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Corrosion stability of electrodeposited cyclic multilayer Zn–Ni alloy coatings

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This paper reports on a study of electrodeposition and characterisation of cyclic multilayer coatings of Zn–Ni alloy from a sulphate bath. Cyclic multilayer alloy coatings were deposited on mild steel through the single bath technique by appropriate manipulation of cathode current densities. The thickness and composition of the individual layers of the CMA deposits were altered precisely and conveniently by cyclic modulation of the cathode current during electrodeposition. Multilayer deposits with sharp change in composition were developed using square current pulses, using thiamine hydrochloride and citric acid as additives. Laminar deposits with different configurations were produced and their corrosion behaviours were studied by AC and DC methods in 5%NaCl solution. It was observed that the corrosion resistance of the CMA coating increased progressively with the number of layers (up to certain optimal numbers) and then decreased. The decrease in corrosion resistance at high degree of layering was attributed to interlayer diffusion due to less relaxation time for redistribution of metal ions at cathode during deposition. The coating configurations have been optimised for peak performance of the coatings against corrosion. It was found that CMA coating developed at cyclic cathode current densities of $3{\cdot}0/5{\cdot}0$ A dm^{-2} with 300 layers showed the lowest corrosion rate ($0{\cdot}112 \times 10^{-2}$ mm/year) which is ~ 54 times better than that of monolithic Zn–Ni alloy, deposited from the same bath. The protection efficacy of CMA coatings is attributed to the difference in phase structure of the alloys in successive layers, deposited at different current densities, evidenced by X-ray diffraction analysis. The formation of multilayers and corrosion mechanism were examined by scanning electron microscopy.

Keywords: Cyclic multilayer alloy, Zn–Ni coating, Corrosion resistance, XRD, SEM

Introduction

Cyclic multilayer alloy (CMA) coatings have been gradually gaining interest among researchers because of the characteristics of the layered structure. These coatings possess improved properties or novel phenomena such as increased mechanical strength, microhardness, giant magneto resistance and corrosion resistance.[1–6] Eliaz and Gileadi[7] have recently reviewed the principles of alloy codeposition and the phenomenon of anomalous codeposition in the frame work of a more comprehensive review of induced codeposition. The term anomalous codeposition was explained by Brenner[8] to describe an electrochemical deposition process in which the less noble metal is deposited preferentially under most plating conditions. This behaviour is typically observed in codeposition of iron group metals or in codeposition of iron group metal with Zn.[9,10] 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 altering composition can be produced in the same bath solution by changing the applied current density (CD), commonly known as cyclic cathode current density (CCCD).[11–13]

Cyclic multilayer alloy coating consists of a large number of thin laminar deposits of metal/alloy layers and each layer has its own distinctive role in achieving preferred performances. During recent decades, electrodeposition of CMA coatings for protection of steel substrates from corrosion has been extensively investigated. Chawa et al.[5] reported that the corrosion resistance of Zn–Ni CMA coatings, electrodeposited from zinc sulphate and nickel sulphamate baths, was better than that of zinc or nickel monolithic coatings of a similar thickness. Kalantary et al.[4] obtained zinc–nickel CMA coatings with an overall thickness of 8 μm by electrodepositing alternate layers of zinc and nickel from zinc sulphate electrolyte and nickel sulphate electrolyte. Ivanov et al.[6] studied the corrosion performance

