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## Development of Nano-Structured Cyclic Multilayer Zn–Ni Alloy Coatings Using Triangular Current Pulses<sup>1</sup>

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**Abstract**—Cyclic multilayer alloy (CMA) deposits of Zn–Ni were developed on mild steel from sulphate bath having thiamine hydrochloride (THC) and citric acid (CA) as additives. CMA coatings were developed galvanostatically using triangular current pulses, under different conditions of cyclic cathode current density (CCCD's) and number of layers. The corrosion behaviors of the coatings were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy methods, and were compared with that of monolayer Zn–Ni alloy of same thickness. At optimal configuration, CMA coating represented as, (Zn–Ni)<sub>2.0/5.0/300</sub> was found to exhibit ~40 times better corrosion resistance compared to monolayer alloy, (Zn–Ni)<sub>3.0</sub>. Cyclic voltammetry study demonstrated that THC and CA have improved the appearance of the deposit by complexation with metal ions. The corrosion protection efficacy of CMA coatings was attributed to the difference in phase structure of the alloy in successive layers, evidenced by XRD analysis. The formation of multilayer and corrosion mechanism was analyzed by Scanning Electron Microscopy (SEM) study.

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### INTRODUCTION

Compositionally modulated multilayer alloys are a class of nano-materials developed by electrolytic methods from aqueous solutions. They consist of successive layers of alloys with alternating composition, developed by bringing modulation in the deposition process itself (usually by a complex pulse sequence) [1]. Because of very fine grain sizes, the compositionally modulated multilayer alloys, or, in other words, cyclic multilayer alloys (CMA), exhibit improved properties not attainable in any of the metallurgical alloys. These include better morphological/structural characteristics, 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, soft-magnetic properties, all as compared with conventionally produced coarse-grained materials [2]. All those properties can be developed in new materials with a view to explore their possible applications in a variety of areas. In effect, those, new materials are difficult to develop by a technique other than electrodeposition. Thus, the multilayer coatings are an extension to a range of surface coatings and their associated applications that were made possible by electroplating. Such multilayers can be produced by means of either of the two main techniques known as the dual

bath technique (DBT) and single bath technique (SBT).

CMA coatings consist of a large number of thin layers of alloys having two or more different compositions, each layer playing its own distinctive role in achieving preferred performances [3]. The resulting changes due to electroplating depend upon the chemical composition of the solution and the operating parameters. During past decades, electrodeposition of CMA coatings for protecting steel substrate from corrosion has been extensively investigated. Kalantary et al. obtained Zn–Ni CMA coatings with an overall thickness of 8  $\mu\text{m}$  by electrodepositing alternate layers of zinc and nickel from zinc sulphate electrolyte and nickel sulphate electrolyte [4]. Chawa et al. reported that the corrosion resistance of Zn–Ni CMA coatings electro-deposited from zinc sulphate and nickel sulfamate baths were better than that of zinc or nickel monolayer coatings of a similar thickness [5]. Ivanov et al. studied the corrosion performance of CMA Zn–Ni coatings with the total thickness of 12  $\mu\text{m}$ , obtained by the successive deposition of individual metals using the DBT [3]. Kalantary et al. deposited Zn–Ni multilayered coatings on a rotating cylinder electrode from a sulphate [6]. In the current density range of 10–50  $\text{A dm}^{-2}$ , the Ni content was between 3–14%, and in the range of 100–130  $\text{A dm}^{-2}$  it was 20–30%. Hayashi observed a higher corrosion resistance of Zn–Ni and Zn–Fe alloys, with respect to pure zinc, under atmospheric exposure conditions, to a higher resistance to the penetration of chloride ions through the coating [7]. Multilayered Zn–Ni deposition from a

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single acidic bath by the potentiostatic method was reported by Prabhu Ganesan et al. who found that the Ni content varied as a function of thickness when applying varying potentials [8]. It was concluded that at higher potentials  $\gamma$ -phase corresponding to (600) planes is preferentially deposited, while lower potentials lead to the deposition of other crystal planes of  $\gamma$ -phases (222). Later, attempts were made to electrodeposite CMA coatings using the SBT, i.e., the bath having ions of both metals [9–11]. Relatively few reports presented some evidence to support the enhanced corrosion resistance due to Zn–Ni CMA coatings. Moreover, not much work has been carried out concerning the optimization of deposition conditions and the required number of layers for the electrolytic synthesis of micro/nano-structured multilayer coatings of zinc–nickel alloy in order to raise corrosion resistance.

Though CMA coatings of Zn–M (where M = Ni, Co or Fe) alloys for improved corrosion resistance have been widely described, very little has been done so far regarding the optimization of the deposition conditions using the SBT. Still, recently, Thangaraj et al., have optimized a stable chloride bath for the production of Zn–Co [12] and Zn–Fe [13] CMA coatings using square current pulses. They have found that the CMA coatings under optimal conditions exhibit much higher corrosion resistance than the respective monolayer alloy coatings of the same thickness. Most of the works available to the authors have been focused on the modulation in composition using square current pulses of two or more current/voltage, i.e., by bringing sudden change in its composition. No work has been found in the available literature on the optimization of coating configuration by a gradual change in the composition, i.e. by using triangular current pulses.

