

Development of anti-corrosive multi-layered coatings of zinc-nickel alloy

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Abstract

Purpose – The purpose of this paper is to develop and optimize anti-corrosive multi-layered coatings of zinc-nickel alloy on carbon steel.

Design/methodology/approach – A variety of composition-modulated multi-layer alloy (CMMA) coatings of zinc-nickel were developed on a carbon steel substrate by cyclic changes in cathode current during electrodeposition, coupled with variation of the thicknesses of the individual layers. The corrosion behavior of the coatings was studied in 5 percent NaCl solution by electrochemical methods. Cyclic cathode current densities (CCCDs) and the number of alloy layers were optimized for highest performance of the coatings against corrosion. The factors responsible for improved corrosion resistance were analyzed in terms of change in the intrinsic electrical properties of the capacitance value at the electrical double layer that was associated with micro/nanometric layering. The formation of the semi-conductive surface film, which was responsible for the improved corrosion resistance, was supported by a Mott-Schottky plot and the cyclic polarization study. The formation of multi-layered deposit and the mechanism of corrosion degradation of the coating were analyzed using scanning electron microscopy.

Findings – CMMA coatings with an optimal configuration of (Zn-Ni)_{2,0/4,0/300} showed ~35 times better corrosion resistance compared to a monolithic (Zn-Ni)_{3,0} alloy coating of the same thickness. The peak performance was attributed to the change in intrinsic electrical properties of the coating and this conclusion was supported by dielectric spectroscopy.

Originality/value – The paper describes the optimization of CCCD and the number of deposited layers by development of electrolytic deposition of anti-corrosive multi-layered zinc-nickel coatings from a single plating technique.

Keywords Steel, Corrosion resistance, Alloys, Coatings, Spectroscopy

Paper type Research paper

1. Introduction

Composition-modulated multi-layer alloy (CMMA) coatings are those in which alloy composition can be varied, either as a step function to produce multilayers, or gradually changed to provide a graded compositional coatings (Jensen *et al.*, 1998). CMMA coating systems are relatively new and are now gradually gaining interest amongst researchers because these layered structure coatings possess improved properties or novel phenomena such as increased mechanical strength, micro-hardness, very high magnetoresistance and corrosion resistance (Bull and Jones, 1996; Gabe and Green, 1998; Nabiyouni *et al.*, 2002; Kalantary *et al.*, 1998; Chawa *et al.*, 1998). CMMA coatings consist of a large number of thin layers of alloys having different composition. Each layer has its own distinctive role in achieving the preferred performance (Ivanov *et al.*, 2002). The ability to achieve these objectives by electrodeposition depends upon the solution chemistry and the operating parameters. During recent decades, electrodeposition of CMMA coatings for the protection of steel substrates from corrosion has been investigated extensively. Kalantary *et al.* (1998), obtained zinc-nickel CMMA coatings with an overall thickness of 8 μm by electrodepositing alternate layers of zinc and nickel from a zinc sulfate and a nickel sulfate electrolytes. Chawa *et al.*

(1998) reported that the corrosion resistance of zinc-nickel CMMA coatings, electrodeposited from zinc sulfate and nickel sulfamate baths, was better than that of zinc or nickel monolithic coatings of similar thickness. Ivanov *et al.* (2002) studied the corrosion performance of CMMA Zn-Ni coatings with total thickness of 12 μm obtained by successive deposition of individual metals using a double bath technique. Later, attempts were made to electrodeposit CMMA coatings using a single bath technique (SBT), i.e. from a bath having ions of both metals (Gabe, 1994; Kalantary *et al.*, 1995; Ivanov and Kirilova, 2003; Feia and Wilcox, 2006). Relatively few reports have reported evidence describing the enhanced corrosion resistance afforded by zinc-nickel CMMA coatings. Moreover, very little work has been reported with regard to optimization of deposition conditions and the number of layers for electrolytic synthesis of micro/nano-structured multi-layer coatings of zinc-nickel alloy for better corrosion resistance. The present work discusses the optimization of cyclic cathode current densities (CCCDs) and number of zinc-nickel CMMA coating deposition layers of for peak performance against corrosion from a single plating bath. The improved corrosion resistance of CMMA coatings is discussed in terms of the changed dielectric properties of such coatings.

