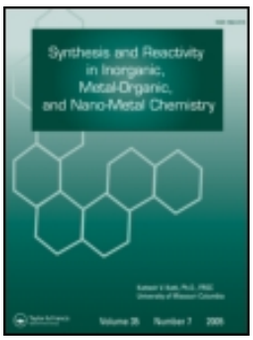

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Development of Nano-structured Zn-Ni Multilayers and their Corrosion Behaviors

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Composition modulated multilayer alloy (CMMA) coatings of Zn-Ni was developed using single bath technique (SBT). CMMA coatings were developed galvanostatically using square current pulses. The cyclic cathode current densities (CCCDs) and number of layers were optimized for highest corrosion resistance. Experimental results showed that CMMA coating, developed at 2.0/5.0 A/dm^2, having 300 layers is ∼29 times higher corrosion resistant than monolithic alloy of same thickness. Tafel and impedance data revealed its good protection ability. The improved corrosion behavior exhibited by multilayers was explained using dielectric spectroscopy. The formation of multilayer and corrosion mechanism was analyzed using scanning electron microscopy (SEM).

Keywords CMMA Zn-Ni coatings, corrosion resistance, dielectric spectroscopy, SEM

1. INTRODUCTION

Composition modulated multilayer alloy (CMMA) coatings consist of alternate layers of two or more metals/alloys having different composition, and each layer has its own distinctive role in achieving preferred performances.[1] The possibility of electrodepositing zinc-based CMMA coatings onto ferrous substrates for protection purpose has been recently investigated.[2]

These CMMA coating systems are a relatively new technique, and is gradually gaining interest amongst researchers because these layered structure coatings possess improved properties or novel phenomenon such as increased mechanical strength, micro-hardness, giant magnetoresistance, and corrosion resistance.[3–9] The ability to do so by electrodeposition depends upon the solution chemistry and the operating parameters. During the last decades, electrodeposition of CMMA coatings for protection of steel substrate from corrosion has been extensively investigated. Kalantary et al.[10] obtained zinc-nickel CMMA coatings by electrodepositing alternate layers of zinc and nickel from zinc sulphate electrolyte and nickel sulphate electrolyte. Chawa et al.[11] reported that the corrosion resistance of zinc-nickel CMMA coatings electrodeposited from zinc sulphate and nickel sulfamate baths were better than that of zinc or nickel monolithic coatings of a similar thickness. Ivanov et al.[12] studied the corrosion performance of CMMA Zn-Ni coatings with total thickness of 12 μm obtained by successive deposition of individual metals using double bath technique (DBT). Later, attempts were made for electrodeposition of CMMA coatings using single bath technique (SBT), i.e., from the bath having ions of both metals.[9,13,14]

Not much work is reported with regard to optimization of deposition conditions and number of layers for synthesis of micro/nano-structured multilayer coatings for better corrosion resistance. The present work discusses the optimization of cyclic cathode current densities (CCCDs) and the number of layers for deposition of zinc-nickel CMMA coating for peak performance against corrosion using SBT. Improved corrosion resistances of the CMMA coatings were discussed in terms of changed dielectric properties of the coatings.

2. EXPERIMENTAL

The electrolytes were freshly prepared from distilled water using analytical grade reagents. Electroplating of mild steel plates was done at pH 5.7 ± 0.3 and temperature 30 ± 2°C. The polished mild steel plates (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) with an exposed surface area of 7.5 cm^2, served as a cathode. The anode was pure Zn with the same exposed area. The depositions were carried out in a rectangular PVC cell containing 250 cm^3 electrolytes, at constant condition of stirring without purging, to maintain a steady-state of mass transport.

All coatings, viz. monolithic and CMMA were carried out galvanostatically using sophisticated power source (N6705A, Agilent Technologies) for 10 minutes (∼20 μm thickness), for comparison purposes. 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).