Hence, the main objective of this study is to optimize the deposition conditions for the development of the monolayer and CMA coatings of Zn–Ni alloys on the mild steel substrate from a sulphate bath for better corrosion resistance using THC and CA, as additives, and to compare the corrosion resistance of CMA coating with that of monolayer alloy coatings of the same thickness.

## EXPERIMENTAL

The electroplating solutions were freshly prepared from distilled water and analytical grade reagents. Electroplating of mild steel plates was done at pH  $3.0 \pm 0.05$  and temperature  $30 \pm 2^\circ\text{C}$ . The polished mild steel plates (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) having exposed surface area of  $7.5\text{ cm}^2$  served as a cathode. The anode was pure Zn with the same exposed area. A rectangular PVC cells containing  $250\text{ cm}^3$  electrolytes were used. All depositions were carried out at constant stirring without purging, so as to maintain a steady-state of mass transport. All

coatings, viz. monolayer and CMA, were made galvanostatically using N6705A (Agilent Technologies) for 10 minutes ( $\sim 12\text{ }\mu\text{m}$  thickness), for comparison. The thickness of the coating was estimated by Faraday's law, then it was verified by measurements, using a digital thickness meter (Coatmeasure model M and C). The compositions of the coatings were determined calorimetrically using a standard method [14]. All electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT<sup>3</sup>, Princeton Applied Research) in a three-electrode configuration cell. All electrochemical potentials referred to in this work are indicated relative to the Ag/AgCl/ $\text{Cl}_{\text{sat}}^-$  electrode. The 5% NaCl solution was used as a corrosion medium. Potentiodynamic polarization study was carried out in a ramped potential of  $\pm 250\text{ mV}$  from an open circuit potential at the scan rate of  $1\text{ mVs}^{-1}$ . Electrochemical Impedances Spectroscopy study was carried out in the frequency range from 100 kHz to 20 mHz, with perturbing signal of 10 mV.

Cyclic Voltammetry (CV) study was performed in a conventional three-electrode cell to better understand the process of electrodeposition and to identify the effect of additives. Pure platinum foil with a surface area of  $1\text{ cm}^2$  was used as the working electrode. Before each experiment, the electrode was activated by immersion in 1 : 1  $\text{HNO}_3$ . The CV experiments were conducted in a quiescent solution, without purging. Initially, three scan rates were evaluated viz. 10, 20 and  $50\text{ mVs}^{-1}$ . However, the peaks in the CV spectra became more distinct when the scan rate was  $10\text{ mVs}^{-1}$ , the same was used for further studies. The phase structure of the electrodeposits under two different current densities was analyzed using the X-ray Diffractometer (Bruker AXS) using  $\text{CuK}_\alpha$ -radiation ( $\lambda = 1.5405\text{ \AA}$ , 30 kV). The formation of multilayers and the corrosion mechanism were examined by the Scanning Electron Microscopy (SEM, Model JSM-6380 LA from JEOL, Japan).

## RESULTS AND DISCUSSION

### *Monolayer Zn–Ni Alloy Coating*

The optimizations of a stable sulphate bath were carried out by the standard Hull cell method [1]. Depositions were carried out galvanostatically at different current densities using an optimized bath, consisting of  $120\text{ gL}^{-1}\text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $100\text{ gL}^{-1}\text{ NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $70\text{ gL}^{-1}\text{ CH}_3\text{COONa}$ ,  $3\text{ gL}^{-1}$  citric acid and  $0.5\text{ gL}^{-1}$  THC. Table 1 shows the effects of current density on wt % Ni, corrosion resistance and appearance of coatings. The alloy of Zn–Ni at  $3.0\text{ A dm}^{-2}$ , represented as  $(\text{Zn–Ni})_{3,0}$ , was found to be more corrosion resistant ( $6.0 \times 10^{-2}\text{ mm y}^{-1}$ ) than any other alloy at other current densities. Hence,  $(\text{Zn–Ni})_{3,0}$  has been taken as the optimal current density for the monolayer Zn–Ni alloy deposition.

**Table 1.** Effect of current density on the deposit characters of monolayer Zn–Ni alloy

c.d. A dm <sup>-2</sup>	Wt. %Ni	$E_{\text{corr.}}$ (Ag/AgCl/Cl <sub>sat</sub> ), V	$i_{\text{corr.}}$ $\mu\text{A cm}^{-2}$	CR, $\times 10^{-2}$ mm y <sup>-1</sup>	Appearance of the deposit
1.0	2.3	-1.242	13.30	19.3	Grayish white
2.0	1.5	-1.286	5.64	8.2	Bright
3.0	1.9	-1.342	4.14	6.0	Bright
4.0	2.7	-1.224	6.34	9.3	Bright
5.0	9.5	-1.316	5.14	9.9	Porous Bright

**Table 2.** Effect of overall number of layering on corrosion properties of Zn–Ni CMA coatings obtained with 2.0–5.0 A dm<sup>-2</sup> and 2.0–4.0 A dm<sup>-2</sup> CCD's