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of zinc–nickel CMA coatings with the total thickness of 12 μm, obtained by successive deposition from dual baths containing zinc sulphate electrolyte and nickel sulphate–chloride electrolyte mainly using the anode potentiodynamic dissolution method. Later, attempts on the electrodepositon of CMA coatings were made by depositing alloy layers under different plating conditions from single bath.[14–17] Kalantary *et al.*[15] deposited controlled Zn–Ni multilayered coatings on a rotating cylinder electrode from a sulphate bath. In the CD range of 1–50 mA dm^{-2}, the Ni content was between 3 and 14%, and in the CD range of 100–130 mA dm^{-2}, it was between 20 and 30%. Hayashi[18] observed the higher corrosion resistance of Zn–Ni and Zn–Fe alloys with respect to pure zinc, under atmospheric exposure conditions, in a higher resistance to the penetration of chloride ions through the coating. Multilayered Zn–Ni deposition from a single acidic bath by the potentiostatic method was reported by Ganesan *et al.*[19] It was found that the Ni content varied as a function of thickness by applying a varying potential sequence. It was concluded that at higher potentials, γ-phases corresponding to (600) planes are preferentially deposited, while depositing at lower potentials leads to the deposition of other crystal planes of γ-phases (222). Although the enhanced corrosion resistance of Zn–M (where M=Ni, Co and Fe) CMA deposits have widely been reported, very little has been done in relation to the optimisation of deposition conditions for development of coatings of good corrosion resistance, using the single bath technique. Recently, Thangaraj *et al.*[20] optimised a chloride bath for the production of Zn–Fe CMA coatings over mild steel, and showed that coatings are ~45 times more corrosion resistant than monolithic Zn–Fe alloy of the same thickness. The corrosion behaviours of some pulse plated Zn–Fe group metal alloys have been studied by Thangaraj by relating pulse parameters and their corrosion performances.[21] Cyclic multilayer Zn–Co alloy coating was developed on mild steel from the single bath using triangular current pulses, and their corrosion performances have been evaluated.[22] The CMA coating with optimal configuration (Zn–Co)$_{2.0/4.0/300}$ showed ~80 times better corrosion resistance compared with monolithic (Zn–Co)$_{3.0}$ alloy obtained from the same bath. The aim of the present study was to optimise the deposition conditions for production of bright corrosion resistant multilayered Zn–Ni alloy, using thiamine hydrochloride (THC) and citric acid (CA) as additives, and to analyse the reasons responsible for better corrosion protection of the coatings.

Experimental

The initial studies were focused on the optimisation of bath composition through visual examination of deposited panels obtained from the standard Hull cell method.[23] The bath composition was: 120 g L^{-1} ZnSO$_4$.7H$_2$O, 100 g L^{-1} NiSO$_4$.7H$_2$O, 70 g L^{-1} CH$_3$COONa, 3 g L^{-1} C$_6$H$_8$O$_7$.H$_2$O (CA) and 0·5 g L^{-1} C$_{12}$H$_{17}$N$_4$OSCl.HCl (THC), and the optimum pH and temperature were 3 and 30°C respectively. The electrolyte was prepared using LR grade chemicals and distilled water. Precleaned mild steel panels with 7·5 cm^2 active surface area were used as cathode. The cathode was mechanically polished with progressively finer grade emery coated mops and, before

deposition, was treated to alkali cleaning. Before immersion, the cathode was neutralised in a 10%HCl solution. After deposition, coatings were washed with distilled water, and dried with hot air. A PVC cell of 250 cm^3 capacity was used for electroplating, with cathode–anode separation of ~5 cm. All depositions were carried out using a high precision power source (N6705A; Agilent Technologies) and other electrochemical characterisations were made using a potentiostat/galvanostat (VersaSTAT3; Princeton Applied Research).

A cyclic voltammetry (CV) study was performed in a conventional three electrode cell to better understand the process of electrodeposition, and to identify the effects of additives. Hence, the process and product of Zn–Ni deposition were studied by adding CA and THC, individually and in combination, into the electrolytic bath. Pure platinum foil with a surface area of 1 cm^2 was used as the working electrode. Before each experiment, the electrode was activated by immersion in 1:1 HNO$_3$ then water rinsed. The CV experiments were conducted in a quiescent solution, without agitation. Initially, three scan rates were evaluated (10, 20 and 50 mV s^{-1}). However, the peaks in the CV spectra became more distinct when the scan rate was 10 mV s^{-1}, and this was used for subsequent studies. The scan began from 0 V in the positive direction, up to +0·5 V. Then, the scan was reversed to the negative direction, down to –1·5 V, and finally reversed back to +0·5 V. The phase structure of the electrodeposits at different CDs was analysed using an X-ray diffractometer (Bruker AXS) using Cu K_α radiation (λ=1·5405 Å, 30 kV). Scanning electron microscopy (SEM; model JSM-6380 LA; JEOL, Japan) was used to examine the multilayer formation and its deterioration after corrosion.

Generally, in electroplating, direct current or constant current results in the coatings having constant composition, called monolithic, or alternatively monolayer coatings. But a periodic change in CD allows the growth of layers on a substrate with periodic change in the chemical compositions,[16] i.e. square current pulses of low CD result in layers of low Ni content, and square current pulses of high CD result in layers of high Ni content. The equipment was set to cycle between two different cathode CDs, called CCCDs, in a repetitive way. While the thickness of each layer was controlled by the duration of one CD, the composition of each layer is decided by the value of CD applied. The total number of layers was fixed appropriately by adjusting the time for each cycle. Thus, CMA coatings of different configurations were produced. Such multilayer coatings are hereafter represented as (Zn–Ni)$_{1/2/n}$, where (Zn–Ni) represents an alloy of Zn and Ni, 1 and 2 represent the cathode CD that is made to cycle between and '*n*' represents the total number of layers formed during the total deposition time (10 min). Monolithic alloy is represented by the notation (Zn–Ni).