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TABLE 1
Corrosion data and deposit characters of Zn-Ni alloy coatings under different conditions of current density

c.d./ A/dm^2	wt. % Ni	Thickness/ μm	Vickers hardness V_{100}	E_{corr}/V vs Ag, AgCl/Cl^-_{sat}	i_{corr}/μA/cm^2	CR/ $\times 10^{-2}$ mm y^{-1}	Nature of the deposit
1. 0	14.64	7.1	135	−1.183	23.72	35.19	Blackish
2. 0	10.68	10.0	145	−1.108	16.96	25.16	Bright
3. 0	10.82	12.2	150	−1.081	9.79	14.53	Bright
4. 0	11.00	15.63	163	−1.163	15.97	23.69	Bright
5. 0	13.07	18.52	168	−0.883	20.84	30.93	Bright

The composition of the coatings was determined colorimetrically using the standard method.[15] The hardness of the deposited alloys was measured using a computer-controlled micro-hardness tester (CLEMEX, Model: MMT-X7). All electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT^3, Princeton Applied Research) in a three-electrode configuration cell, using Ag/AgCl/KCl_{sat} as reference electrode. The 5% NaCl solution was used as corrosion medium throughout the study. Potentiodynamic polarization study was carried out in a potential ramp of ± 250 mV from open circuit potential (OCP) at a scan rate of 1 mVs^{-1}. Electrochemical impedance spectroscopy (EIS) study was made using AC signal of 10 mV amplitude, at a frequency range from 100 kHz to 10 mHz. The formation of multilayer and corrosion mechanism was examined using scanning electron microscopy (SEM, Model JSM-6380 LA from JEOL, Japan).

3. RESULTS AND DISCUSSION

3.1. Development of Monolithic Zn-Ni Alloy Coating

The optimization of a stable zinc chloride bath was carried out by standard Hull cell method.[16] Deposition was carried out at different current densities using optimized bath, consisting of 15 g/L ZnO, 60 g/L $NiCl_2.6H_2O$, 250 g/L NH_4Cl, 20 g/L boric acid (H_3BO_3). The effects of current density (c.d.) on wt. % Ni, deposit thickness, Vickers hardness, corrosion rate and appearance of the coatings are reported in Table 1. Zn-Ni alloy at 3.0 A/dm^2, represented as $(Zn\text{-}Ni)_{3.0,}$ was found to be more corrosion resistant (14.53 × 10^{-2} mm y^{-1}) compared to the alloys obtained at other current densities. Hence, it has been taken as optimal c.d. for deposition of monolithic Zn-Ni alloy. Further, it was observed that both thickness and hardness of the deposit increased with c.d., as a characteristic feature of Zn-Fe group metal alloys.[17] The high wt. % Ni, observed at low c.d. (at 1.0 Amp/dm^2) may be due to tendency of the bath to follow normal codeposition against anomalous codeposition.

3.2. Development of Zn-Ni CMMA Coatings

Coatings having layers with different composition were developed using square current pulses (sharp change in composition is caused by sharp change in c.d.) by proper setting-up of the power source. The power pattern generated for monolithic and CMMA coating systems is shown schematically in Figure 1. The CMMA coating systems developed in the present study is represented as: $(Zn\text{-}Ni)_{1/2/n}$, where 1 and 2 represent cathode current densities between which the current cycles, called-cyclic cathode current densities (CCCD's);n represents the number of layers formed during total plating time (10 min).

3.3. Optimization 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 significant changes in properties due to the change in the phase structure.[18] Thus, by precise control of the cathode current densities, it is possible to develop alternate layers with different compositions and, consequently, different corrosion behaviors. Table 2 demonstrates the effect of the CCCDs on corrosion behavior of the coatings. In order to increase the corrosion resistance, CMMA coatings having 10 layers (arbitrarily chosen) were developed at different sets of CCCDs. Among the various sets tried, the less corrosion rate was measured in the coatings having configurations, $(Zn\text{-}Ni)_{1.0/4.0/10}$ and $(Zn\text{-}Ni)_{2.0/5.0/10}$ (produced at difference of 3.0 A/dm^2 between CCCD's), as shown in Table 2. These coatings were found to be bright and uniform. These sets of CCCDs have been selected

