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Development of Composition Modulated Multilayer Alloy Coatings and their Corrosion Behavior

Subbaiah YOGESHA and Ampar CHITHARANJAN HEGDE*

Electrochemistry Research Laboratory, Department of Chemistry,
National Institute of Technology Karnataka, Surathkal Srinivasnagar - 575025, India

Abstract

Multilayer Zn-Ni alloy coating was developed on mild steel from acid chloride bath containing thiamine hydrochloride, as additive. Composition modulated multilayer alloy (CMMA) coatings, or simply, multilayer coating with gradual change in composition were developed galvanostatically using triangular current pulses from single bath technique. CMMA coatings of Zn-Ni were developed under different conditions, such as cyclic cathode current densities (CCCD's) and a number of layers, and their corrosion behaviors were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy method. Optimal configuration, $(Zn\text{-}Ni)_{2.0/4.0/600}$ was found to exhibit ~50 times better corrosion resistance compared to monolayer $(Zn\text{-}Ni)_{3.0}$ alloy, deposited from the same bath for the same time. The corrosion resistance of CMMA coatings was observed to be better, and results were discussed. Further, decrease of corrosion rate at high degree of layering was found, and was explained by less relaxation time for redistribution of solutes at diffusion layer during plating. The better corrosion resistance of the CMMA coating, developed using triangular current pulses, have been discussed in relation to those obtained by square current pulses. Both formation of multilayer and corrosion mechanisms were analyzed using scanning electron microscopy (SEM).

Key words: Composition modulated multilayer alloy (CMMA), Zn-Ni, Triangular current pulse, Corrosion resistance.

Introduction

A new class of materials with alternate layers of metals/alloys, consisting of a thickness of a few nanometers with ultra fine microstructure, is known as composition modulated multilayer alloys (CMMA) [(1)]. CMMA coating systems are relatively new and are gradually gaining interest amongst researchers, because these layered coatings possess improved properties or novel phenomena such as increased mechanical strength, micro-hardness, giant magnetoresistance and corrosion resistance [(2-6)]. There are different methods for producing multilayered alloy coating; physical vapor deposition (PVD), chemical vapor deposition (CVD), and electrodeposition techniques are some among many others [(7)]. Electrolytically, such alloys can be obtained by using either a single-bath technique (SBT), when deposition takes place in a plating solution containing ions of the alloy components, or a double-bath technique (DBT), when deposition is carried out from separate plating baths by using a manual and automated transfer of the substrate from one bath to another. Both techniques are known to have their own advantages and disadvantages. In most cases, the drawbacks of the DBT have been deemed to outweigh the benefits, so that the SBT approach is used instead [(8)]. Though gradations in composition are possible through modulation in cathode current density, agitation, temperature etc, the composition can be better controlled, with a great degree of accuracy and reproducibility using microprocessor controlled power sources [(9)]. In principle, this technique is straightforward to design and fabricate. The multilayered alloy coating can be developed from SBT using square, triangular and trapezoidal current pulses. Accordingly, it is possible to tailor the properties of coatings in order to meet desired engineering properties by proper manipulation of current/voltage pulse patterns.

Substantial work has already been documented to support the enhanced corrosion resistance of CMMA coatings of Zn-M (where M = Fe group metals like Fe, Co and Ni) alloy using SBT [(10-14)]. Recently, the development of multilayered Zn-Ni alloy coatings from various

*Corresponding author E-mail: achegde@rediffmail.com

baths has been reported, using square current pulses i.e. by bringing sudden change in composition for improved corrosion resistance [15-18]. No work is reported with regard to optimization of coating configuration for development of CMMA coatings using triangular current pulses. Hence this paper discusses the optimization of deposition conditions for development of monolayer and multilayer coatings of Zn–Ni alloy using triangular current pulses from chloride bath, containing THC as additive. Better corrosion resistance of multilayer coating over the monolayer was identified, and results were discussed with emphasis on corrosion stability of the coatings, developed using square current pulses.