The corrosion behaviour of coatings was measured by electrochemical DC and AC techniques, in a three electrode configuration cell. All electrochemical potentials reported in this work are indicated relative to the Ag/AgCl/Cl$_{sat}^{-1}$ electrode. A 5%NaCl solution (30°C) was used as corrosion medium throughout the study. The potentiodynamic polarisation study was carried out in a potential ramp of ±250 mV from open circuit potential (OCP) at a scan rate of 1 mV s^{-1}. Impedance
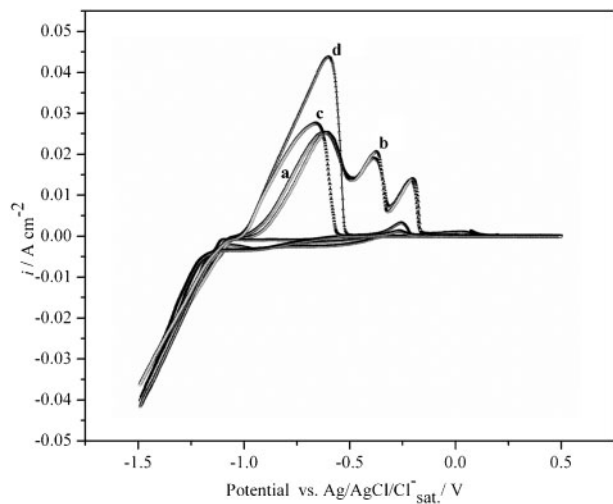
a without additive; *b* with CA; *c* with THC; *d* with CA+THC

1 Cyclic voltammograms of Zn–Ni alloy bath, demonstrating effects of THC and CA addition: working electrode: Pt, pH=3·0, *T*=30°C, *v*=10 mV s⁻¹

behaviour was studied in the frequency range from 100 kHz to 10 mHz. The chemical composition of the coatings was determined by stripping the known mass of electrodeposit into 2 N HCl, and wt-%Ni was estimated colorimetrically.[24] While the thickness of the coating was estimated by Faraday's law, it was verified by measurements, using a Digital Thickness Meter (model M & C; Coatmeasure). A close agreement was found between calculated and measured values.

Results and discussion

Cyclic voltammetry study

It was observed that THC in combination with CA has a significant effect on the homogeneity and brightness of the coatings. When no CA was added, the electrochemical oxidation curve showed multiple peaks, as shown in Fig. 1*a*. This corresponds to the dissolution of the metals in the alloy via different intermediate phases.[25] When only CA was added, a slight change in the shape of the voltammogram was found (Fig. 1*b*), indicating that CA has involved in complexation of metal ions. Furthermore, when THC was added, the shape of the voltammogram changed drastically, with one major peak at −0·68 V and one minor peak at −0·28 V, corresponding to dissolution of different phases of the alloy (Fig. 1*c*). Finally, when CA and THC were added in combination, the intensities of the first and second peaks increased, with slight distortion to the right (Fig. 1*d*). Hence, it may be inferred that THC improves the deposit character, by forming a complex with metal ions, and CA acts as a brightener by becoming incorporated into the crystal lattice by the action of the THC.

X-ray diffraction (XRD) study

The corrosion resistance of the Zn–Ni alloy depends practically on its phase structure, depending on the percentage of Ni in the deposit.[26] X-ray diffraction patterns of Zn–Ni alloy coatings as a function of deposition CD are shown in Fig. 2. It may be observed that the intensity of the peak corresponding to Zn
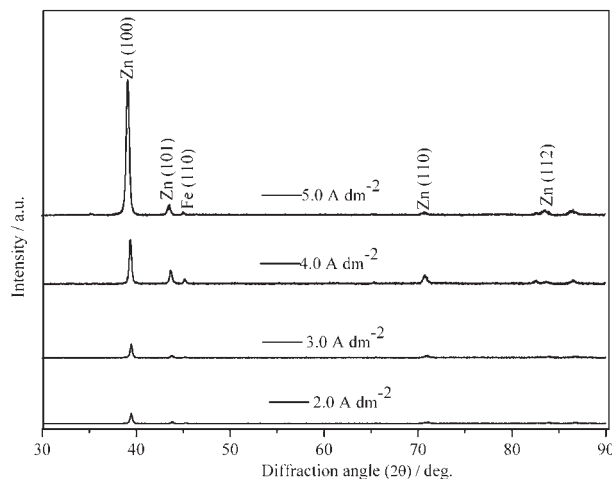
2 X-ray diffraction profiles of Zn–Ni alloy electrodeposits, developed from optimal bath at different CDs