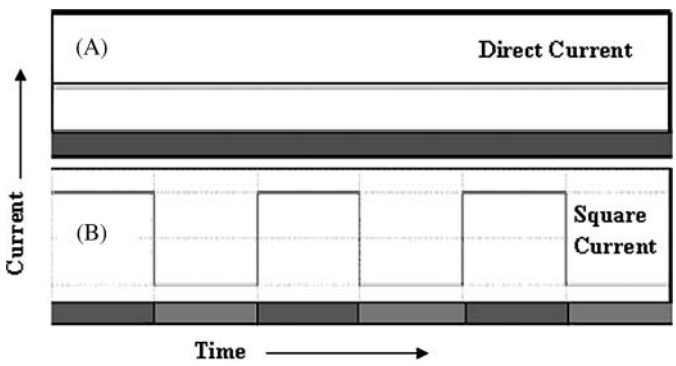

FIG. 1. Schematic representation of different power patterns used and corresponding modulation in composition of alloy: (a) Monolithic at constant current density, and (b) CMMA with sharp change in composition using square current pulses.

TABLE 2
Corrosion rates of CMMA Zn-Ni coatings at different set of CCCDs (with 10 layers each)

CMMA Zn-Ni coatings developed at a difference of 3.0 A/dm^2 between CCCDs			
CCCDs/ A/dm^2	E_{corr}/V vs Ag, AgCl / KCl$_{sat}$	i_{corr}/ μA/cm^2	CR/ $\times 10^{-2}$ mm y^{-1}
(Zn-Ni)$_{1.0/4.0/10}$	−0.914	6.554	13.22
(Zn-Ni)$_{2.0/5.0/10}$	−0.911	7.555	11.20

for studying the effect of layering, as described in the following subsection.

3.4. Optimization of Number of Layers

The physico-mechanical properties of CMMA coatings, including their corrosion behavior may often be increased substantially by increasing the number of layers (usually up to an optimal limit), without sacrificing the demarcation between each layer. Therefore, 1.0/4.0 A/dm^2 and 2.0/5.0 A/dm^2 have been selected for layering. Zn-Ni CMMA coatings having 10, 20, 60, 120, 300, and 600 layers were developed and their corrosion rates were measured by Tafel's extrapolation method. It was observed that in both sets of CCCDs, the corrosion rates decreased, as number of layers increased up to only 300 layers, and then increased, as shown in Table 3. However, at 2.0/5.0 A/dm^2, corrosion rate reached saturation (beyond which no decrease of corrosion rate with layering was observed) value at 300 layers with minimum corrosion rate (0.502×10^{-2} mm y^{-1} relative to 14.53×10^{-2} mm y^{-1}, for monolithic alloy for same thickness). Though there is substantial decrease of corrosion rate (CR) at 1.0/4.0 A/dm^2, as shown in Table 3, the result pertaining to 2.0/5.0 A/dm^2 is more encouraging, due to better appearance, homogeneity, and less CR. However, an effort of increasing the corrosion resistance further by increasing number of layers (up to 600 layers) in each set of CCCDs has resulted in increase of CR. Therefore, (Zn-Ni)$_{2.0/5.0/300}$ has been proposed as the optimal configuration of CMMA coating, with individual layer thickness ~ 66 nm; with peak performance against corrosion.

TABLE 3
Decrease of corrosion rate with increase in number of layers in CMMA Zn-Ni coating system

Coating configuration	No. of layers	E_{corr}/V vs Ag, AgCl / KCl$_{sat}$	i_{corr}/ μA/cm^2	CR/ $\times 10^{-2}$ mm y^{-1}
Effect of number of layers at 1.0 – 4.0 A/dm^2				
(Zn-Ni)$_{1.0/4.0}$	10	−0.914	6.554	13.22
(Zn-Ni)$_{1.0/4.0}$	20	−0.881	4.580	6.791
(Zn-Ni)$_{1.0/4.0}$	60	−1.003	3.067	4.550
(Zn-Ni)$_{1.0/4.0}$	120	−0.823	2.539	3.767
(Zn-Ni)$_{1.0/4.0}$	300	−0.799	1.2225	1.816
(Zn-Ni)$_{1.0/4.0}$	600	−1.176	10.129	15.02
Effect of number of layers at 2.0 – 5.0 A/dm^2				
(Zn-Ni)$_{2.0/5.0}$	10	−0.911	7.555	11.20
(Zn-Ni)$_{2.0/5.0}$	20	−0.956	2.634	3.902
(Zn-Ni)$_{2.0/5.0}$	60	−0.938	1.397	2.073
(Zn-Ni)$_{2.0/5.0}$	120	−0.928	1.153	1.170
(Zn-Ni)$_{2.0/5.0}$	300	−0.942	0.379	0.502
(Zn-Ni)$_{2.0/5.0}$	600	−0.968	4.046	6.00