2. Methodology

2.1 Materials

Initial studies focused on the optimization of an electrolytic bath using the standard Hull cell method. The bath

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composition was: 15 g/L ZnO, 60 g/L NiCl₂, 150 g/L NH₄Cl, 20 g/L boric acid, 10 g/L citric acid and 2 g/L thiamine hydrochloride (THC). An optimum pH of 3 and a temperature of 30 °C were maintained throughout the study. The addition of a small amount of THC was found to deliver a significant improvement on the brightness and homogeneity of the deposit. The electrolyte was prepared using LR-grade chemicals and distilled water. Steel panels with an active surface of 7.5 cm² were used as cathodes after suitable pretreatment. A PVC cell of 250 cm³ capacity was used for the electroplating work, with cathode-anode space of ~ 5 cm.

2.2 Development of monolithic and multi-layered coatings

Zn-Ni alloy coatings (monolithic and CMMA) were carried out galvanostatically using a sophisticated power supply (N6705A, Agilent Technologies). All depositions were made for 10 min (~12 μm thickness) for comparison purposes. Deposition conditions were kept constant, except for current density (CD). Monolithic Zn-Ni alloys were developed at a specific cathode CD and CMMA coatings were developed by applying alternately the predetermined cathode CDs, by careful control of the power supply. Laminar deposits with alternate layers of alloys (with different composition) are represented as: (Zn-Ni)_{1/2/n} (where 1 and 2 indicate the first and second cathode CDs, respectively, and “n” represents the number of layers formed during total plating time, i.e. 10 min).

2.3 Electrochemical tests

2.3.1 Corrosion study

All electrochemical tests were carried out using a potentiostat/galvanostat (VersaSTAT-3, Princeton Applied Research) in a three-electrode configuration. All electrochemical potentials referred in this work are indicated relative to Ag, AgCl/KCl_{sat} electrode. The working electrode was the test specimen. Platinum foil was used as the counter electrode. The corrosion behavior of coatings was measured by electrochemical DC and AC techniques. A 5 percent NaCl solution (open to air at 28 ± 2 °C) was used as the corrosive medium. Potentiodynamic polarization studies were carried out using a potential ramp of ± 250 mV from open-circuit potential at scan rate of 1 mVs⁻¹. Corrosion rates (CRs) were determined by the Tafel extrapolation method. The corrosion resistance afforded by the CMMA coatings was evaluated using cyclic polarization studies over a potential range of -1.3V to -0.2V. Electrochemical impedance measurements were made over the frequency range 100 KHz-5 mHz using a perturbation of 10 mV.

2.3.2 Mott-Schottky plot

Data on the electronic properties of the CMMA coating were obtained by evaluation of the capacitance of the electrical double layer (EDL). The relationship between the capacitance C, and the potential drop in a semiconductor can be written in the form of Mott-Schottky equation (Morrison, 1980):

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N} (E - E_{fb} - kT/e) \quad (1)$$

where e is the elementary charge (+ e for electrons and - e for holes), ε is the dielectric constant, ε₀ the permittivity in vacuum (8.854 × 10⁻¹² Fm⁻¹), N is the acceptor or

donor concentration, E is the applied potential and E_{fb}, the flat band potential.

The donor or acceptor concentrations can be estimated from the slopes of the straight lines obtained. The double-layer capacitance measurements were carried out at 100 Hz within the potential range from +0.5 to -0.5 V.

2.3.3 Dielectric study

The relative permittivity, ε_r of the Zn-Ni alloy coatings was calculated from film thickness, δ and area, A, and coating capacitance C, using the equation:

$$\epsilon_r = \frac{C\delta}{A\epsilon_0} \quad (2)$$

The improved corrosion resistance of the CMMA coatings was evaluated in terms of the effect of the time dependent electric field (i.e. frequency).

2.4 SEM analysis

The formation of multi-layer coating and the mechanism of corrosion attack were analyzed using scanning electron microscopy (SEM, model JSM-6380 LA from JEOL, Japan). Examination of the microscopic appearance of the surface after the corrosion test was used to investigate the reasons for the increased corrosion resistance of the CMMA coatings. The corroded specimen was washed with distilled water and then examined under SEM.