(100) increases progressively with CD (from 2·0 to 5·0 A dm⁻²), and has become most prominent at 5·0 A dm⁻². In addition, peaks corresponding to Zn (101), Zn (110) and Zn (112) may be distinctly observed at 5·0 A dm⁻², compared with the deposit produced at 3·0 A dm⁻². Thus, the XRD study clearly indicates that a significant change in the corrosion resistance of CMA (Zn–Ni)$_{3·0/5·0/300}$ coatings is the consequence of change in the phase structures of the coatings in alternate layers, i.e. at 3·0 and 5·0 A dm⁻², in the present study.

Partial CD study

The partial CDs i_p for deposition of Zn and Ni at different CDs has been calculated using the equation

$$i_i = \frac{w}{At} \frac{c_i \, n_i \, F}{M_i} \tag{1}$$

where w is the measured mass of the deposit (g), A is the surface area of the cathode (cm²), t is the deposition time (s), c_i is the weight fraction of the element in the alloy deposit, n_i is the number of electrons transferred per atom of each metal, M_i is the atomic mass of that element and F is the Faraday's constant (96 485 C/equivalent). i_p is the partial CD of element (A cm⁻²). It was found that, in the case of both metals, the i_p increased as the applied CD was increased up to 4·0 A dm⁻², and the i_p of Zn was found to increase more rapidly than Ni, possibly due to its preferential deposition. However, at high CD (>4·0 A dm⁻²), the partial CD for deposition of Zn decreased, with preferential deposition of Ni. Thus, it was found that the depositions of the two metals at extreme ends of CD are at different mass transportation limits, which is key for the modulation of composition in multilayer coatings.

Monolithic Zn–Ni coating

The wide spectrum of Zn–Ni alloy formed on the preliminary Hull cell panels showed that CD plays an important role in deciding the properties of the deposit. The effects of CD on wt-%Ni, thickness, corrosion rate (CR) and appearance of the coatings are reported in Table 1. The corrosion data showed that monolithic alloy at 3·0 A dm⁻² gives the lowest CR (6·0×10⁻²

mm/year) with bright appearance and has been taken as optimal.

Cyclic multilayer alloy coatings

Optimisation of CCCDs

As mentioned earlier in the case of alloys of Zn–M, even a small change in the concentration of the latter may result in significant amending of properties due to the change in the phase structure. Initially, multilayer alloy coatings having 10 layers were developed at different sets of CCCDs to increase their corrosion resistance. Among the various sets tried, the lowest CR was measured in the coatings produced with difference of $2 \cdot 0$ A dm^{-2} between CCCDs (i.e. at $3 \cdot 0/5 \cdot 0$ A dm^{-2} and $2 \cdot 0/4 \cdot 0$ A dm^{-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 section and given in the data in Table 2.

Optimisation of overall number of layers

The properties of CMA electrodeposits, including their corrosion resistance, may often be improved by increasing the total number of layers (usually, up to an optimal number), as long as the adhesion between layers does not deteriorate. Thus, at the optimal combination of CDs ($3 \cdot 0/5 \cdot 0$ A dm^{-2}), CMA coatings with 10, 20, 60, 120, 300, 400 and 600 layers were produced. As observed in Table 2, the CR decreased drastically as the number of layers increased only up to 300 layers, and then increased. The lowest CR ($0 \cdot 11 \times 10^{-2}$ mm/year) was obtained for a multilayer coating, represented by the $(Zn–Ni)_{3 \cdot 0/5 \cdot 0/300}$ configuration, while for the same number of layers at CCCDs of $2 \cdot 0/4 \cdot 0$ A dm^{-2}, the CR was $0 \cdot 63 \times 10^{-2}$ mm/ year, which is higher. Hence, the CMA $(Zn–Ni)_{3 \cdot 0/5 \cdot 0/300}$ configuration is taken as optimal. From the total

observed thickness (~ 15 μm), the average thickness of each layer in the $(Zn–Ni)_{2 \cdot 0/5 \cdot 0/300}$ coating was calculated. At this configuration, the average thickness of each layer is found to be ~ 50 nm (Table 2).

