for deposition of CMA coatings with gradually changing compositions

Development of Zn-Co CMA coatings

The CMA coatings were developed by causing the cathodic current to change gradually from one CD to another by appropriate set-up of the power source. Multilayer coatings having alternate layers of alloys with different compositions were developed using triangular current pulses (gradual change in composition is effected by gradual change in CD). The power pattern generated for CMA coating is shown schematically in Fig. 1. In the present study, the CMA coating systems are represented as: $(\text{Zn-Co})_{1/2/n}$, where 1 and 2 represent cathode CDs between the cathode current cycles and n represents the number of layers formed during total plating time.

Optimisation of CCCDs

In the case of alloys of Zn-M (where M=Ni, Co and Fe), it is well known that even a small change in the concentration of the latter may result in a significant change in properties due to the change in the phase structure. Thus, by precise control of the CCCDs, it is possible to develop alternate layers of alloys with different compositions and, consequently, different properties. Table 2 demonstrates the effect of the CCCDs on the corrosion behaviour of the coatings. Multilayer coatings having 10 layers were developed at different sets of CCCDs to increase their corrosion



2 Potentiodynamic polarisation curves of CMA $(\text{Zn-Co})_{2.0/4.0}$ coatings with different numbers of layers

resistance. Among the various sets tested, the lowest corrosion rate (CR) was measured in the coatings produced at differences of 2.0 and 4.0 A dm^{-2} 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.

Optimisation of overall number of layers

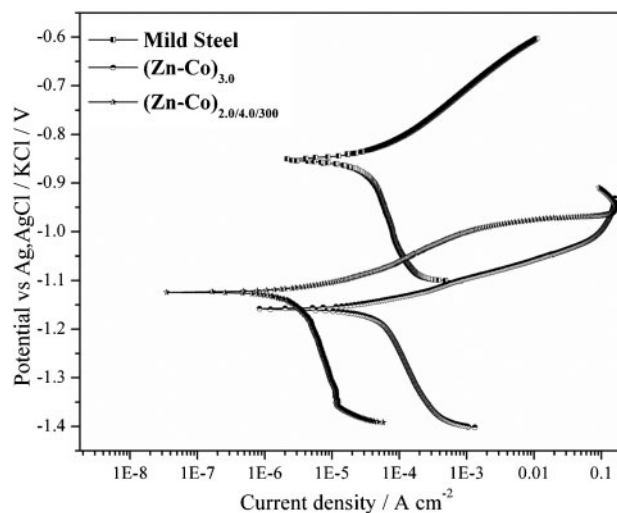
The physicomechanical properties of CMA coatings, including their corrosion resistance, may often be increased substantially by increasing the number of layers (usually, up to an optimal limit), without sacrificing the demarcation between layers. Therefore, a few sets of CCCDs such as 2.0/4.0 and 2.0/6.0 A dm^{-2} were selected for layering. Zn-Co CMA coatings with 20, 60, 120 and 300 layers were developed and their CRs were measured by Tafel's extrapolation method. The CR of coatings was found to decrease with the number of layers in each set of CCCDs as shown in Table 3. However, at 2.0/4.0 A dm^{-2} , the coating with 300 layers showed minimum CR of 0.243×10^{-2} mm/year relative

Table 1 Effect of CD on deposit characteristics of monolithic Zn-Co alloy

CD/ A dm^{-2}	Weight per cent of Co/ wt-%	Thickness/ μm	Vickers hardness/HV0.1	$E_{\text{corr}}(\text{Ag,AgCl/KCl}_{\text{sat}})/$ V	$i_{\text{corr}}/$ $\mu\text{A cm}^{-2}$	CR/ $\times 10^{-2}$ mm/year	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	Semibright

Table 2 Corrosion rate of CMA Zn-Co coatings at different sets of CCCDs (with 10 layers)