Cyclic cathode current densities (CCCD's)	Number of layers	Average thickness of each layer, nm	$E_{\text{corr}}$ V vs. Ag/AgCl/Cl <sub>sat</sub>	$i_{\text{corr.}}$ / $\mu\text{A cm}^{-2}$	CR, $\times 10^{-2}$ mm y <sup>-1</sup>
(Zn–Ni)2.0/5.0	10	3000	-1.100	3.78	5.50
	20	1500	-1.149	2.40	3.49
	60	500	-1.194	0.77	1.12
	120	250	-1.218	0.23	0.33
	300	100	-1.212	0.10	0.15
	600	50	-1.197	5.96	8.69
(Zn–Ni)2.0/4.0	10	3000	-1.120	4.56	6.69
	20	1500	-1.132	3.67	5.38
	60	500	-1.183	2.87	4.21
	120	250	-1.164	1.76	2.58
	300	100	-1.224	1.08	1.58
	600	50	-1.198	6.03	8.84

### CMA Zn–Ni Coatings

CMA coatings were developed by making the cathodic current to change gradually from one current density to another by proper setting-up of the power source. Multilayer coatings having alternate layers of alloys with gradually changing composition were developed using triangular current pulses (gradual change in the composition of metals is achieved by a gradual change in current density). In the present study, the CMA coating systems are represented as (Zn–Ni)<sub>1/2/n</sub>, where 1 and 2 are two cathode current density between which the cathode current is cycling; “n” is the number of layers formed during the total plating time, i.e. 10 minutes.

#### Optimization of the Cathode Current Densities

The electrochemical deposition of CMA coatings was accomplished by galvanodynamic cycling of the working electrode between pre-set current ranges in an aqueous solution containing Zn<sup>2+</sup> and Ni<sup>2+</sup> ions. Thus, by the precise control of the cathode current densities (CCD's), the deposits with alternate layers of

alloys, having different compositions and, consequently, different properties were developed. Table 2 shows the effect of the CCD's on the corrosion behavior of the coatings. To understand the effect of layering on the corrosion resistance, to begin with, the coating with only 10 layers was developed at different sets of CCD's. Among the various sets tried, the lowest corrosion rate was measured in the coatings produced with difference of 3.0 and 2.0 A dm<sup>-2</sup> between CCD's. These coatings were found to be bright and uniform. Therefore, this combination of CCD's has been selected to study the effect of layering, as described in the following subsection and in Table 2.

#### Optimization of Overall Number of Layers

The metallurgical properties of CMA coatings, including their corrosion resistance, may often be increased substantially by increasing the degree of layering (usually, up to an optimal limit), without sacrificing the demarcation between each layers. Therefore, 2.0–4.0 A dm<sup>-2</sup> and 2.0–5.0 A dm<sup>-2</sup> have been selected for layering. CMA coatings of Zn–Ni having 10, 20, 60, 120, 300 and 600 layers have been devel-

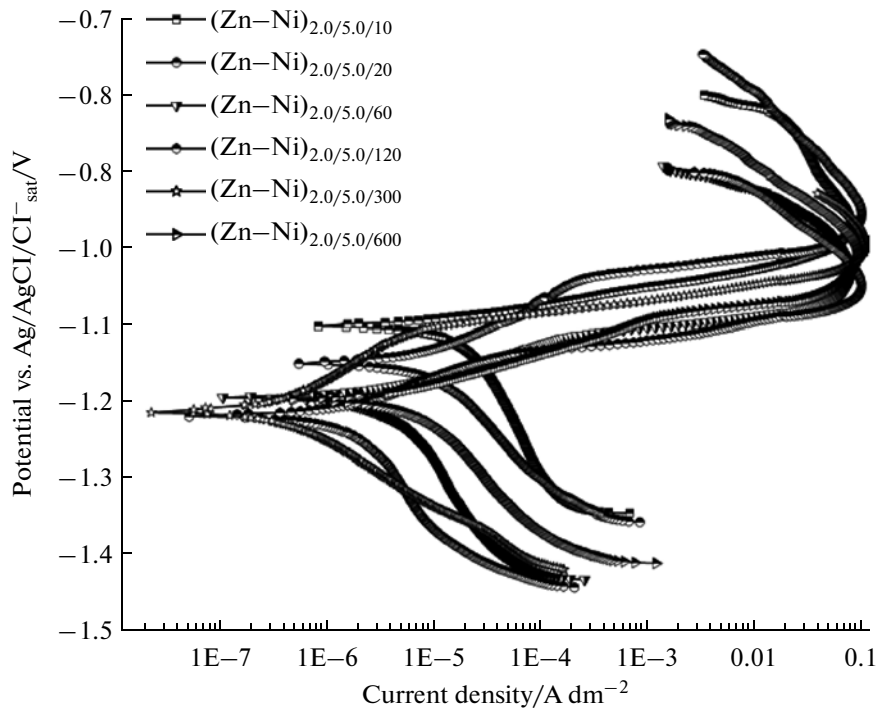


Fig. 1. Potentiodynamic polarization curves of CMA  $(\text{Zn-Ni})_{2.0/5.0}$  coatings with different number of layers.