Materials and Experimental Procedures

Materials

The prepared electrolytic bath composition having 15g/L ZnO, 60g/L $NiCl_2$, 150g/L NH_4Cl, 20g/L boric acid, 10g/L citric acid and 2g/L Thiamine hydrochloride (THC) was used for electrodeposition. The electrolyte was prepared using LR-grade chemicals and distilled water. Mild steel panels with 7.5 cm^2 active surface area were used as cathode after pretreatment. A PVC cell of 250 cm^3 capacity was used for electroplating with a cathode-anode space of ~ 5cm.

Equipment

DC power analyzer (Model N6705A, Agilent Technologies, USA) was used for development of both monolayer and multilayer coatings. Potentiostat/Galvanostat (VersaSTAT-3, Princeton Applied Research) with three-electrode cell was used to evaluate corrosion behavior of the coatings. Other equipment used for coating characterization includes micro pH meter (Model 362, Systronics), Scanning electron microscopy (SEM) (Model JSM-6380 LA from JEOL Japan), Digital Thickness Tester (Coatmeasure M&C, ISO-17025/2005), and Micro Hardness Meter (CLEMEX).

Experimental Design and Procedure

All depositions were made using optimized bath for a duration of 10 minutes (thickness of ~20µm), for the purpose of comparison. All deposition conditions were kept constant, except current density. Predetermined cathode current densities were applied alternatively by proper setting-up of the power source. Both monolayer and multilayer coatings having graded composition have been developed, using DC and triangular current pulses, respectively, as shown schematically in Figure 1.

Zn-Ni multilayer coating having alternatively different compositions were represented as: $(Zn\text{-}Ni)_{1/2/n}$ (where 1 and 2 indicate the first and second cathode current density, and 'n' represents the number of gradations formed during total plating time i.e. 10 min). Zn-Ni CMMA coatings with different configuration (i.e. under different sets of CCCD's and number of layers) were developed and characterized.

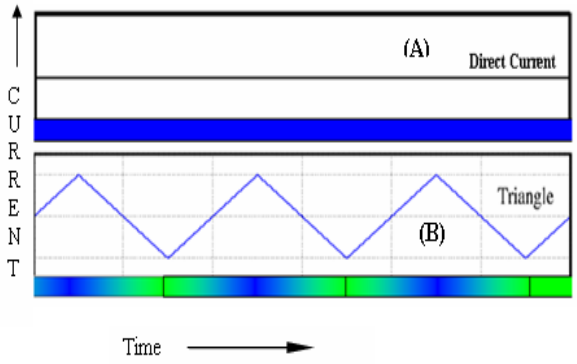

Figure 1. Schematic representation of (A) Monolayer Zn-Ni alloy using constant current, and (B) Composition graded multilayer coating using triangular current pulses, cycling between pre-defined current densities.

Characterization and Properties Evaluation

The corrosion behavior of coatings was measured by electrochemical polarization and impedance spectroscopy techniques in a three-electrode cell. All electrochemical potentials referred in this work are relative to Ag, $AgCl/KCl_{sat.}$ The 5% NaCl solution (open to air at 30±2 °C) was used as corrosion medium.

Potentiodynamic polarization study was carried out in a potential ramp of ± 250 mV from open circuit potential (OCP) at a scan rate of $1mVs^{-1}$. Impedance behavior was studied in the frequency range from 100 KHz to 10 mHz. Composition of the coatings was determined colorimetrically using standard method [19]. Data on the electronic properties of the protective film were obtained by capacitance measurements as a measure of the charge distribution in the film. The relationship between the capacitance C and the potential drop in the semiconductor can be written in the following form [20]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 eN}(E - E_{fb} - kT/e) \qquad (1)$$

representing the Mott-Schottky equation, where e is the elementary charge (+ e for electrons and – e for holes), ε. is the dielectric constant, ε_0 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 Mott-Schottky plots were obtained by performing a potential scan in the cathodic direction. The capacitance measurements were carried out at 100 Hz within the potential range from + 0.5 to - 0.5 V. A perturbing signal of 10 mV was used. The formation of multilayer and corrosion mechanism was examined by scanning electron microscopy. The thickness of the coatings was assessed through Faradays law and cross-examined using digital thickness tester.