The CR was found to increase at a higher degree of layering (i.e. >300), as shown in Table 2. This may be attributed to the shorter relaxation time for redistribution of metal ions at the diffusion layer during plating.[27] The phenomenon may be explained as follows: during plating, metal ions from the bulk of the electrolyte diffuse towards the cathode and get discharged as metal atom, and this process of diffusion is mainly controlled by the cathode CD. As the number of layers increases, the time for the deposition of each layer, say, $(Zn–Ni)_1$ is small (as the total time for deposition remains the same at 10 min). At a higher degree of layering, there is not sufficient time for metal ions to relax (against diffusion under given CD) and to form deposit on cathode with modulation in composition. As a result, at a higher degree of layering modulation in composition is not likely to take place. In other words, under these conditions, the CMA deposit is tending towards the monolithic, showing lower corrosion resistance.
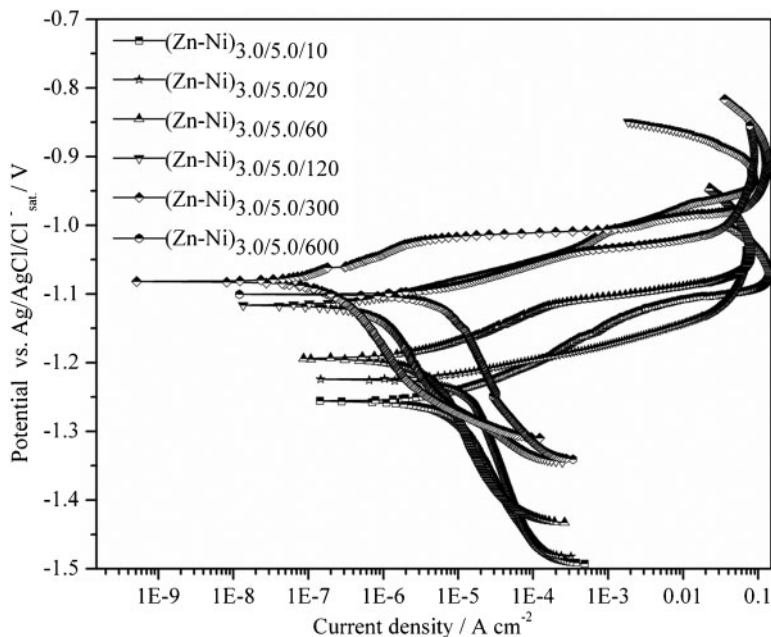
Corrosion study

Tafel polarisation study

The polarisation behaviours of $(Zn–Ni)_{3 \cdot 0/5 \cdot 0}$ CMA coatings with different degrees of layering (representative only) are shown in Fig. 3. It was observed that the corrosion resistance of the coatings increased with the number of layers as evidenced by their i_{corr} values (Table 2). The increase in E_{corr} value with increasing number of layers showed that the CMA coatings provide sacrificial anodic protection to the substrate. Furthermore, the progressive decrease in corrosion current i_{corr} with the number of layers indicated that

**Table 1 Effect of CD on deposit characteristics of monolithic Zn–Ni alloy**

CD/ A dm^{-2}	Weight percentage of Ni/wt-%	Thickness/ μm	Vickers hardness/ HV0·1	E_{corr} (Ag/AgCl/ KCl$_{sat}$)/V	i_{corr}/μA cm^{-2}	CR/ $\times 10^{-2}$ mm/year	Appearance of the deposit
1. 0	2·3	6·2	131	−1·24	13·30	19·3	Greyish white
2. 0	1·5	11·8	146	−1·26	5·64	8·2	Bright
3. 0	1·9	19·2	160	−1·32	4·13	6·0	Bright
4·0	2·7	24·8	180	−1·24	6·34	9·3	Bright
5·0	9·5	28·3	198	−1·36	5·14	9·9	Porous Bright

Table 2 Effect of overall number of layering on corrosion properties of Zn–Ni CMA coatings obtained with 3·0/ 5·0 A dm^{-2} and 2·0/4·0 A dm^{-2} CCCDs