oped and their corrosion rates have been measured by Tafel's extrapolation method. It was observed that the corrosion rates decrease substantially, with increasing the number of layers only up to 300 layers, and then they increase in both sets of CCD's, as shown in Table 2. However, at  $2.0\text{--}5.0 \text{ A dm}^{-2}$ , the corrosion rate has reached the saturation point at 300 layers (beyond which no decrease of corrosion rate with layering was observed), with the minimum corrosion rate of  $0.15 \times 10^{-2} \text{ mm y}^{-1}$  relative to  $6.0 \times 10^{-2} \text{ mm y}^{-1}$  for monolayers. Though there is a substantial decrease of the corrosion rate at  $2.0\text{--}4.0 \text{ A dm}^{-2}$ , as shown in Table 2, the result pertaining to  $2.0\text{--}5.0 \text{ A dm}^{-2}$  is more encouraging due to a better brightness and lower corrosion rate. However, an effort to further increase the corrosion resistance by increasing the number of layers in each set of CCD's has resulted in the increase of the corrosion rate.

The rise of the corrosion rate at a higher degree of layering (e.g. 600 layers) is attributed to a shorter relaxation time needed to redistribute solutes in the diffusion layer during plating [1]. As the number of layers increases, the time for the deposition of each layer, say,  $(\text{Zn-Ni})_1$ , shrinks while the total time for deposition remains the same. At a higher degree of layering, there is no sufficient time for metal ions to relax (against diffusion under a given current density) and to get deposited on the cathode, with modulation in composition. As a result, at a higher degree of layering the modulation in composition is unlikely to take place. In other words, CMA deposit is tending to become monolayer.

Therefore,  $(\text{Zn-Ni})_{2.0/5.0/300}$  has been proposed as the optimal configuration of CMA coating, with individual layer thickness  $\sim 100 \text{ nm}$  (obtained from total thickness  $30 \mu\text{m}$ ); for peak performance against corrosion.

## CORROSION STUDY

### Tafel's Polarization Study

Potentiodynamic polarization curves of CMA  $(\text{Zn-Ni})_{2.0/5.0}$  coating system with different number of layers is shown in Fig. 1. Tafel's extrapolation on such curves resulted in determination of the corrosion potential,  $E_{\text{corr}}$  corrosion current density,  $i_{\text{corr}}$  and CR, as listed in Table 2. A progressive decrease of corrosion current,  $i_{\text{corr}}$  and hence, the CR was observed with up to 300 layers, and then increased.

### Electrochemical Impedance Spectroscopy (EIS)

EIS, also referred to as an AC impedance spectroscopy, is a suitable technique to gain valuable information on the capacitance behavior of a double layer responsible for the improved corrosion resistance of the coatings and behavior of inhibitors [15]. Information about the interaction of coating with the corrosion medium is obtained from Nyquist plots [16]. In this technique it is common to plot the data as imaginary impedance versus real impedance, with the provision to distinguish the polarization resistance contribution ( $R_p$ ) from the solution resistance ( $R_s$ ). It may be observed that in  $(\text{Zn-Ni})_{2.0/5.0}$  coating systems, the

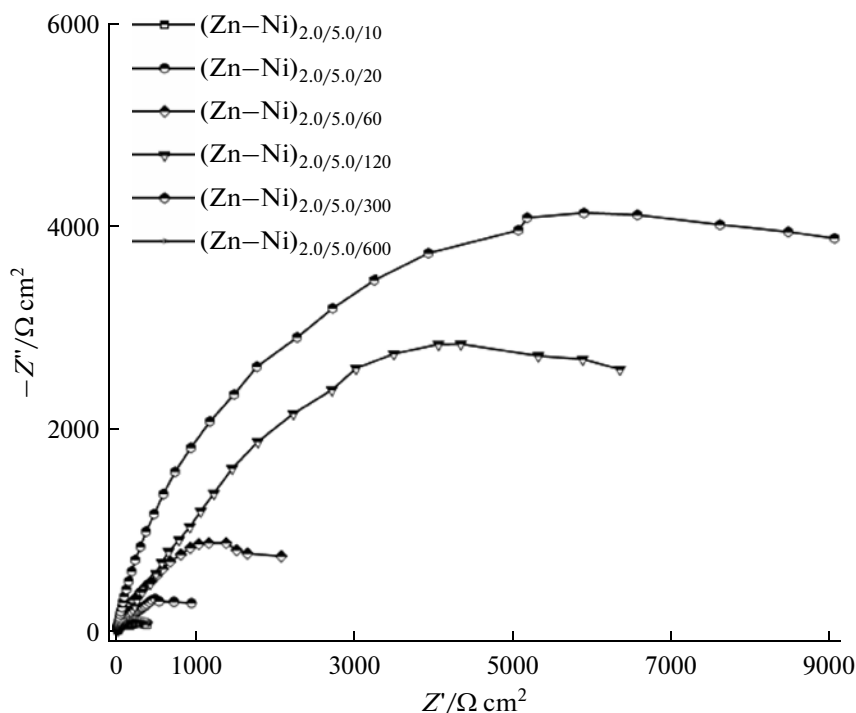


Fig. 2. Real versus imaginary resistance values of CMA  $(\text{Zn-Ni})_{2.0/5.0}$  coatings with different number of layers measured as function of frequency.

radius of the semi-circle increases with number of layers of up to 300 and then decreases as shown in Fig. 2. Polarization resistance,  $R_p$ , increases as the number of layers increases. However, for deposit with 600 layers, the radius of the semi-circle decreases drastically, indicating its poor corrosion resistance, as shown in Fig. 2.