Results and Discussion

Deposition of Monolayer Zn-Ni Alloy

A wide spectrum of Zn-Ni alloy formed on Hull cell panel, which shows that current density (c.d.) plays an important role in deciding the properties of the deposit.

Monolayer, or monolithic Zn-Ni alloys were developed galvanostatically onto pre-cleaned mild steel at different c.d. and were then tested. The effects of c.d. on wt. % Ni, thickness, Vickers hardness, corrosion resistance and appearance of the coatings are reported in Table 1. The corrosion data show that at 3.0 A/dm^2, the coating exhibits the least corrosion rate (15.18 X 10^{-2} mmy^{-1}) with bright appearance, which has been taken as its optimal corrosion rate.

Deposition of CMMA coating

Optimization of Cyclic Cathode Current Densities (CCCD's)

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 properties change due to change in the phase structure. Thus, by precise control of the CCCD's it is possible to develop alternate layers of alloys with different compositions and, consequently, different properties. Experimental study of multilayer Zn-Ni alloy, developed using square current pulses (sharp change in current) has revealed that they are more corrosion resistant (by several folds) than corresponding monolayer coating of the same thickness. Hence, in the present study modulation in composition is effected by gradual change in composition using triangular current pulses. Accordingly, multilayer coatings having 10 layers (5 bi-layers) were developed at different sets of CCCD's and corresponding corrosion data are reported in Table 2. Among the various sets tried, the lowest corrosion rate was measured in the coatings produced with a difference of 2.0 A/dm^2 and 4.0 A/dm^2 between CCCD's, as shown in Table 2. This combination of CCCD's has been selected for studying the effect of layering, as described in the following subsection and in Table 3.

Optimization of Total Number of Layers

The metallurgical properties of CMMA 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 layer. Therefore, several sets of CCCD's such as 2.0/4.0 and 2.0/6.0 A/dm^2 have been selected for layering. Zn-Ni CMMA coatings with 20, 60, 120, 300 and 600 layers were developed and their corrosion rates were measured by Tafel's extrapolation method. The corrosion rate (CR) of coatings was found to decrease with the number of layers in each set of CCCD's, as shown in Table 3. However, at 2.0/4.0 A/dm^2, the coating with 600 layers showed minimum CR of $0.28x\ 10^{-2}$ mmy^{-1} relative to 15.18×10^{-2} mmy^{-1} for monolithic Zn-Ni alloy coatings (shown in Table 1). Though there is

substantial decrease of CR with layering at other sets of CCCD's also (i.e. at 2.0/6.0 A/dm^2 with 300 layers as shown in Table 3), the result pertaining to 2.0/4.0 A/dm^2 is more encouraging due to better homogeneity and brightness of the deposit. However, an effort of increasing the corrosion resistance further by increasing the number of layers in each set of CCCD's has resulted in decrease of corrosion rate, may be due to the diffusion of individual layers (tended towards monolithic). $(Zn\text{-}Ni)_{2.0/4.0/600}$ has been proposed as the optimal configuration of CMMA deposit (with individual layer thickness ~50 nm) from the proposed bath for peak performance against corrosion.

Table 1. Effect of c.d. on the deposit characters of monolithic Zn-Ni alloy deposited from optimized bath at 303K.

c.d. /A/dm^2	wt. % Ni	Thickness/ µm	Vickers Hardness V_{100}	$-E_{corr}$ /V vs Ag,AgCl / KCl_{sat}	I_{corr} /µA/cm^2	CR /x 10^{-2} mmy^{-1}	Nature of the deposit
2. 0	5.15	6.5	177	1.306	11.29	15.46	Semi Bright
3. 0	3.16	10.8	180	1.245	11.08	15.18	Bright
4. 0	3.23	12.4	182	1.225	13.23	18.13	Bright
5.0	3.81	15.9	190	1.196	14.83	20.31	Semi Bright
6.0	4.00	16.1	195	1.264	14.94	22.16	Semi Bright
7.0	5.05	16.8	170	1.344	18.3	25.06	Grayish Bright
8.0	5.13	17.5	165	1.060	22.29	30.52	Grayish Bright

Table 2. Corrosion rate of CMMA Zn-Ni coatings at different set of CCCD's (with 10 layers).