2.5 Analysis of coatings

The wt% Ni present in the monolithic Zn-Ni alloy deposited at different CDs was estimated spectrophotometrically by stripping the deposit into dilute HCl (Vogel, 1951). The thickness of deposits was assessed using Faradays law and cross correlated using a digital thickness tester (Coatmeasure M&C, ISO-17025/2005).

3. Results

3.1 Corrosion behavior of monolithic and CMMA coatings

Effect of CD on wt% Ni, thickness, corrosion resistance and the appearance of the coatings are summarized in Table I. CMMA Zn-Ni coatings having ten layers (five bi-layers) were developed at different sets of CCCD'. Those (such as 2.0/4.0, 2.0/6.0 and 4.0/6.0 A/dm²) at which the coating showed least corrosion attack was considered to be optimal CCCD's and the results are presented in Table II. The corrosion resistance of the coatings was further increased by nano/micrometric layering (such as 10, 20, 60, 120, 300 and 600 layers) and the corresponding CRs are shown also in Table II. The corrosion resistance performance of CMMA (Zn-Ni)_{2,0/4,0} coatings was observed to be more encouraging than were other sets of CCCD's, as reported in Table III. The potentiodynamic polarization results and impedance responses of the coatings having different number of layers at CCCD's of 2.0/4.0 A/dm² are shown in Figures 1 and 2, respectively. The relative rates of corrosion for coating systems having (Zn-Ni)_{3,0} and CMMA (Zn-Ni)_{2,0/4,0/300} configurations (both optimized) are given in Table IV, and corresponding impedance responses are shown in Figure 3.

Table I Effect of CD on the deposit characters of monolithic Zn-Ni alloy

c.d./A/dm ²	Wt% Ni	Thickness/ μ m	E _{corr} /V vs Ag,AgCl/KCl _{sat}	I _{corr} / μ A/cm ²	CR/ $\times 10^{-2}$ mmy ⁻¹	Nature of the deposit
2.0	5.70	8.5	-1.306	11.29	15.46	Semi-bright
3.0	3.16	10.8	-1.245	11.08	15.18	Bright
4.0	3.23	12.4	-1.225	13.23	18.13	Bright
5.0	3.81	15.9	-1.196	14.83	20.31	Semi-bright
6.0	4.00	16.1	-1.264	14.94	22.16	Semi-bright
7.0	5.05	16.8	-1.344	18.3	25.06	Grayish bright
8.0	5.13	17.5	-1.060	22.29	30.52	Grayish bright

Table II CR of CMMA Zn-Ni coatings at different set of CCCD's

CCCD's/A/dm ²	E _{corr} /V vs Ag,AgCl/KCl _{sat}	I _{corr} / μ A/cm ²	CR/ $\times 10^{-2}$ mmy ⁻¹
CMMA Zn-Ni coatings developed at difference of 2.0 A/dm² between CCCD's			
(Zn-Ni) _{2.0/4.0/10}	-1.256	7.363	10.92
(Zn-Ni) _{6.0/8.0/10}	-1.244	8.665	12.84
CMMA Zn-Ni coatings developed at difference of 4.0 A/dm² between CCCD's			
(Zn-Ni) _{2.0/6.0/10}	-1.286	16.92	10.10