The increase of CR at high degree of layering may be explained as follows:[16] During plating, metal ions (Zn^{+2} and Ni^{+2}) from the bulk of the electrolyte diffuse towards cathode and get discharged as metal atoms. This process is mainly controlled by the cathode current density, as it is the driving force for deposition. As the number of layers increased, the time for the deposition of each layer, say, for (Zn-Ni)$_1$ is small, due to constant total time of deposition (10 min). Therefore, at a high degree of layering due to rapid cycling of cathode current density, there is no sufficient time for metal ions to relax against diffusion (at given current density), and to deposit with modulation in composition. As a result, at high degree of layering no modulation in composition is likely to take place. In other words, the coating at higher degree of layering is tending towards monolithic, and consequently exhibits less corrosion resistance.

3.5. Corrosion Study

3.5.1. Potentiodynamic polarization study

Potentiodynamic polarization curves of CMMA (Zn-Ni)$_{2.0/5.0}$ coating system with different number of layers is shown in Figure 2. Tafel extrapolation on such curves resulted

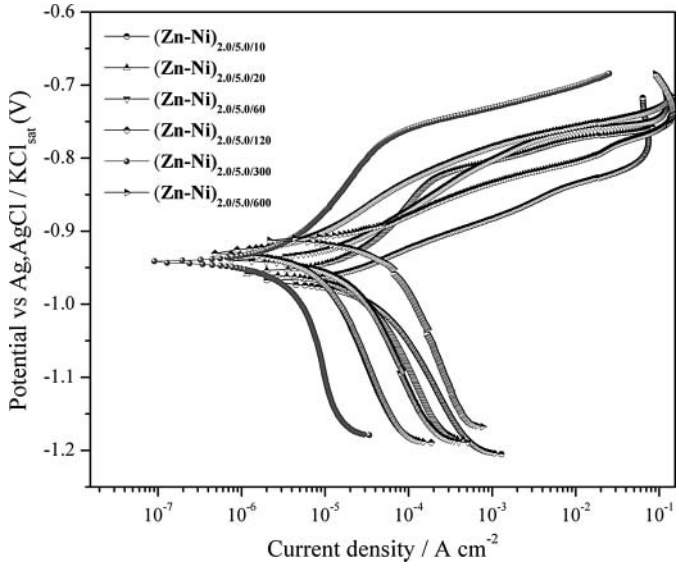

FIG. 2. Potentiodynamic polarization curves of CMMA (Zn-Ni)$_{2.0/5.0}$ coatings having a different number of layers.

in determination of the corrosion potential, corrosion current density and CR, as listed in Table 3. A progressive decrease of corrosion current, i_{corr} and hence, the CR was observed up to 300 layers. But as number of layers has increased to 600, the i_{corr} has value increased drastically, as shown in Figure 2. The observed increase of corrosion rate at high degree of layering is attributed to interlayer diffusion. It may be recalled that the most important requirement for multilayered material to exhibit novel properties is to have thin structured layers with clear demarcation between each layer. Failing to which generally leads to the decreased novel properties of materials.[4,10] Hence, the observed high corrosion rate at higher number of layers (>300) is due to diffusion of layers for the reasons explained in Section 3.4.