CMMA Zn-Ni coatings developed at difference of 2.0 A/dm^2 between CCCD's			
CCCD's /A/dm^2	$-E_{corr}$ /V vs Ag,AgCl / KCl_{sat}	I_{corr} /µA/cm^2	CR /x 10^{-2} mmy^{-1}
$(Zn\text{-}Ni)_{2.0/4.0/10}$	1.143	8.213	12.14
CMMA Zn-Ni coatings developed at difference of 4.0 A/dm^2 between CCCD's			
$(Zn\text{-}Ni)_{2.0/60/10}$	1.139	8.695	12.75

Table 3. Decrease of corrosion rate (CR) of CMMA coatings with increase of layers.

Current density /A/dm^2	No. of layers	-E_{corr} /V vs Ag,AgCl / KCl_{sat}	I_{corr} /μA/cm^2	CR /x 10^{-2} mmy^{-1}
Optimization of layer thickness at CCCD's of 2.0 - 4.0 A/dm^2				
$(Zn\text{-}Ni)_{2.0/4.0/10}$		1.143	8.213	12.14
$(Zn\text{-}Ni)_{2.0/4.0/20}$		1.119	5.128	7.60
$(Zn\text{-}Ni)_{2.0/4.0/60}$		1.109	1.553	2.30
$(Zn\text{-}Ni)_{2.0/4.0/120}$		1.166	0.774	1.14
$(Zn\text{-}Ni)_{2.0/4.0/300}$		1.190	0.404	0.60
$(Zn\text{-}Ni)_{2.0/4.0/600}$		1.209	0.189	0.28
Optimization of layer thickness at CCCD's 2.0 – 6.0 A/dm^2				
$(Zn\text{-}Ni)_{2.0/6.0/10}$		1.139	8.695	12.75
$(Zn\text{-}Ni)_{2.0/6.0/20}$		1.157	2.813	4.17
$(Zn\text{-}Ni)_{2.0/6.0/60}$		1.156	1.555	2.30
$(Zn\text{-}Ni)_{2.0/6.0/120}$		1.163	0.504	0.74
$(Zn\text{-}Ni)_{2.0/6.0/300}$		1.207	0.256	0.38

Corrosion Study

Tafel's Polarization Study

The polarization behavior $(Zn\text{-}Ni)_{2.0/4.0}$ of CMMA coatings with different degrees of layering is shown in Figure 2. It was observed that the corrosion resistance of the deposits increased with the number of layers as evidenced by their i_{corr} values, reported in Table 3. Decrease of E_{corr} value with increase of number of layers showed that the CMMA deposits provide sacrificial anodic protection to the substrate. Further, the progressive decrease of corrosion current (i_{corr}) with the number of layers indicated that improved corrosion resistances are due to layering of alloys, having distinctive properties. The polarization curve shown in Figure 2 indicates that CMMA deposit with $(Zn\text{-}Ni)_{2.0/4.0/600}$ configuration possesses the highest corrosion resistance.

Electrochemical Impedance Spectroscopy (EIS)

EIS, also referred to as AC impedance spectroscopy, is a suitable technique to gain valuable information on the capacitance behavior of double layer responsible for improved corrosion resistance of the deposits and behavior of inhibitors [21]. In this technique, it is common to plot the data as imaginary impedance versus real impedance with provision to distinguish the polarization resistance contribution (R_p) from the solution resistance (R_s). These plots are often called Nyquist diagrams. Nyquist diagrams of $(Zn\text{-}Ni)_{2.0/4.0}$ deposits with different number of layers were studied (Figure 3). Impedance signals clearly indicate that the capacitance of the double layer has decreased progressively with increase of number of layers. This is to say the real component of the impedance, Z_{real} increases with number of layers as shown in Figure 3. In other words, capacitive reactance, X_c increases with layering.