#### Cyclic Voltammetry Study

It was observed that THC and CA have significant effect on the homogeneity and brightness of the coatings. Hence, the process and product of Zn–Ni deposition was studied by the CV method, on adding CA and THC, both individually and in combination, into the electrolytic bath. In the absence of CA, the electrochemical oxidation curve showed multiple peaks, as shown in Fig. 3a. This corresponds to the dissolution of the metals in the alloy via different intermediate phases [17]. After adding CA, a small change in the shape of the voltammogram was found (Fig. 3b). It indicates that CA has been involved in complexation of metal ions. Further, when THC was added, the shape of voltammogram has changed drastically, with one major peak at  $-0.68$  V and one minor peak at  $-0.28$  V, corresponding to the dissolution of different phases of the alloy (Fig. 3c). Lastly, when CA and THC were added in combination, the intensities of the first and second peaks have increased, with a slight distortion to the right (Fig. 3,d). Hence, it may be noted

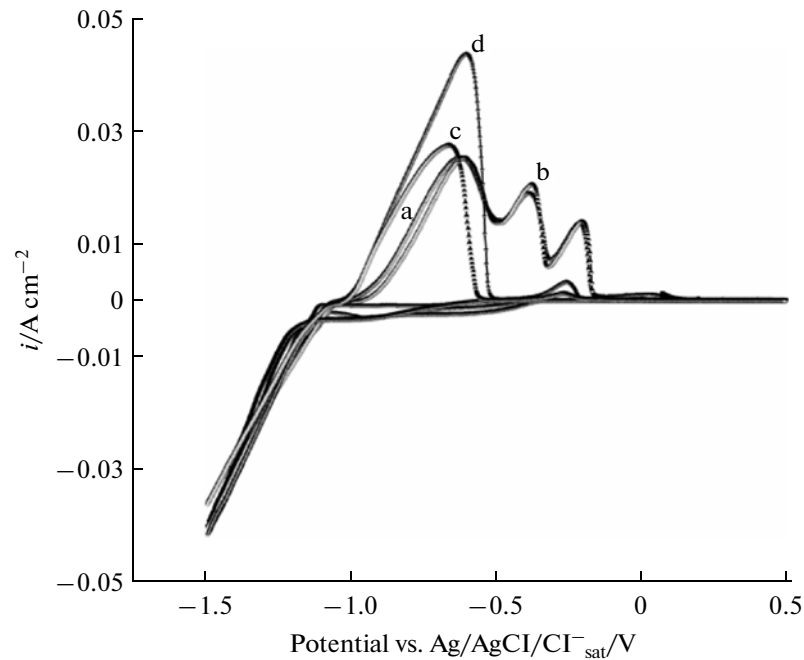
that THC and CA have improved the deposit characters, by forming complexes with metal ions.

#### X-ray Diffraction Study

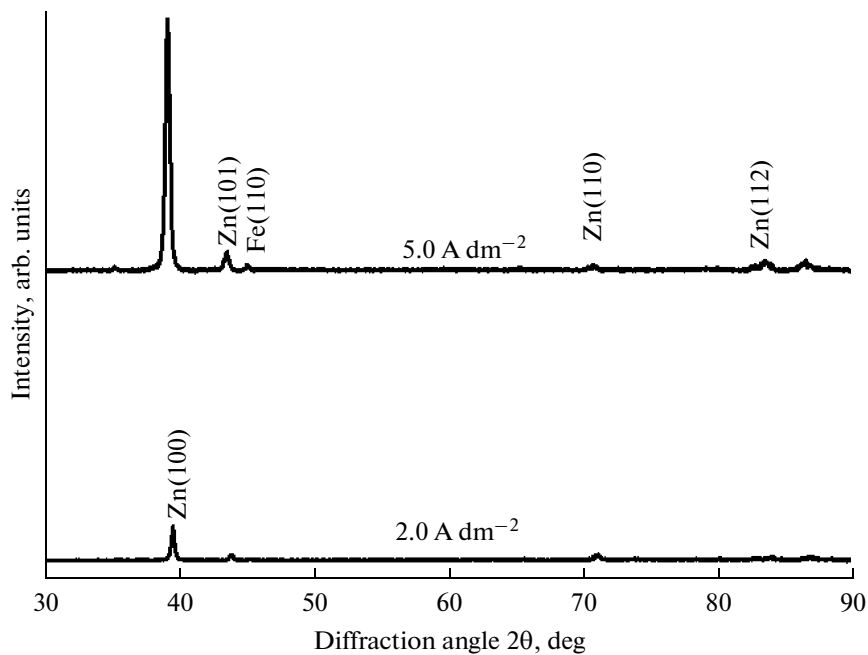
The corrosion resistance of Zn–Ni alloy depends, in effect, on its phase structure and also on the wt % Ni in the deposit [18]. X-ray diffraction patterns of Zn–Ni alloy coatings as a function of deposition current density 2.0 and 5.0  $\text{A dm}^{-2}$  are shown in Fig. 4. It may be observed that the peak corresponding to Zn (100) intensify at current density 5.0  $\text{A dm}^{-2}$  compared to the deposit has been obtained at 2.0  $\text{A dm}^{-2}$ . Besides, peaks corresponding to Zn (101), Zn (110) and Zn (112) may be distinctly observed at 5.0  $\text{A dm}^{-2}$ , comparing to that at 2.0  $\text{A dm}^{-2}$ . Thus it may be inferred that the drastic change in corrosion resistance of CMA  $(\text{Zn-Ni})_{2.0/5.0/300}$  coatings is due to the consequent change in the phase structures of the coatings in alternate layers, i.e. at 2.0 and 5.0  $\text{A dm}^{-2}$ , which is responsible for the modulation of composition, and consequently, the properties of alloys in a multilayer.