CCCDs/ A dm^{-2}	$E_{\text{corr}}(\text{Ag,AgCl/KCl}_{\text{sat}})/$ V	$i_{\text{corr}}/\mu\text{A cm}^{-2}$	CR/ $\times 10^{-2}$ mm/year
CMA Zn-Co coatings developed at difference of 2.0 A dm^{-2} between CCCDs $(\text{Zn-Co})_{2.0/4.0/10}$	-1.125	8.300	12.314
CMA Zn-Co coatings developed at difference of 4.0 A dm^{-2} between CCCDs $(\text{Zn-Co})_{2.0/6.0/10}$	-1.028	11.674	17.320



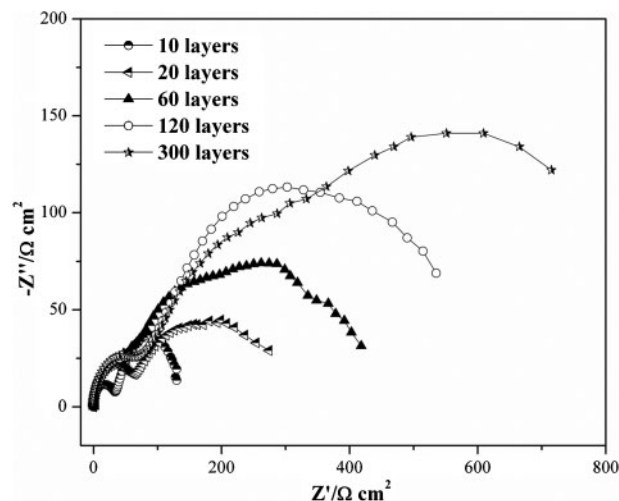
3 Comparison of potentiodynamic polarisation curves of monolithic (Zn–Co)_{3,0}, CMA (Zn–Co)_{2,0/4,0/300} coatings (of same thickness) and mild steel in 5% NaCl

to 19.51×10^{-2} mm/year for monolithic Zn–Co alloy coatings (Table 1). Though there is a substantial decrease in CR also with layering at other sets of CCCDs (i.e. at 2.0/6.0 A dm⁻² with 300 layers as shown in Table 3), the result pertaining to 2.0/4.0 A dm⁻² is more encouraging due to better homogeneity, and brightness of the deposit. However, an effort of increasing the corrosion resistance further by increasing the number of layers in each set of CCCDs has resulted in an increase in CR, possibly due to less relaxation time for redistribution of solutes in the diffusion double layer, during plating. Hence, (Zn–Co)_{2,0/4,0/300} has been proposed as the optimal configuration of CMA coating from the proposed bath for peak performance against corrosion.

Corrosion study

Tafel polarisation study

The polarisation behaviours of (Zn–Co)_{2,0/4,0} CMA coatings with different degrees of layering are shown in Fig. 2. It may be observed that the corrosion current i_{corr} values decreased with increasing number of layers. This progressive decrease in i_{corr} with number of layers indicated that improved corrosion resistances are due to layering of alloys, having distinctive properties. The slight variation of E_{corr} value with number of layers (Table 3) showed that the CMA coatings provide sacrificial protection to the substrate. The polarisation



4 Real versus imaginary resistance values of CMA (Zn–Co)_{2,0/4,0} coatings with different numbers of layers measured as function of frequency

curve shown in Fig. 2 indicates that the CMA coating with (Zn–Co)_{2,0/4,0/300} configuration is the most corrosion resistant. Potentiodynamic polarisation behaviours of monolithic and CMA coatings (both under optimal conditions) in comparison with that of mild steel are shown in Fig. 3. It may also be noted that both i_{corr} and E_{corr} values of electroplates have changed considerably compared with that of base metal.