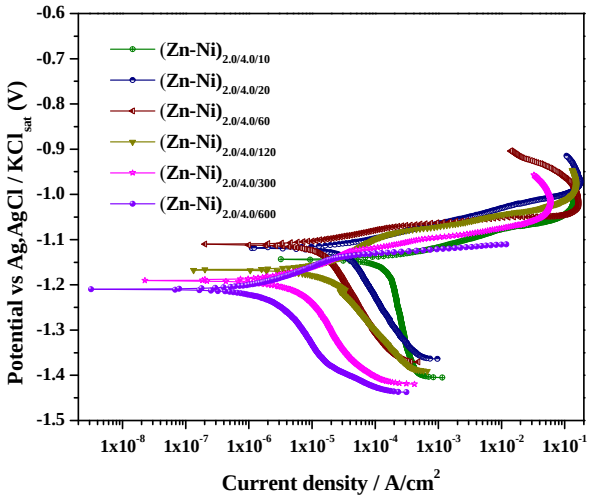

Figure 2. Potentiodynamic polarization curves of CMMA $(Zn\text{-}Ni)_{2.0/4.0}$ coatings with different number of layers.

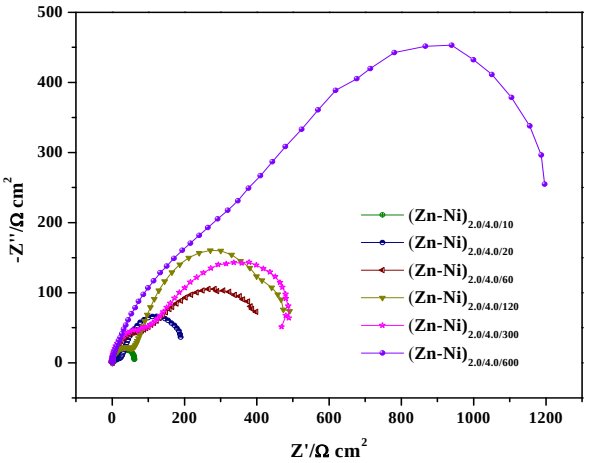

Figure 3. Real versus imaginary resistance values of CMMA $(Zn\text{-}Ni)_{2.0/4.0}$ coatings with different number of layers measured as function of frequency.

Mott-Schottky Behavior and Passivity

It is well known that the corrosion product film on most alloys exhibits semiconductive behavior. The most common *in situ* method for probing the electronic properties of the corrosion product film is Mott-Schottky's analysis. The linear relation between $1/C^2$, where C is the interfacial capacitance, and the applied potential E is expressed as Mott-Schottky (M-S) equation. The significantly lower corrosion rate observed at optimal configuration, CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ is attributed to the semiconductor property of film (coatings) at the interface, evidenced by M-S plot shown in Figure 4. Further, the straight line with positive slope revealed that the protective semiconductor layer operative at the interface is n-type in nature.

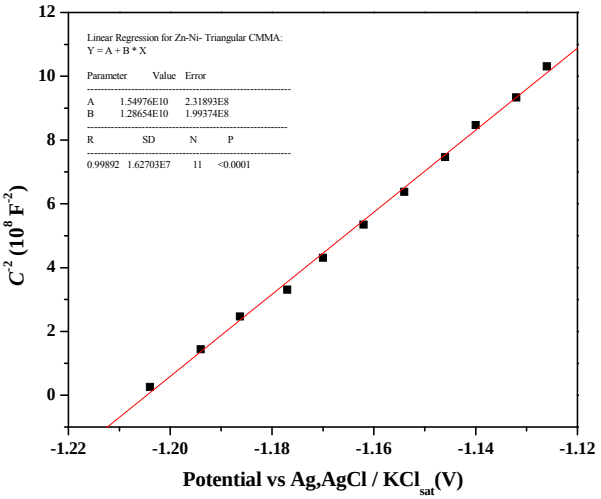

Figure 4. Mott- Schottky plot for CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ coating developed at optimal bath conditions.