#### Comparison Between Monolayer and CMA Zn–Ni Coatings

The corrosion rates of a monolayer Zn–Ni alloy at 3.0  $\text{A dm}^{-2}$  and CMA  $(\text{Zn-Ni})_{2.0/5.0/300}$  coatings developed (both under optimal conditions) from the same bath are given in Tables 1 and 2, respectively. The CMA (Zn–Ni) coating, having 300 layers, deposited



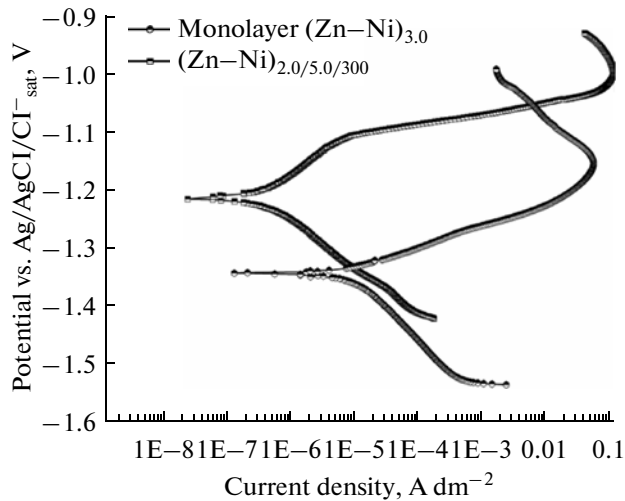
**Fig. 3.** Cyclic voltammograms of Zn–Ni alloy bath, demonstrating the effects of THC and CA. Working electrode: Pt, pH = 3.0,  $T = 30^\circ\text{C}$ ,  $v = 10 \text{ mV s}^{-1}$ . (a) Without additive, (b) with CA, (c) with THC, (d) with CA + THC.



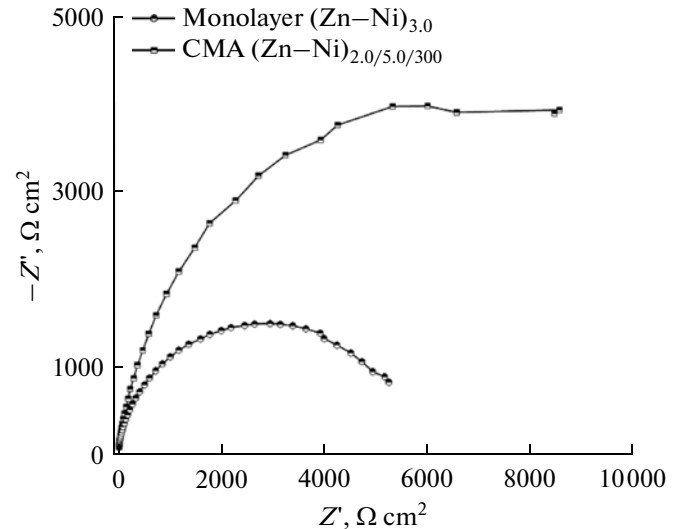
**Fig. 4.** X-ray diffraction profiles of Zn–Ni alloy electrodeposits, developed from the optimal bath at two different current density.

at CCD's 2.0 and 5.0  $\text{A dm}^{-2}$  was found to show the lowest corrosion rate ( $0.15 \times 10^{-2} \text{ mm y}^{-1}$ ) compared to that of a monolayer alloy ( $6.0 \times 10^{-2} \text{ mm y}^{-1}$ ) of the same thickness. The relative responses for the potentiodynamic polarization and the EIS study of the monolayer Zn–Ni, represented as  $(\text{Zn–Ni})_{3.0}$  and  $(\text{Zn–Ni})_{2.0/5.0/300}$  coatings, are shown in Figs. 5 and 6,