Electrochemical impedance spectroscopy study

Electrochemical impedance spectroscopy is one of the most powerful tools for studying the electrochemical behaviour of materials. In this technique, impedance behaviour is studied by the application of an AC signal (sinusoidal wave).²³ The form of the current–voltage relationship of the impedance in an electrochemical system can also be expressed as

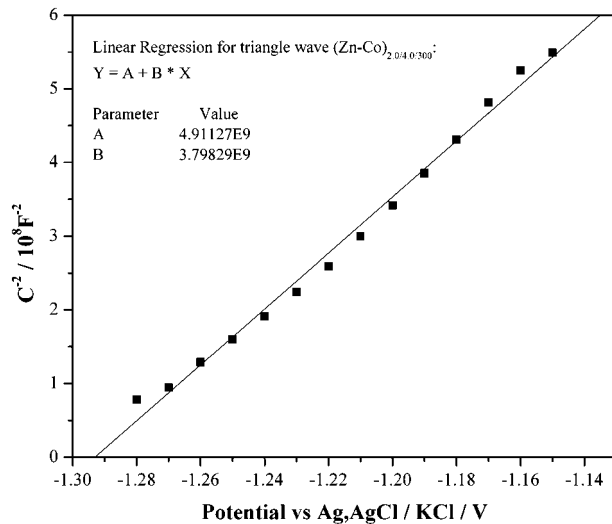
$$Z(\omega) = \frac{V(t)}{I(t)}$$

where $V(t)$ and $I(t)$ are the measurements of voltage and current in an AC 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 dataset $Z(Z_{\text{re},i}, Z_{\text{im},i}, \omega_i)$, ($i=1, 2, \dots, n$) of n points measured at different frequencies, with each

Table 3 Decrease in corrosion rate (CR) of CMA Zn–Co coatings with increasing number of layers

CD/A dm ⁻²	No. of layers	$E_{\text{corr}}(\text{Ag,AgCl/KCl}_{\text{sat}})/\text{V}$	$i_{\text{corr}}/\mu\text{A cm}^{-2}$	CR/ $\times 10^{-2}$ mm/year
Optimisation of layer thickness at CCCDs of 2.0–4.0 A dm ⁻²				
(Zn–Co) _{2,0/4,0/10}		-1.125	8.300	12.314
(Zn–Co) _{2,0/4,0/20}		-1.140	5.047	7.488
(Zn–Co) _{2,0/4,0/60}		-1.132	1.317	1.954
(Zn–Co) _{2,0/4,0/120}		-1.116	0.599	0.889
(Zn–Co) _{2,0/4,0/300}		-1.124	0.178	0.243
Optimisation of layer thickness at CCCDs of 2.0–6.0 A dm ⁻²				
(Zn–Co) _{2,0/6,0/10}		-1.028	11.674	17.32
(Zn–Co) _{2,0/6,0/20}		-1.084	9.358	13.88
(Zn–Co) _{2,0/6,0/60}		-1.055	5.962	8.846
(Zn–Co) _{2,0/6,0/120}		-1.050	2.613	3.877
(Zn–Co) _{2,0/6,0/300}		-1.042	0.639	0.948



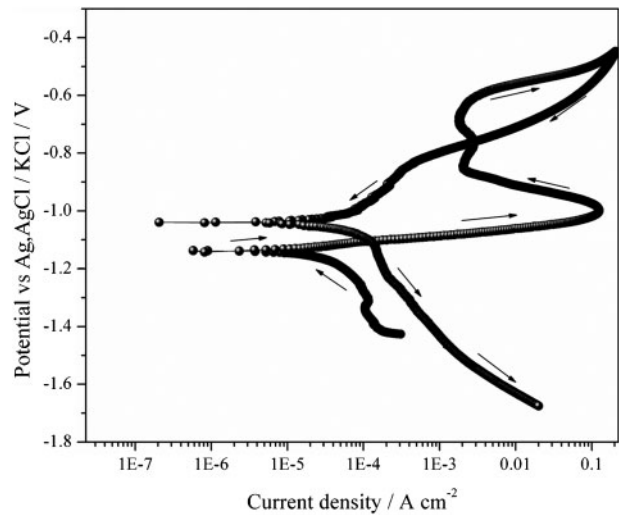
5 Mott-Schottky plot of CMA coating under optimal condition, having configuration of CMA (Zn-Co)_{2.0/4.0/300}

point representing the real and imaginary parts of the impedance ($Z_{re,i}, Z_{im,i}$) at a particular frequency ω_i . A Bode plot is an alternative representation of the impedance in a plot of phase angle θ versus $\log \omega$, describing the frequency dependences 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.