Note: With ten layers

Table III Decrease in CR of CMMA coatings with increase in the number of layers

CD/A/dm ²	No. of layers	E _{corr} /V vs Ag,AgCl/KCl _{sat}	I _{corr} / μ A/cm ²	CR/ $\times 10^{-2}$ mmy ⁻¹
Optimization of layer thickness at CCCD's of 2.0 – 4.0 A/dm²				
(Zn-Ni) _{2.0/4.0/10}		-1.256	7.363	10.92
(Zn-Ni) _{2.0/4.0/20}		-1.225	4.899	7.26
(Zn-Ni) _{2.0/4.0/60}		-1.320	0.972	1.44
(Zn-Ni) _{2.0/4.0/120}		-1.331	0.546	0.74
(Zn-Ni) _{2.0/4.0/300}		-1.348	0.318	0.45
Optimization of layer thickness at CCCD's 2.0 – 6.0 A/dm²				
(Zn-Ni) _{2.0/6.0/10}		-1.286	16.922	10.10
(Zn-Ni) _{2.0/6.0/20}		-1.273	5.967	8.85
(Zn-Ni) _{2.0/6.0/60}		-1.241	5.145	7.63
(Zn-Ni) _{2.0/6.0/120}		-1.288	3.869	5.74
(Zn-Ni) _{2.0/6.0/300}		-1.048	0.646	2.95
(Zn-Ni) _{2.0/6.0/600}		-1.372	0.379	1.93
Optimization of layer thickness at CCCD's 6.0 – 8.0 A/dm²				
(Zn-Ni) _{6.0/8.0/10}		-1.244	8.665	12.84
(Zn-Ni) _{6.0/8.0/20}		-0.951	1.163	2.72
(Zn-Ni) _{6.0/8.0/60}		-1.296	0.645	1.95

3.2 Cyclic polarization study

The cyclic polarization curve shown in Figure 4 illustrates that during the forward scan, the value of CD moved from negative to positive, which showed that the oxidizing reaction of passive film occurred with increase in potential. During backward scan, the value of CD moved from positive to negative, indicating that the reducing reaction of the high-valence oxide in the passive film occurred with the a decrease in potential.

Figure 1 Potentiodynamic polarization curves of CMMA (Zn-Ni)_{2.0/4.0} coating with different numbers of layers

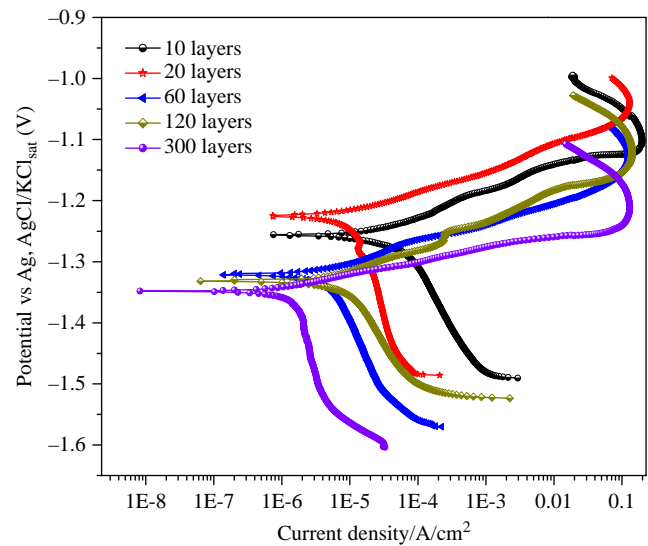
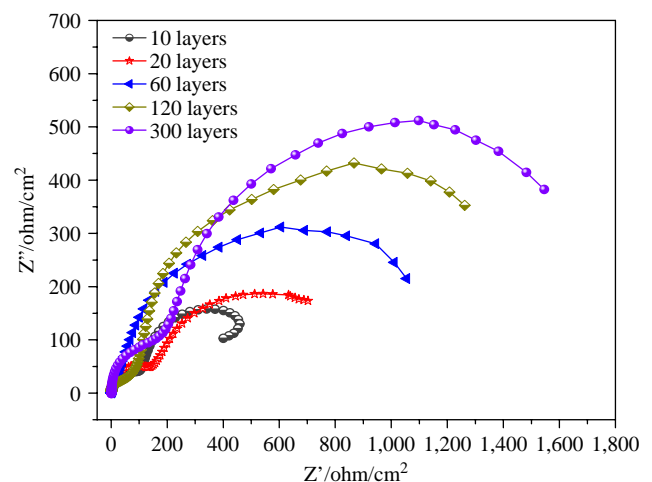


Figure 2 Real versus imaginary resistance values of CMMA (Zn-Ni)_{2.0/4.0} coatings with different number of layers measured as function of frequency