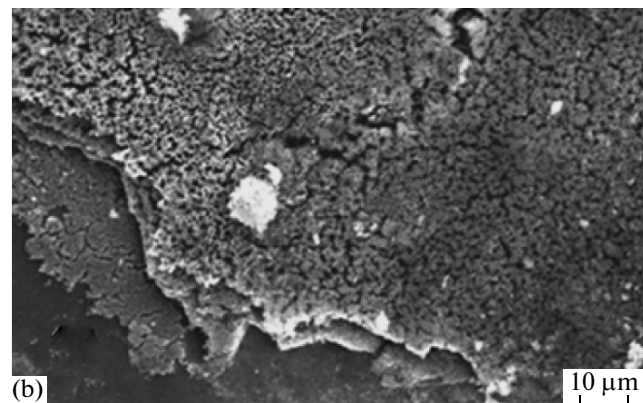
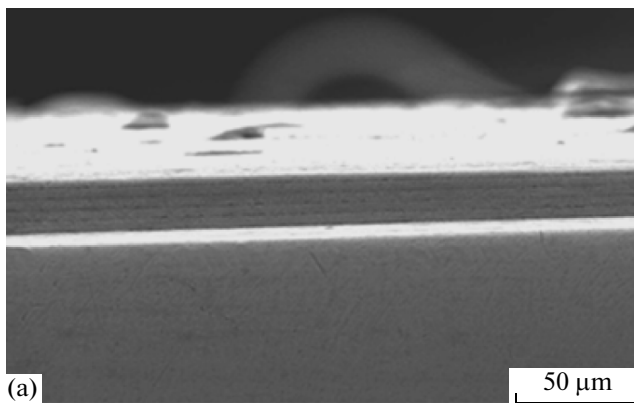
respectively. The behavior of Nyquist plots showed that significant decrease of the corrosion rate of the CMA coating, in relation to a monolayer alloy, is due to a large reactance of an electrical double layer capacitor at the interface of the base metal and the medium. The high corrosion resistance of CMA coatings can be envisaged since the formation of pores, crevices



**Fig. 5.** Comparison of potentiodynamic polarization curves of monolayer  $(\text{Zn-Ni})_{3.0}$ , and CMA  $(\text{Zn-Ni})_{2.0/5.0/300}$  coatings (of same thickness).



**Fig. 6.** Comparison of Nyquist response of monolayer  $(\text{Zn-Ni})_{3.0}$ , CMA  $(\text{Zn-Ni})_{2.0/5.0/300}$  coatings (of same thickness).



**Fig. 7.** SEM images of CMA  $(\text{Zn-Ni})$  coatings: Cross-sectional view of alloy having 10 layers (a), CMA  $(\text{Zn-Ni})_{2.0/5.0/4}$  after corrosion test (b).

occurring in one layer is blocked or neutralized by the successively deposited coating layers, and thus the corrosion agent's path is delayed or blocked. The improved corrosion resistance afforded by CMA coatings can be also explained in terms of the formation of alternate layers of alloys with low and high wt % of Ni [19]. A small compositional change in layers has brought a significant change in the phase structure of the alloys, as evidenced by the XRD study.

#### SEM Study

Formation of alternate layers of alloys, having different composition, was confirmed by using SEM. Cross-sectional view of CMA  $(\text{Zn-Ni})_{2.0/5.0/10}$  is shown in Fig. 7a. The poor contrast may be due to the marginal difference in the chemical composition of alloys in each layer. Inspection of the microscopic

appearance of the surface after corrosion tests has helped to understand the reason for the improved corrosion resistance of CMA coatings. The coatings with CMA  $(\text{Zn-Ni})_{2.0/5.0/4}$  configuration are subjected to anodic polarization at +250 mV vs. open circuit potential in the 5% NaCl solution. The corroded specimens were washed with distilled water and examined under SEM. Figure 7b shows four layers for CMA  $(\text{Zn-Ni})_{2.0/5.0/4}$  configuration after corrosion test. The image in Fig. 7b exposes alternate layers formed during the process of deposition. It is evident that the layers with a lower concentration of Ni have been preferentially dissolved, although, eventually, the steel substrate was exposed. Short et al. reported that an improved barrier layer was formed on Zn-Ni deposits under anodic control due to dezincification, thus reducing the rate of anodic dissolution properties of CMA coatings [20].

## CONCLUSIONS

The following conclusions have been drawn from the present study:

(1) CMA coatings of Zn–Ni have been developed on mild steel by the proper manipulation of cathodic current densities and number of layers using single bath technique.

(2) CMA (Zn–Ni) coatings, having 300 layers, deposited at 2.0 and 5.0 A dm<sup>-2</sup>, have been found to show the lowest corrosion rate ( $0.15 \times 10^{-2}$  mm y<sup>-1</sup>) compared to that of a monolayer alloy ( $6.0 \times 10^{-2}$  mm y<sup>-1</sup>) of the same thickness.

(3) Corrosion resistance of CMA coatings increases with the number of layers but only up to a certain optimal level of 300 layers and then decreases. This may be attributed to a shorter relaxation time for the redistribution of metal ions at the diffusion layer during deposition. In other words, at a higher layering, the CMA coating tends to become a monolayer.