Dielectric Barrier of CMMA Coatings

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

$$\varepsilon_r = \frac{C_c \delta}{A \varepsilon_0} \qquad (2)$$

Where, ε_0 is permittivity of the vacuum. Improved corrosion resistance of CMMA coatings can be explained in terms of the effect of time dependent electric field (i.e. frequency response). Figure 5 shows the variation of relative permittivity versus frequency of the coatings having a different number of layers. It was observed that the value of ε_r for all coatings is high at a low frequency; values are diminished as the frequency is increased. At low frequency side, the decrease of ε_r with increase of number of layers indicates that the dielectric barrier of coatings has increased with layering. This attributes to the increased interfacial polarization effect, caused by the heterogeneous media consisting of phases with different dielectric permittivity [22].

There are many causes for heterogeneity in materials, but CMMA coatings pertaining to present work, it is related to interfaces created by electron charge density. Thus it may be concluded that the peak corrosion resistance of CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ coating is due to the decreased permittivity of the coating.

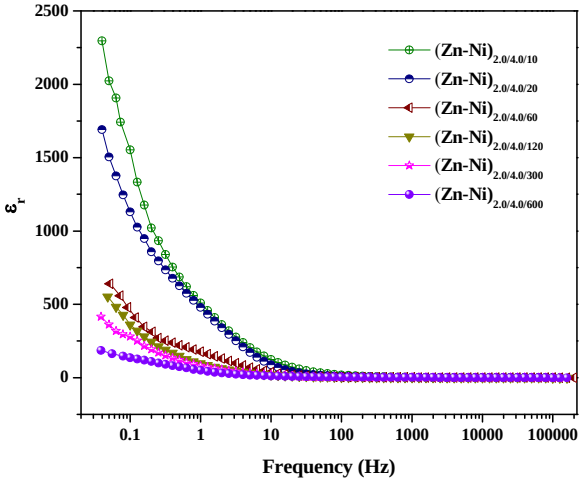

Figure 5. Relative permittivity of CMMA $(Zn\text{-}Ni)_{2.0/4.0}$ coatings with varying number of layers as function of frequency

Cyclic Polarization Study

The peak corrosion resistance exhibited by CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ coating may be better understood by investigating the cyclic polarization study over a potential range of -1.3V to -0.2V as shown in Figure 6. In the forward scanning, the value of current density went through from negative to positive, which showed that the oxidizing reaction of the passivation film occurred with increasing potential. During backward scanning, the value of current density went through from positive to negative, indicating that reducing reaction of the high valence oxide in the passivation film occurred with the falling potential.

In the range of -0.2 to -0.5 V, the current density of backward scanning is higher than that of the forward scanning, indicating that the dissolving of oxides had occurred in the process of forward scanning, so self-repairing occurred in the process of backward scanning, and the increased anodic current appeared. In the range of -0.5 to -0.8 V, current density of backward scanning was lower than that of forward scanning, which illustrates that metal could form a protective passive film below this value. But current density of backward scanning was lower than forward scanning at the same potential, which indicates that passive film had a more compact structure after anodic polarization.

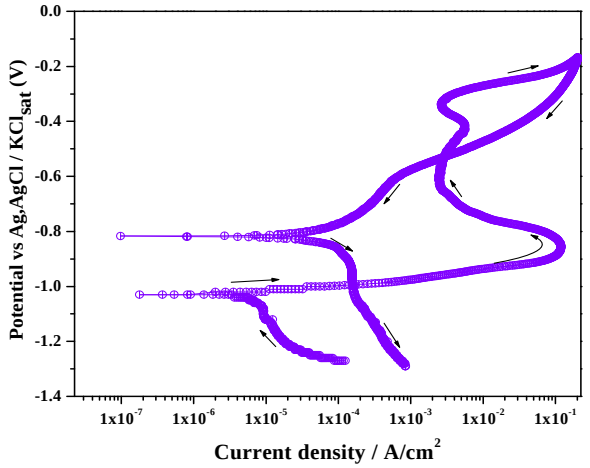

Figure 6. Cyclic polarization curve of CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ coating developed at optimal bath condition.