Coating configuration	No. of layers	Deposition time for each layer/s	Average thickness of layer/nm	E_{corr} (Ag/AgCl/KCl$_{sat}$)/V	i_{corr}/μA cm^{-2}	CR/ $\times 10^{-2}$ mm/year
$(Zn–Ni)_{3 \cdot 0/5 \cdot 0}$	10	60	1500	−1·25	2·11	3·07
	20	30	750	−1·22	2·08	3·03
	60	10	250	−1·19	1·07	1·57
	120	5	125	−1·11	0·19	0·29
	300	2	50	−1·08	0·07	0·11
	400	1·5	37·5	−1·10	1·29	1·89
	600	1	25	−1·10	2·33	1·93
$(Zn–Ni)_{2 \cdot 0/4 \cdot 0}$	10	60	1500	1·12	4·95	7·21
	20	30	750	1·32	4·11	5·99
	60	10	250	1·30	1·00	1·46
	120	5	125	1·26	0·75	1·09
	300	2	50	1·32	0·44	0·63
	400	1·5	37·5	1·32	1·85	1·24
	600	1	25	1·32	2·93	1·36

3 Potentiodynamic polarisation curves of CMA (Zn–Ni)$_{3\cdot0/5\cdot0}$ coatings with different numbers of layers (at 1 mV s^{-1})
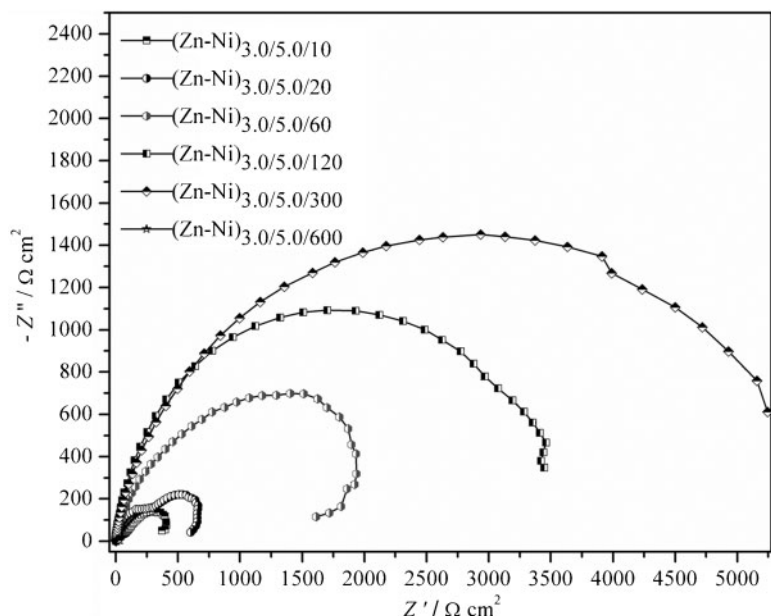
4 Nyquist plots of CMA Zn–Ni coatings with (Zn–Ni)$_{3\cdot0/5\cdot0}$ configuration having different numbers of layers

the improved corrosion resistance is due to layering of alloys with distinct properties. It may be observed that the passivation current of the Zn–Ni coatings remained almost the same, regardless of the number of layers. This shows that the improved corrosion resistance is not due to the corrosion product formed, but due to the delayed, or blocked path of the corrosion agent due to layering, as will be discussed later. The polarisation curve shown in Fig. 3 demonstrates that the CMA coating with (Zn–Ni)$_{3\cdot0/5\cdot0/300}$ configuration is more corrosion resistant than all other coatings.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy, also referred to as AC impedance spectroscopy, is a suitable technique to gain valuable information on the capacitance behaviour of the double layer responsible for

improved corrosion resistance of the coatings and behaviour of inhibitors. In this technique, it is common to plot the data as imaginary impedance versus real impedance with provision to distinguish the polarisation resistance contribution R_p from the solution resistance R_s. These plots are often called Nyquist diagrams. Nyquist responses (representative only) of (Zn–Ni)$_{3\cdot0/5\cdot0}$ coatings with different numbers of layers are shown in Fig. 4. The impedance signals showed that the polarisation resistance of the coatings increased progressively with the number of layers only up to 300 layers, and then decreased (i.e. >300).