3.5.2. Electrochemical Impedance Spectroscopy (EIS)

EIS, also referred to as AC impedance spectroscopy, is a suitable technique to gain valuable information about the interface (between substrate and medium); responsible for improved corrosion resistance, on the basis of electrical double layer (EDL) capacitance.[19] Information about the interaction of coating with corrosion medium is obtained from Nyquist plots.[20] It may be observed that in $(Zn\text{-}Ni)_{2.0/5.0}$ coating systems, the radius of the semi-circle increased with number of layers, up to 300 layers, as shown in Figure 3. It should be noted that the solution resistance R_s is nearly identical in all cases, as the same bath chemistry and cell configuration were used. It may be noted that the radius of the capacitive loops increases with number of layers, indicating increase of polarization resistance, R_P. Further, the impedance points lying away from the real axis, at lower frequency limit, shows that both capacitance and resistance are responsible for improved corrosion resistance.[20]

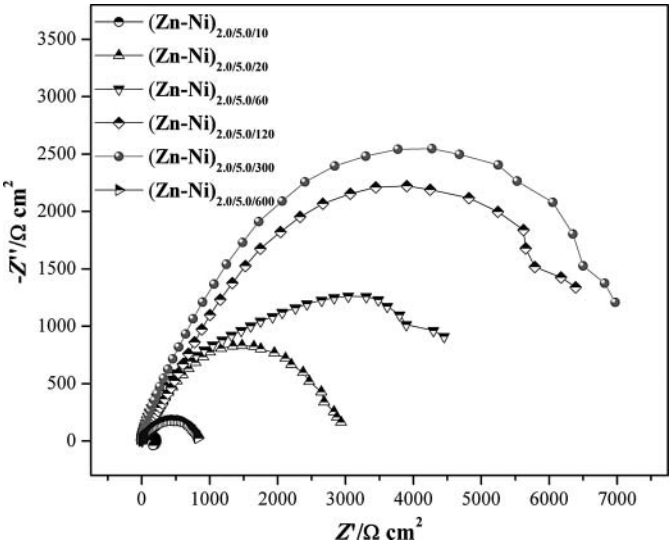

FIG. 3. Electrochemical impedance response of CMMA $(Zn\text{-}Ni)_{2.0/5.0}$ coating systems measured at frequency range of 100 kHz −10 mHz, and perturbing voltage of 10 mV.

But, as the number of layers increased, the radius of the semicircle decreased drastically, demonstrating its high corrosion rate with less $R_{P,}$ as shown in Figure 3. The enhanced corrosion resistance of CMMA coatings may be interpreted in terms of changed dielectric property of the coatings, due to layering as explained in next section.

3.6. Dielectric Study of CMMA Coating

EIS data points can also be used to study the dielectric properties of materials, and the technique is called dielectric spectroscopy.[21] It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. This technique measures the relative dielectric constant, ε_r of a system over a range of frequencies, and the frequency response of the system, including the energy storage and dissipation properties, can be identified. The capacitance is inversely proportional to the electric field between the plates, and the presence of the dielectric reduces the effective electric field. The capacitance C may expressed as,

$$C = \frac{k\varepsilon_0 A}{d} = \frac{\varepsilon_r A}{d} \qquad [1]$$

Where k is dielectric constant of the medium, ε_0 is permittivity of vacuum, A is surface area of parallel plates and d is the spacing distance. When coating having definite dielectrics is placed between charged plates having electric field E, the polarization of the medium produces an electric field, opposing the field of the charges on the plate. The relative dielectric constant is a characteristic of space between plates, and is a way to characterize the reduction of electric field due to polarization, represented as $E_{\text{polarizatioin.}}$ Then the effective electric field, $E_{\text{effective}}$ is given by relation,

$$E_{\text{effective}} = E - E_{\text{polarization}} = \frac{\sigma}{k\varepsilon_0} = \frac{\sigma}{\varepsilon_r} \qquad [2]$$

Here σ is the surface charge density; or quantity of charge per unit area of capacitor plate (C/m^2). Then a decrease of effective electric field between the plates will increase the capacitance of the parallel plate structure. Therefore, dielectric must be a good electric insulator to minimize any DC leakage current through a capacitor.[22]