The Nyquist response of CMA (Zn-Co)_{2.0/4.0} with different numbers of layers is shown in Fig. 4. At high frequency limit of Z' , all electroplates exhibited $R_{real}=0$, indicating that the solution resistance R_s is the same for all the analyses. The increase in the radius of the semicircle with increasing number of layers showed that the capacitive reactance of the double layer, responsible for improved corrosion resistance, increased with layering. The highest corrosion resistance at optimal layers (300 layers) is evidenced by a bigger incomplete semicircle, caused by large capacitive reactance. However, the radius of the semicircle increased with number of layers, and this is due to the increased capacitive reactance. The presence of Nyquist plots with incomplete semicircles at low frequency limit of Z' indicated that the corrosion behaviour of the coatings is not only controlled by charge transfer resistance R_{ct} but also by capacitive reactance or due to double layer capacitance C_{dl} .

Mott-Schottky behaviour of passive film

The marked increase in corrosion resistance of all the CMA coatings is attributed to the semiconductor behaviour of the passive film at the metal/medium interface during corrosion. In general, passive films are always semiconductors.^{24,25} The semiconductor property of a passive film, i.e. the relationship between space charge capacitance C and applied potential E can be



6 Cyclic polarisation curve of CMA coating under optimal condition, having configuration of CMA (Zn-Co)_{2.0/4.0/300}

described using the Mott-Schottky equation^{26,27}

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

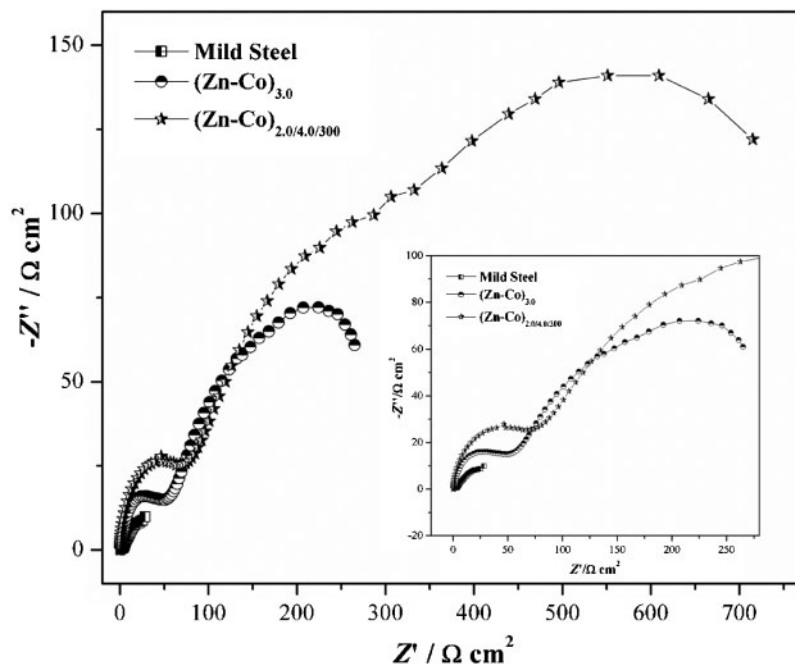
$$\text{p-type: } \frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_A} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (2)$$

where e is the elementary charge ($+e$ for electrons and $-e$ for holes), ϵ is the dielectric constant of the passive film, ϵ_0 is the permittivity in vacuum (8.854×10^{-12} F m⁻¹), N_D and N_A stand for the donor and acceptor electron density, E_{fb} is the flat band potential, k is the Boltzmann constant and T is the absolute temperature. The donor or acceptor concentrations can be estimated from the slopes of the straight lines obtained in C^{-2} versus E plots.