3.3 Mott-Schottky plot and dielectric study

The significantly lower CR that was observed with optimal configuration CMMA (Zn-Ni)_{2.0/4.0/300} was attributed to the semiconductor properties of the film (i.e. the coatings) at the interface, as evidenced by the Mott-Schottky plot shown in Figure 5. Further, the straight line with positive slope reveals

Table IV Comparison of CRs of (Zn-Ni)_{3.0} (monolithic) and CMMA (Zn-Ni)_{2.0/4.0/300} coatings of same thickness

Coating configuration	E_{corr}/V vs Ag,AgCl/KCl _{sat}	$i_{corr}/\mu A/cm^2$	CR/ $\times 10^{-2}$ mmy ⁻¹
(Zn-Ni) _{3.0} (monolithic)	-1.196	11.02	15.18
CMMA (Zn-Ni) _{2.0/4.0/300}	-1.348	0.31	0.43

Figure 3 Nyquist response for CMMA (Zn-Ni)_{2.0/4.0/300} and monolithic (Zn-Ni)_{3.0} coatings of same thickness

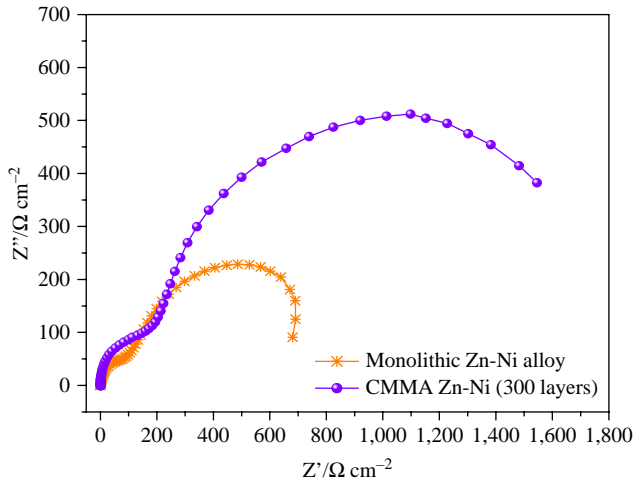
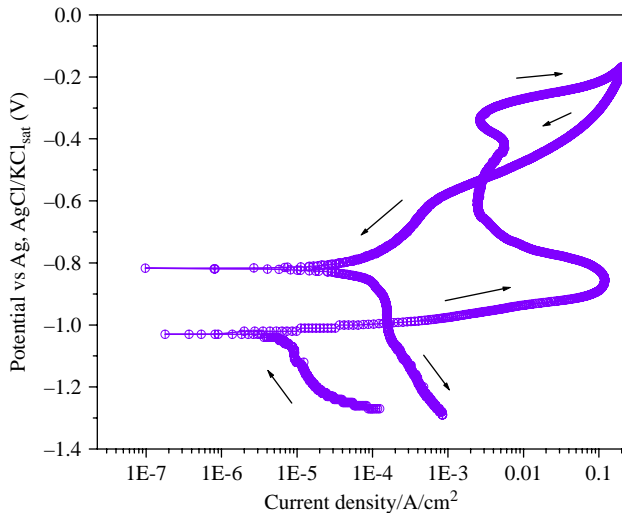


Figure 4 Cyclic polarization curve of CMMA (Zn-Ni)_{2.0/4.0/300} coating



that the protective semiconductor layer operative at the interface is n-type in nature. The decrease of the relative permittivity of the CMMA coatings with increase in number of layers is shown in Figure 6.

3.4 SEM study

The formation of multilayers in the CMMA coating was confirmed by the SEM study. A cross-sectional view of the coating with (Zn-Ni)_{2.0/4.0/30} configuration is shown in Figure 7(a). Figure 7(b) shows the decayed alternate layers (formed during process of CMMA deposition), after corrosion testing.