The variation of ε_r vs. frequency (from 10 mHz to 100 kHz) for different coating systems is shown Figure 4. It may be observed that at a high frequency limit, ε_r is independent of number of layers. It is due to the fact that at high frequencies, there is no charging of the capacitor, and the capacitance is effectively like that of an open circuit (vacuum). Therefore, ε_r is almost same for all coatings, irrespective of the number of layers. At a low frequency side, the frequency response of the capacitor was found to dependent of $\varepsilon_{r,}$ as shown in Figure 4. This is due to the fact that at low frequency, AC becomes equivalent to

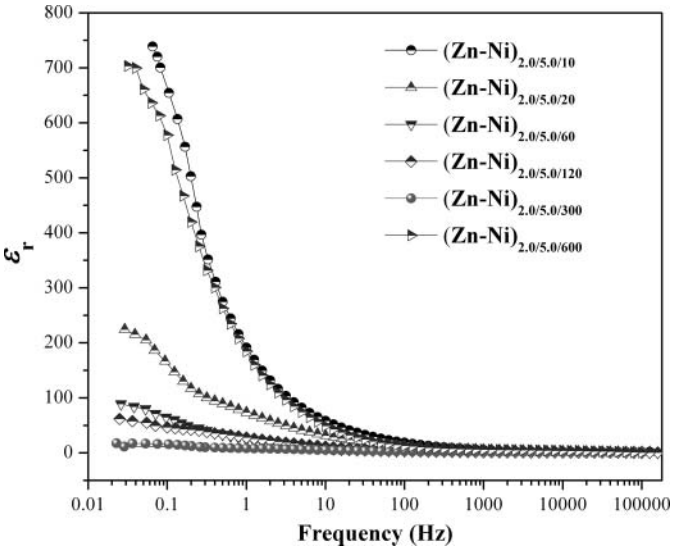

FIG. 4. Frequency response of relative dielectric constant of CMMA (Zn-Ni) $_{2.0/5.0}$ coatings having different number of layers.

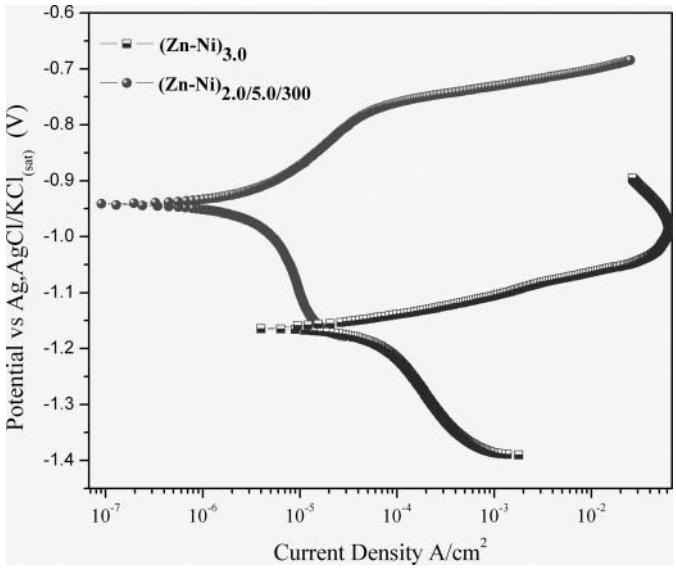

FIG. 5. Comparison of potentiodynamic polarization curves for monolithic $(Zn\text{-}Ni)_{3.0}$ and CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$ coating systems of same thickness.

DC. Hence, the increase of ε_r with number of layers indicates the increased polarizing ability of the corresponding electrical double layer (EDL) capacitor. Therefore, less ε_r of CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$ compared to other coating systems indicates that coating behaves as good dielectric barrier for passage of current through the capacitor, leading to less corrosion tendency.

3.7. Comparison between Monolithic and CMMA Coatings

A substantial change in corrosion rate was observed when coatings are changed from monolithic to multilayer type, and is supported by the corrosion data reported in Table 4. Potentiodynamic polarization behaviors of both monolithic and CMMA coatings (both under optimal conditions) is shown in Figure 5. It may be observed that both i_{corr} values of CMMA coatings have decreased compared to monolithic alloy. It was found that corrosion protection of coatings with $(Zn\text{-}Ni)_{2.0/5.0/300}$ configuration is ∼29 times better (0.502×10^{-2} mm y^{-1}) than monolithic $(Zn\text{-}Ni)_{3.0}$ alloy (14.53×10^{-2} mm y^{-1}), obtained from same bath, for the same time.