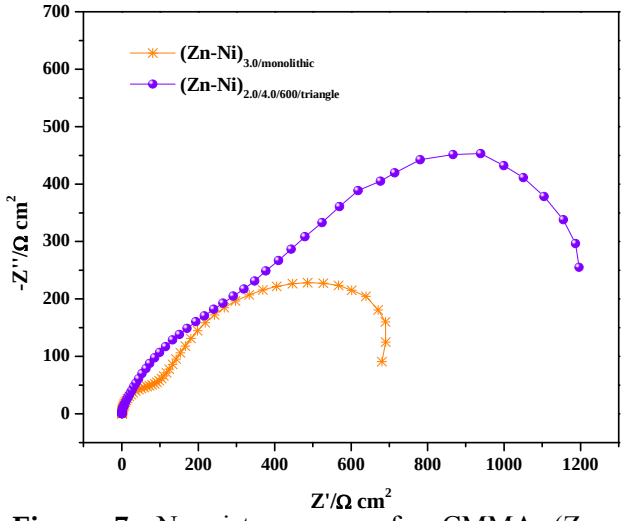

Figure 7- Nyquist response for CMMA $(Zn\text{-}Ni)_{2.0/4.0/600/triangular}$ and monolithic $(Zn\text{-}Ni)_{3.0}$ coatings of the same thickness.

Comparison between Monolithic and CMMA Zn-Ni Coatings

The corrosion rates of multilayer coating developed using triangular current pulse, represented as $(Zn\text{-}Ni)_{2.0/4.0/600/triangular}$ is given in comparison with those developed using square current pulses, represented as CMMA $(Zn\text{-}Ni)_{2.0/4.0/300/square\ pulse}$ and constant current, represented as $(Zn\text{-}Ni)_{3.0}$ (all under optimal conditions); these are displayed in Table 4. It was found that corrosion protection of $(Zn\text{-}Ni)_{2.0/4.0/600}$ configuration is ~50 times better (0.28×10^{-2} mmy^{-1}) than that of monolithic $(Zn\text{-}Ni)_{3.0}$ alloy (15.18×10^{-2} mmy^{-1}) obtained from the same bath, during the same time. No significant difference in the protection efficacy of multilayer coating was found, when the current pulse was changed from square to triangular type, as compared to monolayer and multilayer coating. This supports the fact that modulation in composition in individual layer is no significant factor responsible for improved corrosion resistance; instead, the number of interfaces separating two compositions is of significance.

Relative impedance response of $(Zn\text{-}Ni)_{3.0/monolithic}$ and $(Zn\text{-}Ni)_{2.0/4.0/600/triangular}$ coating systems are given in Figure 7. The decrease of corrosion rate is attributed to the changes in the intrinsic electrical properties of CMMA coatings, as evidenced by dielectric spectroscopy. Impedance signals showed that the substantial decrease of the corrosion rate is caused by the increased dielectric barrier at the interface.

SEM Study

The surface morphology and formation of alternate layers of alloys having distinctive properties was confirmed by scanning electron microscopy (SEM). The SEM image of $(Zn\text{-}Co)_{2.0/4.0/30}$ coating without corrosion, marked as 8 (A), displayed a uniformly rough surface. Cross-sectional view of CMMA $(Zn\text{-}Co)_{2.0/4.0/30}$ is shown in Figure 8 (B). The poor contrast may be due to marginal difference in chemical composition of alloys in each layer. Inspection of the microscopic appearance of the surface of monolithic and multilayer after corrosion tests were used to understand the reason for the improved corrosion resistance of the CMMA coatings.

The coatings are subjected to anodic polarization at +250 mV vs OCP in 5% NaCl solution. The corroded specimens were washed with distilled water and examined under SEM. Figures 8(C) and 8(D) show the surface image of monolayer and multilayer coatings after corrosion tests, respectively. Figure 8 (C) exhibits corrosion of the coating, whereas Figure 8(D) exhibits the decay of alternate layers formed during the process of deposition. It was observed that the layer with lower concentration of Ni is preferentially dissolved, although eventually the steel substrate was exposed. Short et al. [23] 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 CMMA coatings, evidenced by its dielectric and impedance spectroscopy.

Table 4. Comparison of corrosion rates of $(Zn\text{-}Ni)_{3.0}$ (monolithic) and Triangular waveform CMMA $(Zn\text{-}Ni)_{2.0/4.0/600}$ coatings of the same thickness.