When equations (1) and (2) are adapted to describe the electronic properties of metal surface passivation films, 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 greatly. It is clear that by plotting C^{-2} versus 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} versus E plot. Figure 5 shows the C^{-2} versus E profile for the optimal configuration CMA (Zn-Co)_{2.0/4.0/300} coating system, deposited at optimised processing parameters. The linear plot with positive slope indicated that protection efficacy of coatings is due to formation

Table 4 Comparison of CRs of monolithic (Zn-Co)_{3.0} and CMA (Zn-Co)_{2.0/4.0/300} coatings of same thickness with mild steel

Coating configuration	$E_{corr}(\text{Ag,AgCl/KCl}_{sat})/\text{V}$	$i_{corr}/\mu\text{A cm}^{-2}$	$\text{CR}/\times 10^{-2} \text{ mm/year}$
Mild steel	-0.851	43.08	50.67
Monolithic (Zn-Co) _{3.0}	-1.158	13.15	19.51
CMA (Zn-Co) _{2.0/4.0/300}	-1.124	0.178	0.243



7 Comparison of Nyquist responses of monolithic (Zn-Co)_{3.0}, CMA (Zn-Co)_{2.0/4.0/300} coatings (of same thickness) and mild steel: inset shows part in high frequency limit

of n-type semiconductor film at the interface during corrosion.

Cyclic polarisation study

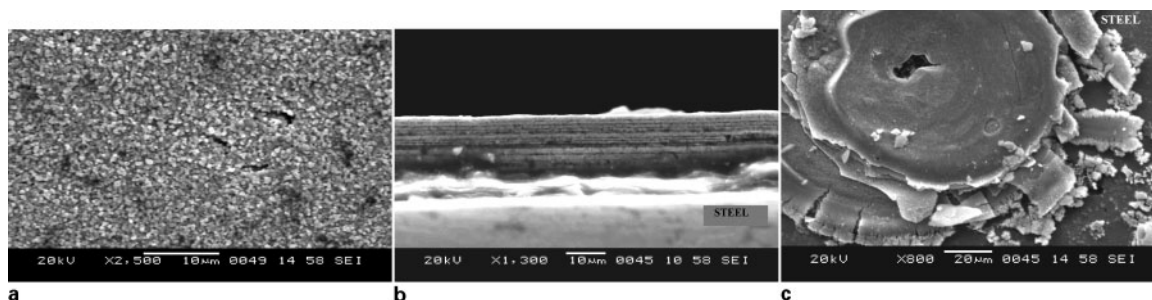
The peak corrosion resistance exhibited by the CMA (Zn-Co)_{2.0/4.0/300} coating may be better understood by investigating the cyclic polarisation study over a potential range from -1.42 to -0.44 V as shown in Fig. 6. In the forward scanning, the value of CD has gone through from negative to positive, which showed that the oxidising reaction of the passivation film occurred with increasing potential. During backward scanning, the CD has gone through from positive to negative, indicating that reducing reaction of the high valence oxide in the passivation film occurred with decreasing potential.

In the range from -0.44 to -0.75 V, the CD of backward scanning was higher than that of the forward scanning, indicating that the dissolving of oxides had occurred in the process of forward scanning, so self-repairing occurred in the process of backward scanning and the increased anodic current appeared. In the range from -0.75 to -1.04 V, the CD of backward scanning was lower than that of the forward scanning, showing that metal could form a protective passive film below

this value. However, the CD of the backward scanning was lower than that of the forward scanning at the same potential, which indicated that the passive film had a more compact structure after anodic polarisation.