Prabhu Genesan et al.[18] have reported that by X-ray diffraction (XRD) analysis, a small compositional difference in the layers of alloys brings a significant change in the phase structure of the coatings, and consequently, the corrosion behavior of the coating as a whole. Hence, the extended corrosion stability of CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$ coatings is due to alternate layers of alloys having, respectively, 10.68 and 13.07 wt. % Ni. The micrographic characteristics of Zn-Ni CMMA coatings after corrosion test revealed that the protection efficacy of the coatings are due to the barrier effect of alloy layers having high wt. % Ni (noble layers) and sacrificial effect of alloy layers having low wt. % Ni (active layers). Thus, the protection efficacy of CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$ coatings may be explained by the barrier effect of Zn-Ni layer, with high wt. % Ni (13.07) and the sacrificial effect of Zn-Ni layer, with less wt. % Ni (10.68). A small change in wt. % noble metal in the alloy layer is good enough to bring large change in the phase structures of the alloys and thereby their properties.

TABLE 4
Comparison of corrosion rates of monolithic $(Zn\text{-}Ni)_{3.0}$ and CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$ coating systems, deposited for same times

Coating configuration	E_{corr}/V vs Ag, AgCl / KCl_{sat}	i_{corr}/ μA/cm^2	CR/ $\times 10^{-2}$ mm y^{-1}
$(Zn\text{-}Ni)_{3.0}$ (Monolithic)	−1.081	9.79	14.53
CMMA $(Zn\text{-}Ni)_{2.0/5.0/300}$	−0.942	0.379	0.502

3.8. SEM Study

Surface morphology of $(Zn\text{-}Ni)_{2.0/5.0/10}$ coating without corrosion displayed a uniform and crack-free morphology, as shown in Figure 6a. A cross-sectional view of CMMA $(Zn\text{-}Ni)_{2.0/5.0/10}$ (for better distinction only 10 layers have been built) is shown in Figure 6b. It should be noted that the unequal thickness of the individual layers in Figure 6b is attributed to large difference in deposition current density. The poor contrast may be due to marginal difference in chemical composition of layers. To understand the reason for the improved corrosion resistance, the CMMA coatings were examined under SEM after corrosion test. The coatings having $(Zn\text{-}Ni)_{2.0/5.0/4}$ configuration are subjected to anodic polarization at +250 mV vs. OCP in 5% NaCl solution. The corroded specimen was washed with distilled water and examined. Partial dissolution of layers due to corrosion, corresponding to CMMA $(Zn\text{-}Ni)_{2.0/5.0/4}$ was