Comparison between monolithic and CMA Zn–Ni coatings

The CRs of monolithic Zn–Ni alloy, at $3\cdot0$ A dm^{-2} and CMA (Zn–Ni)$_{3\cdot0/5\cdot0/300}$ coatings, developed under optimal conditions from the same bath are given in Tables 1 and 2
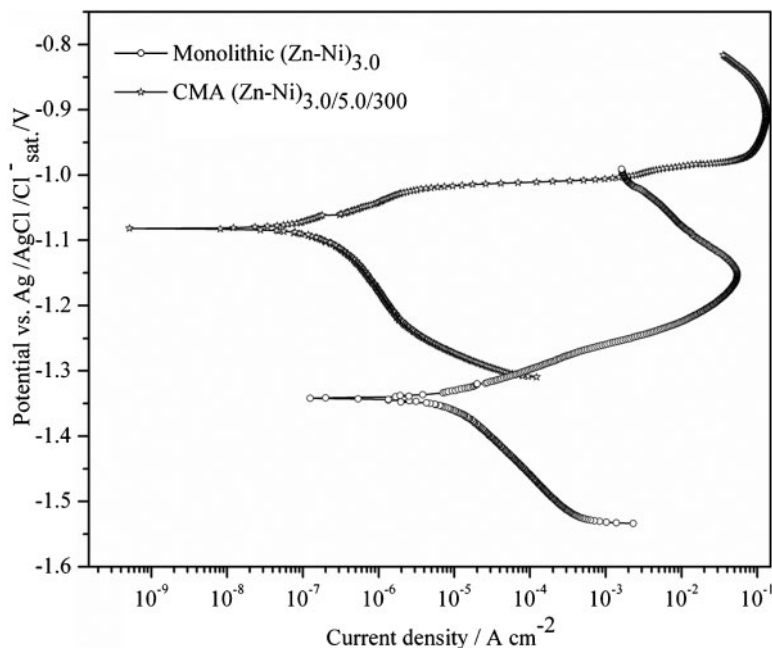
5 Comparison of polarisation behaviours of monolithic (Zn–Ni)$_{3\cdot0}$ alloy and CMA (Zn–Ni)$_{3\cdot0/5\cdot0}$ coatings of same thickness
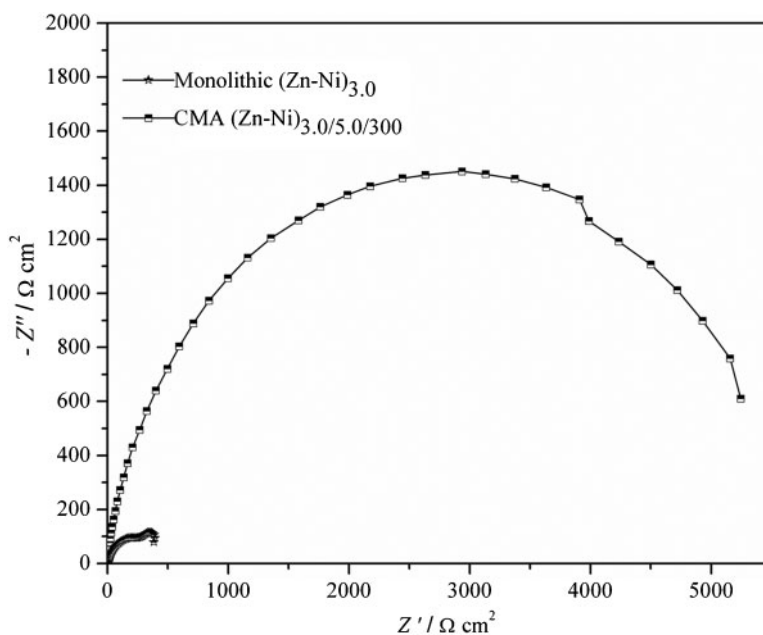

6 Comparison of Nyquist behaviours for monolithic (Zn–Ni)$_{3\cdot0}$ alloy and CMA (Zn–Ni)$_{3\cdot0/5\cdot0}$ coatings of same thickness

respectively. It was found that the CMA (Zn–Ni) coating, having 300 layers, deposited at 3·0 and 5·0 A dm^{-2}, showed the least CR ($0\cdot11\times10^{-2}$ mm/year) compared with that of monolithic alloy ($6\cdot0\times10^{-2}$ mm/year) of the same thickness. The relative response from the potentio-dynamic polarisation and electrochemical impedance spectroscopy studies of monolithic Zn–Ni, represented as (Zn–Ni)$_{3\cdot0}$ and (Zn–Ni)$_{3\cdot0/5\cdot0/300}$ coatings, are shown in Figs. 5 and 6 respectively. Nyquist behaviours showed that significant decrease in CR of the CMA coating, in relation to the monolithic alloy is due to the large reactance of the electrical double layer capacitor, at the interface of the base metal and the medium. The high corrosion resistance of CMA coatings can be explained by failures like pores, crevices occurring in one layer being blocked or neutralised by the successively deposited coating layers, and thus the path of the corrosion agent is delayed or blocked. The improved corrosion resistance afforded by the CMA coating can also be explained in terms of the formation of alternate layers of alloys with low and high wt-%Ni.[28] A small compositional change in layers has brought a significant change in the phase structure of the alloys, as evidenced by the XRD study.