Comparison between monolithic and CMA Zn-Co coatings

The CRs of coating systems having CMA (Zn-Co)_{2.0/4.0/300} and (Zn-Co)_{3.0} configurations (both optimised) in comparison with mild steel are given in Table 4. It was found that corrosion protection of coatings with (Zn-Co)_{2.0/4.0/300} configuration is ~80 times better (0.243×10^{-2} mm/year) than that of a monolithic (Zn-Co)_{3.0} alloy (19.51×10^{-2} mm/year) obtained from the same bath, during the same time. A higher CR (50.67×10^{-2} mm/year) observed in the case of mild steel shows that both monolithic and multilayer coatings offer protection to the base metal against corrosion. The relative impedance responses of mild steel in comparison with those of monolithic (Zn-Co)_{3.0} alloy and CMA (Zn-Co)_{2.0/4.0/300} coating systems are given in Fig. 7 respectively. The protection efficacy of the CMA (Zn-Co) coatings was related to the barrier effect of the alloys having alternate alloy configuration [i.e. (Zn-Co)_{2.0/4.0} and (Zn-Co)_{4.0/2.0}]. Impedance signals showed that the substantial decrease in



a surface morphology of (Zn-Co)_{2.0/4.0/16} coatings; b cross-sectional view of alloy having 16 layers; c CMA (Zn-Co)_{2.0/4.0/5} after corrosion test

8 Images (SEM) of CMA (Zn-Co) coatings

CR is due to the increased polarisation resistance, evidenced by the shape of the Nyquist plots shown in Fig. 7.

SEM study

The surface morphology and formation of alternate layers of alloys having distinctive properties was confirmed by SEM. The surface of $(\text{Zn–Co})_{2.0/4.0/16}$ coating without corrosion (Fig. 8a) displayed a smooth, uniform and crack free morphology. A cross-sectional view of CMA $(\text{Zn–Co})_{2.0/4.0/16}$ is shown in Fig. 8b. The poor contrast may be due to marginal difference in chemical composition of alloys in 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 the CMA coatings. The coatings with CMA $(\text{Zn–Co})_{2.0/4.0/5}$ configuration were subjected to anodic polarisation at +250 mV versus OCP in 5% NaCl solution. The corroded specimens were washed with distilled water and examined under SEM. Figure 8c shows a sample with CMA $(\text{Zn–Co})_{2.0/4.0/5}$ configuration, after the corrosion test. The image in Fig. 8c 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. Short *et al.*²⁸ reported that an improved barrier layer was formed on Zn–Co deposits under anodic control due to dezincification, thus reducing the rate of anodic dissolution properties of CMA coatings, as shown by their impedance spectroscopy data.

Conclusions

The corrosion resistance of CMA Zn–Co coatings produced by the single bath technique was shown to be higher than that of the monolithic Zn–Co coatings with the same thickness. For example, CMA coatings with optimal configuration $(\text{Zn–Co})_{2.0/4.0/300}$ showed ~80 times better corrosion resistance compared with monolithic $(\text{Zn–Co})_{3.0}$ alloy obtained from the same bath. The corrosion resistances of coatings were found to increase with the number of layers up to a certain degree of layering, and then decreased. The decrease in corrosion resistance at high degree of layering is attributed to less relaxation time for redistribution of solutes in the diffusion double layer, during plating. Even a small change in the weight per cent of Co in the layer was sufficient to change the corrosion resistance significantly. The better corrosion resistances of multilayered coatings were attributed to high electron donor density at the interface, evidenced by Mott–Schottky plots. The protection efficacy of the CMA $(\text{Zn–Co})_{2.0/4.0}$ coatings was related to the barrier effect of the $(\text{Zn–Co})_{4.0}$ layers and the sacrificial behaviour of the $(\text{Zn–Co})_{2.0}$ layers. Surface and cross-section microstructures of the coatings before and after corrosion tests have revealed the formation of composition modulated multilayers and mechanism of corrosion. It was demonstrated that optimisation

of coating condition is possible through proper manipulation of the cyclic cathode CDs and number of layers.

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