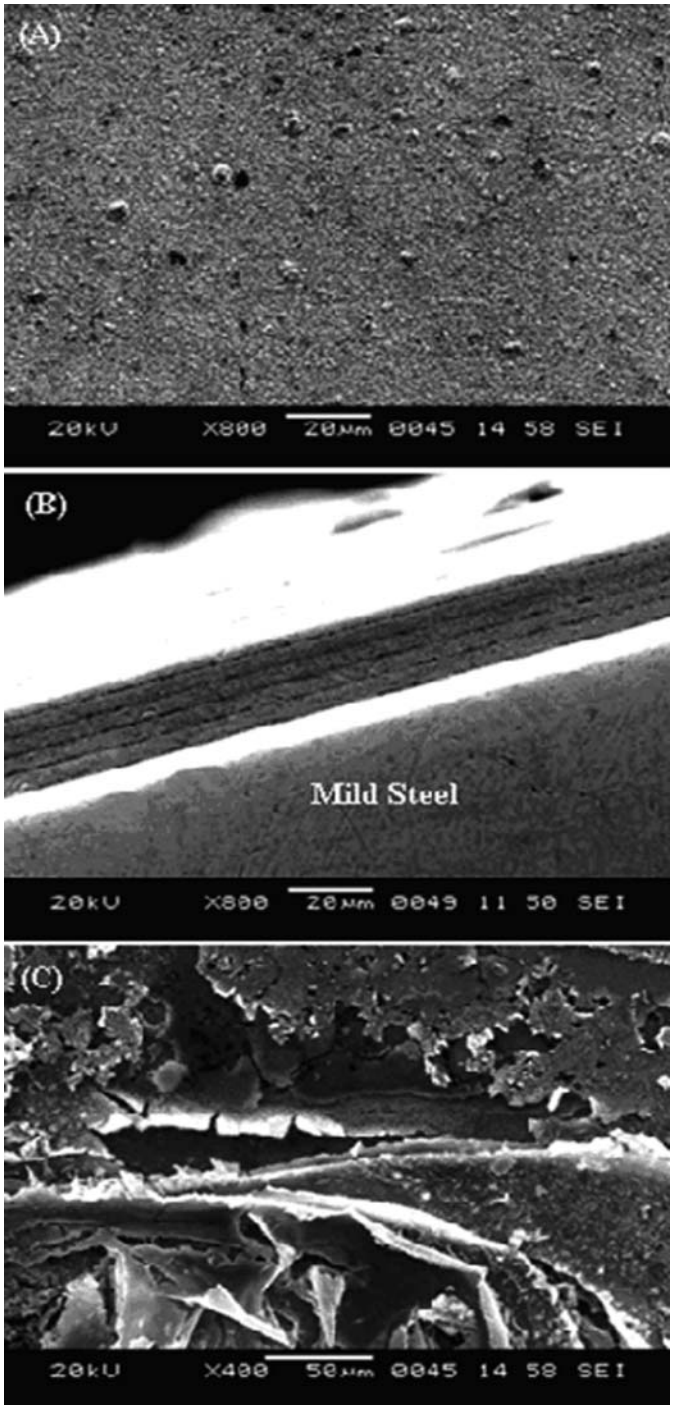

FIG. 6. SEM images of CMMA (Zn-Ni) coatings: (a) Surface morphology of (Zn-Ni) $_{2.0/5.0/10}$ coatings, (b) cross-sectional view showing 10 layers, and (c) surface morphology of CMMA (Zn-Ni) $_{2.0/5.0/4}$ after corrosion test.

confirmed, as shown in Figure 6c.

The possibility of high corrosion prevention of CMMA coating is due to the fact that the failures like pores and crevices developed on coatings of single layer at a particular current density will be covered by the successively deposited layers. Thus, the corrosion agent's path is longer or blocked.[23] That is why with multilayer coating, the corrosive agent needs more time to penetrate through coating defects into the substrate material, than in monolayer coating. In other words, the corrosive agent path is extended. Zn-Ni alloy layer, with less wt. % Ni beneath the high wt. % Ni top layer dissolves through the pores and micro-cracks existing in the CMMA coatings existing during corrosion.[24]

4. CONCLUSIONS

The following conclusions were drawn from the present study:

a) A stable electrolytic bath, without any brightener, has been proposed for deposition of bright and uniform coatings of Zn-Ni on mild steel.
b) Under optimal conditions, the corrosion resistance of CMMA (Zn-Ni)$_{2.0/5.0/300}$ coating (with average layer thickness of about 66 nm) was found to be about 29 times better than the corresponding monolithic coating of same thickness.
c) The corrosion stability of the coatings increased with number of layers, up to an optimal level, and then decreased. The increase of corrosion rate at high degree of layering is attributed to less relaxation time for redistribution of metal ions during plating.
d) The improved corrosion resistance of CMMA coatings is due to alternate layers of alloys having differences in composition, and consequently the phase structure.
e) The protection efficacy of CMMA coatings may be explained by the barrier effect of Zn-Ni layer, with high wt. % Ni (13.07) and the sacrificial effect of Zn-Ni layer, with less wt. % Ni (10.68).
f) The protection stability of the multilayer coatings may be explained by the delayed path of corrosion agent, due to successively deposited layers having different degrees of pores and crevices.
g) The high corrosion resistance of Zn-M CMMA coating is attributed to its decreased dielectrics due to layering, supported by dielectric spectroscopy.

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