Scanning electron microscopy study

The formation of alternate layers of alloys having distinctive properties was confirmed by SEM. A cross-sectional view of (Zn–Ni)$_{3\cdot0/5\cdot0/10}$ is shown in Fig. 7a. The poor contrast may be due to the small difference in chemical composition (1·9 wt-%Ni at 3·0 A dm^{-2} and 9·5 wt-%Ni at 5·0 A dm^{-2}) of the alloys in each layer. Inspection of the microscopic appearance of the surface,
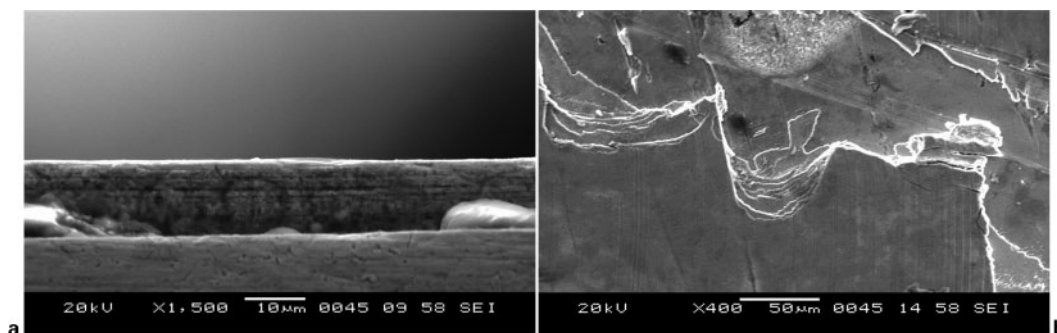
a cross-sectional view and *b* after corrosion test displaying layer formation
7 Image (SEM) of CMA (Zn–Ni)$_{3/5/10}$ coating

after corrosion tests, was used to demonstrate the formation of successive layers of alloys, during deposition, and to understand the reason for improved corrosion resistance. By subjecting the coating with (Zn–Ni)$_{3\cdot0/5\cdot0/10}$ configuration to dissolution by the corrosion test, a region displaying the layers, was obtained. This has been accomplished by the anodic polarisation up to $+250$ mV(OCP) in 5%NaCl. Then the corroded specimen was washed with distilled water and examined under SEM. Figure 7*b* exhibits the surface after the corrosion test. Short *et al.* have reported that the improved corrosion resistances of Zn–Ni coatings are due to dezincification.[29] Hence, it may be inferred that the improved corrosion resistance afforded by the CMA coating is due to the selective dissolution of metals in alternate layers of alloys, having low and high wt-%Ni in the deposit.

Conclusions

The following conclusions were drawn from the present study.

1. The CMA coatings of Zn–Ni have been developed on mild steel by appropriate manipulation of square current pulses of different CDs and number of layers using the single bath technique.

2. A CV study demonstrated that additives CA and THC improve the deposit character, by complexing metal ions.

3. The CMA (Zn–Ni) coating, having 300 layers, deposited at 3·0 and 5·0 A dm^{-2} was found to be $\sim$54 times more corrosion resistant than the monolithic alloy of the same thickness.

4. Corrosion resistance of CMA coating increased with the number of layers only up to a certain optimal level (300 layers) and then decreased. This may be attributed to less relaxation time for redistribution of metal ions (Zn^{+2} and Ni^{+2}) at the diffusion layer, during deposition. In other words, at higher layering, the CMA coating tends to become monolithic.

5. The XRD study revealed that the improved corrosion resistance afforded by the CMA coating is due to the formation of alternate layers of alloys, having different phase structures.

6. The SEM analysis confirmed the formation of multilayers during deposition, and showed evidence of the enhanced protection, by successively deposited alloy coating layers having different extents of pores and crevices.

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