Figure 5 Mott-Schottky plot for CMMA (Zn-Ni)_{2.0/4.0/300} coating

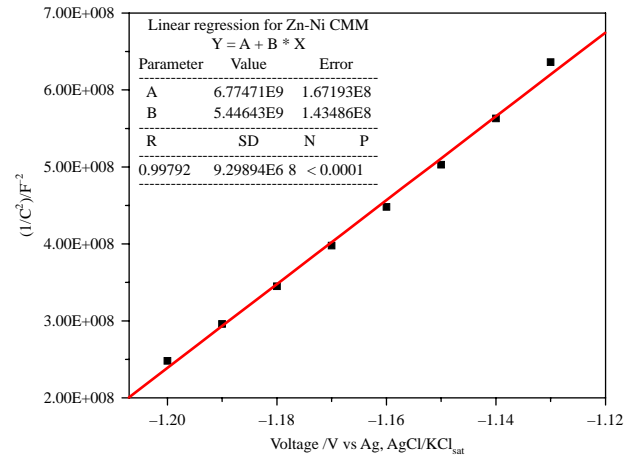
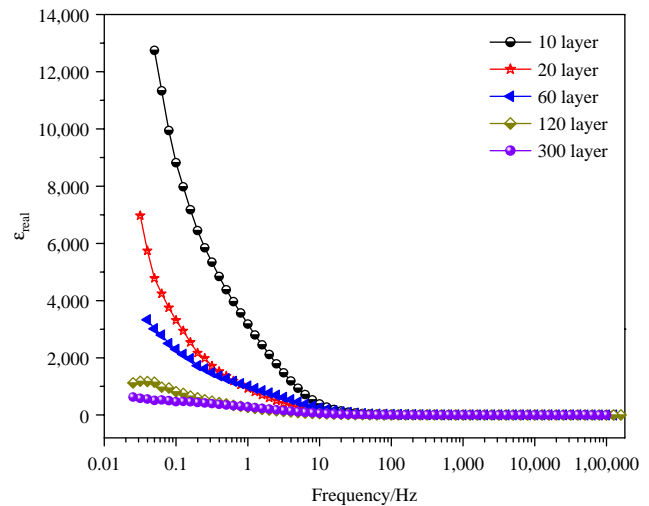


Figure 6 Relative permittivity of CMMA (Zn-Ni)_{2.0/4.0} coatings with varying number of layers as function of frequency

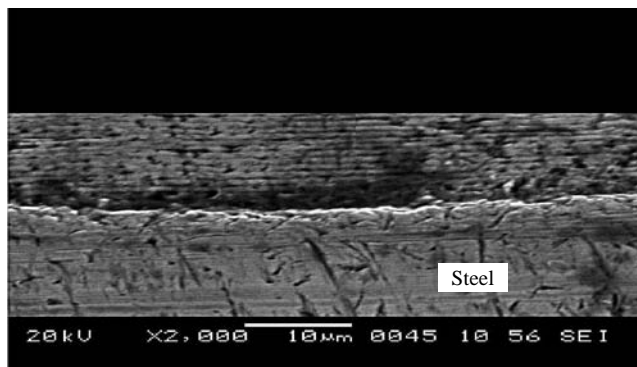


3.5 Analysis of monolithic alloy

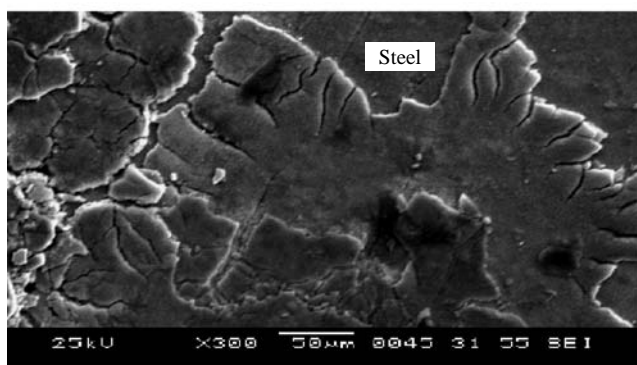
It was found that the wt% Ni in the deposit increased slightly with increasing CD, as shown in Table I. This was due to the fact that at high CD, the more readily deposited metal (zinc) is depleted at the cathode site, which is characteristic feature of anomalous codeposition observed in Zn-M (where M = Ni, Co and Fe) alloys (Brenner, 1963). However, at 2.0 Amp/dm², the Ni content was ~ 5.7 percent. This may be due to less hydrogen formation, which is unable to cause large alkalization effects (a hydroxide suppression mechanism) (Horans, 1981). The thickness of deposit was observed to exhibit direct dependency on the CD, as shown in Table I. The observed dependency of the thickness with CD is due to the adsorption of metal hydroxide at the cathode (caused by a steady increase in pH due to evolution of hydrogen gas).