(4) The CV study has demonstrated that both THC and CA have improved the deposit character, by forming complexes with metal ions.

(5) The X-ray diffraction study has revealed that the improved corrosion resistance afforded by CMA coatings is due to the formation of alternate layers of alloys having different phase structures.

(6) The SEM analysis has confirmed the formation of a multilayer during deposition and evidenced the extended protection by successively deposited alloy coating layers with different extent of pores and crevices.

## REFERENCES

- Nasser Kanani, *Electroplating: Basic Principles, Processes and Practice*, Berlin, Germany: Elsevier Ltd, 2006.
- Injeti, G. and Leo, B., Electrodeposition of Nanostructured Coatings and Their Characterization—a Review, *Sci. Technol. Adv. Mater.*, 2008, vol. 9, pp. 1–11.
- Ivanov, I., Valkova, T., and Kirilova, I., Corrosion Resistance of Compositionally Modulated Zn–Ni Multilayers Electrodeposited from Dual Bath, *J. Appl. Electrochem.*, 2002, vol. 32, pp. 85–89.
- Kalantary, M.R., Wilcox, G.D., and Gabe, D.R., Alternate Layers of Zinc and Nickel Electrodeposited to Protect Steel, *Britt. Corros. J.*, 1998, vol. 33, pp. 197–201.
- Chawa, G., Wilcox, G.D., and Gabe, D.R. Compositionally modulated zinc alloy coatings for corrosion protection. *Trans. Inst. Met. Finish.* 1998, 76, 117–121.
- Kalantary, M.R., Wilcox, G.D., and Gabe, D.R., Production of Compositionally Modulated Alloys by Simulated High Speed Electrodeposition from a Single Solution, *Electrochim. Acta*, 1995, vol. 40, no. 11, pp. 1609–1616.
- Hayashi, K., The Cosmetic Corrosion Mechanism and Corrosion Resistance of Zinc Alloy Coated Steel Sheet, *Int. J. Mater. Prod. Technol.*, 1991, vol. 6, no. 1, pp. 9–25.
- Prabhu Ganeshan, Swaminatha P., Kumaraguru, and Popov, B.N., Development of Compositionally Modulated Zn–Ni Multilayer Deposits as Replacement for Cadmium, *Surf. Coat. Technol.*, 2007, vol. 201, pp. 7896–7904.
- Gabe, D.R., Protective Layered Electrodeposits, *Electrochim. Acta*, 1994, vol. 39, nos. 8–9, pp. 1151–1121.
- Ivanov, I. and Kirilova, I., Corrosion Resistance of Compositionally Modulated Multilayered Zn–Ni Alloys Deposited from Single Bath, *WJ. Appl. Electrochem.*, 2003, vol. 33, nos. 3–4, pp. 239–244.
- Jing-yin, Fei, and Wilcox, G.D., Electrodeposition of Zinc–Nickel Compositionally Modulated Multilayer Coatings and Their Corrosion Behaviors, *Surf. Coat. Technol.*, 2006, vol. 200, pp. 3533–3539.
- Thangaraj, V., Eliaz, N., and Chitharanjan Hegde, A., Corrosion Behavior of Composition Modulated Multilayer Zn–Co Electrodeposits Produced Using a Single-Bath Technique, *J. Appl. Electrochem.*, 2009, vol. 39, no. 3, pp. 339–345.
- Thangaraj, V., Ravishankar, K., and Chitharanjan Hegde, A., Surface Modification by Compositionally Modulated Multilayered Zn–Fe Alloy Coatings, *Chin. J. Chem.*, 2008, vol. 26, pp. 1–10.
- Vogel, A.I., *Quantitative Inorganic Analysis*, London: Longmans Green and Co, 1951.
- Craig, B.D., *Fundamental Aspects of Corrosion Films in Corrosion Science*, New York: Plenum Press, 1991.
- Yuan, X., Song, C., Wang, H., and Zhang, J., *Electrochemical Impedance Spectroscopy in PEM Fuel Cells—Fundamentals and Applications*, London: Springer Publications, 2010.
- Trejo, G., Ortega, R., Meas, Y., Ozil, P., and Chainet, E., Effect of Benzyl Ideneacetone on the Electrodeposition Mechanism of Zn–Co Alloy, *J. App. Electrochem.*, 2003, vol. 33, pp. 373–379.
- Felloni, L., Fratesi, R., Quadrini, E., and Roventi, G., Electrodeposition of Zinc–Nickel Alloys from Chloride Solution, *J. Appl. Electrochem.*, 1987, vol. 17, no. 3, pp. 574–582.
- Jingyin, Fei, Liang, Guozheng, Xin, Wenli, and Liu, Jianghong, Corrosion Performance of Zinc and Zinc-cobalt Alloy Compositionally Modulated Multilayer (CMM) Coatings, *Journal of Wuhan University of Technology—Mater. Sci.*, 2006, vol. 21, no. 4, pp. 40–44.
- Short, N.R., Abibsi, A., and Dennis, J.K., Corrosion Resistance of Electroplated Zinc alloy Coatings, *Trans. Inst. Met. Fin.*, 1984, vol. 67, no. 1, pp. 73–77.