4. Discussion

The wide spectrum of Zn-Ni alloys formed on the Hull cell panels showed that CD plays an important role in deciding

Figure 7 SEM images of CMMA (Zn-Ni)_{2.0/4.0/30} coatings

(a)



(b)

Notes: (a) Cross-sectional view of alloy having 30 layers; (b) CMMA (Zn-Ni)_{2.0/4.0/4} after corrosion test

the properties of the deposit. The corrosion data showed that the monolithic Zn-Ni alloy formed at 3.0 A/dm², showed lowest CR ($15.18 \times 10^{-2} \text{ mmy}^{-1}$) and had a bright appearance. This was taken as its optimal low CR.

It is well established that, in the case of alloys of Zn-M (where M = Ni, Co and Fe), even a small change in the concentration of the latter may result in significant change in coating properties, due to changes in the phase structure of the deposit. Thus, by precise control of the CCCD's it is possible to develop alternate layers of alloys with different compositions and, consequently, different properties. Table II demonstrates the effect of the CCCD's on the corrosion behavior of the coatings. Among the various sets tried, the lower CR was measured in coatings produced at differences of 2.0 and 4.0 A/dm² between CCCD's, as shown in Table II.

The metallurgical properties of CMMA coatings, including their corrosion resistance, often may be increased substantially by increasing the degree of layering (usually, up to an optimal limit), without sacrificing the demarcation between each layers. The CRs of coatings were observed to decrease consistent with the number of layers in each set of CCCD's, as shown in Table III. At 2.0/4.0 A/dm², the coating with 300 layers showed the minimum CR of $0.45 \times 10^{-2} \text{ mmy}^{-1}$, as opposed to $15.18 \times 10^{-2} \text{ mmy}^{-1}$ for monolithic Zn-Ni alloy coatings (shown in Table I). Though there was also a substantial decrease in CR with layering at other set of CCCD's, (i.e. at 2.0/6.0 A/dm² with 600 layers and at

6.0/8.0 A/dm² with 60 layers as shown in Table III), the result pertaining to 2.0/4.0 A/dm² was more encouraging in terms of the homogeneity and brightness of the deposit. However, an effort to increase corrosion resistance further by increasing the number of layers in each set of CCCD's resulted in an increase in CR, which may have been due to the diffusion of individual layers (i.e. a tendency towards the formation of a monolithic coating). Hence, (Zn-Ni)_{2.0/4.0/300} has been proposed as the optimal configuration of CMMA coating from the proposed bath, with individual layer thickness of ~ 40 nm, for highest performance against corrosion.

It was observed that the corrosion resistance of the coatings increased with number of layers in each set of CCCDs, as evidenced by their i_{corr} values (Table III). The decrease in E_{corr} value with increasing number of layers showed that the CMMA coatings provided sacrificial anodic protection to the substrate. Furthermore, the progressive decrease of corrosion current (i_{corr}) with the increasing number of layers, as shown in Figure 1, indicated that the improved corrosion resistance was due to the layered alloys having distinctive properties. The CMMA coating with a (Zn-Ni)_{2.0/4.0/300} configuration was found to be the most corrosion resistant, as is evident from Table III.

The impedance measurement technique is useful to gain information about the capacitance behavior of the EDL the improved corrosion resistance of the coatings, and the behavior of inhibitors (Craig, 1991). It is common to plot the data as imaginary impedance vs real impedance, with provision to distinguish the polarization resistance contribution (R_p) from the solution resistance (R_s). These plots are known as Nyquist plots. Nyquist plots of (Zn-Ni)_{2.0/4.0} coatings with different number of layers were studied. The impedance spectra shown in Figure 2 clearly indicate that the capacitance of the EDL decreased progressively with increase in the number of layers. The relative impedance response of monolithic (Zn-Ni)_{3.0} and CMMA (Zn-Ni)_{2.0/4.0/300} coating systems are shown in Figure 3. The substantial decrease of the CR of the CMMA coating is due to the decreased capacitance and the increased dielectric barrier at the interface.

Cyclic polarization (Figure 4) showed that over the potential range -0.2 to -0.5 V, the CD of the backward scan was higher than was that of the forward scan, indicating that the dissolution of oxides had occurred during the forward scan, so self-repair occurred during the reverse portion of the scan. Over the range -0.5 to -0.8 V, the CD of the reverse portion of the scan was lower than was that of the forward portion of the scan, which showed that metal could form a protective passive film below this value. However, the CD of the reverse scan was lower than was that of the forward scan at the same potential, which indicated that the passive film had a more compact structure after having been anodically polarized.

It was observed that the degree of corrosion protection afforded by coatings with (Zn-Ni)_{2.0/4.0/300} configuration was ~ 35 times better ($0.43 \times 10^{-2} \text{ mmy}^{-1}$) than that of the monolithic (Zn-Ni)_{3.0} alloy ($15.18 \times 10^{-2} \text{ mmy}^{-1}$) obtained from same bath, during same plating time. The decrease in CR with multi-layered coating may be best explained by dielectric spectroscopy. It is well known that the corrosion product film on most alloys exhibits semiconductor behavior. The most common *in situ* method for probing the electronic properties of the corrosion product film is the Mott-Schottky analysis. The linear relation between $1/C^2$ vs E for the optimal

configuration $(\text{Zn-Ni})_{2.0/4.0/300}$ indicates that anticorrosion behavior of multi-layer CMMA coatings is attributable to the semiconductor property of the film at the interface, as evidenced by the Mott-Schottky plot shown in Figure 5. Further, the straight line with positive slope reveals that the protective layer that is operative at the interface is n-type in nature.

The improved corrosion resistance of CMMA coatings can be explained in terms of the effect of the time-dependent electric field (i.e. frequency response). Variations in the relative permittivity with frequency show that the value of ϵ_r for all of the coatings is high at low frequency, and the variability is diminished as the frequency is increased. At low frequencies, the dielectric barrier of the coatings increases number of layers. This is attributable to the increased interfacial polarization effect caused by the heterogeneous media, consisting of phases with different dielectric permittivity (Kouloumbi *et al.*, 1996). There are many causes for heterogeneity in materials, but concerning the CMMA coatings developed in the present work, it is related to interfaces created by electron charge density. Thus, it may be summarized that the anti-corrosion behavior of CMMA coatings is associated with its decreased permittivity.

The SEM micrographs shown Figure 7(a) illustrate the formation of alternate layers of alloys having $(\text{Zn-Ni})_{2.0/4.0/30}$ configuration. The poor contrast between the layers may be due to the marginal difference in chemical composition of the alloy in each layer. Inspection of the corroded surface (Figure 7(b)) reveals that the protection efficacy of the CMMA coating is due to the selective dissolution of alloys in the different layers (i. e. layers with low wt% Ni dissolve preferentially, compared to layers with high wt% Ni), though eventually the steel substrate is exposed.

5. Conclusion

The corrosion resistance of CMMA coatings produced by the SBT was shown to be higher than that of the monolithic (Zn-Ni) coatings with the same thickness. For example, CMMA coatings with the optimal configuration $(\text{Zn-Ni})_{2.0/4.0/300}$ showed ~ 35 times better corrosion resistance, compared to monolithic $(\text{Zn-Ni})_{3.0}$ alloy of same thickness that had been obtained from the same bath. The CR of the CMMA coating decreased as the number of layers was increased. Even a small change in the wt% Ni in the layer was sufficient to change the corrosion resistance significantly. The electrochemical stability of the CMMA coatings was explained in terms of their changed intrinsic electrical properties, as evidenced by Mott-Schottky plots and dielectric spectroscopy. The protection efficacy of the CMMA $(\text{Zn-Ni})_{2.0/4.0}$ coatings was associated with the barrier effect of the $(\text{Zn-Ni})_{4.0}$ layers and the sacrificial behavior of the $(\text{Zn-Ni})_{2.0}$ layers. It was demonstrated that optimization of the corrosion resistance is possible through careful manipulation of the CCCD's and number of layers.

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