Coating configuration	$-E_{corr}$ /V vs Ag,AgCl / KCl_{sat}	I_{corr} /μA/cm^2	CR /x 10^{-2} mmy^{-1}
$(Zn\text{-}Ni)_{3.0/monolayer}$	1.245	11.08	15.18
CMMA $(Zn\text{-}Ni)_{2.0/4.0/600/square\ pulse}$	1.348	0.31	0.43
CMMA $(Zn\text{-}Ni)_{2.0/4.0/600/\ triangular\ pulse}$	1.209	0.19	0.28

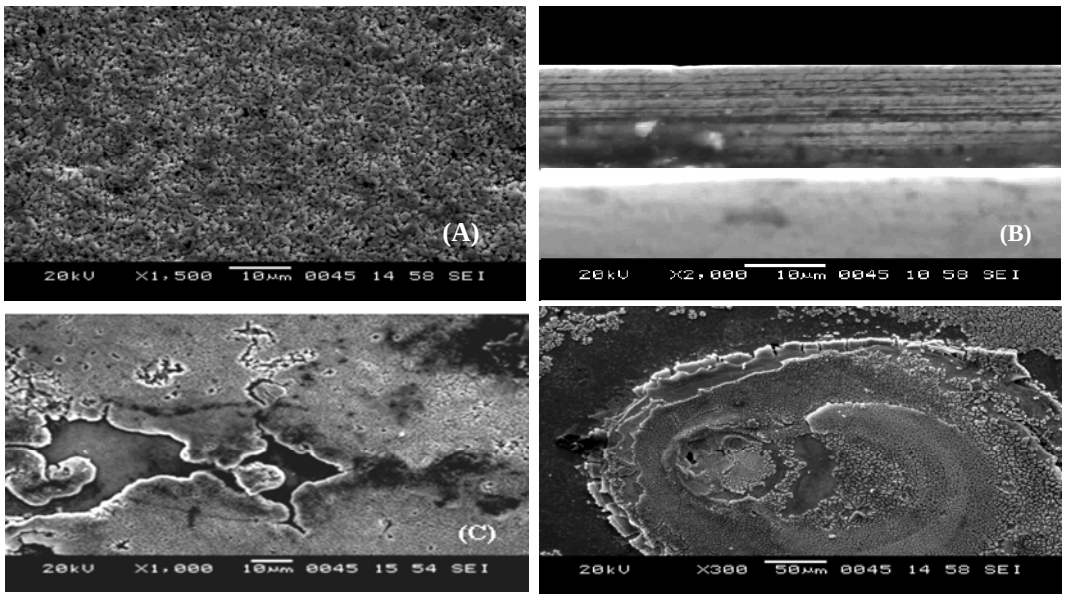

Figure 8. SEM image of $(Zn\text{-}Ni)_{2.0/4.0/30}$ (A), cross-sectional view of $(Zn\text{-}Ni)_{2.0/4.0/30/triangular}$ (B) and monolayer $(Zn\text{-}Ni)_{3.0}$ and CMMA $(Zn\text{-}Ni)_{2.0/4.0/6,}$ after corrosion test [(C) and (D)].

Conclusions

The corrosion resistance of CMMA coatings produced using triangular current pulses was shown to be much higher than that of the monolithic (Zn-Ni) coatings with the same thickness, i.e. CMMA coatings with optimal configuration $(Zn\text{-}Ni)_{2.0/4.0/600}$ showed ~50 times better corrosion resistance compared to monolithic $(Zn\text{-}Ni)_{3.0}$ alloy obtained from the same bath.

The electrochemical stability of the CMMA coatings was explained in terms of changed intrinsic electrical property, evidenced by M-S plot and dielectric spectroscopy. The protection efficacy of the CMMA $(Zn\text{-}Ni)_{2.0/4.0}$

coatings was related to the barrier effect of the $(Zn\text{-}Ni)_{4.0}$ layers and the sacrificial behavior of the $(Zn\text{-}Ni)_{2.0}$ layers. No significant difference in the protection efficacy of multilayer coatings was found, whether the current pulse used is square, or of triangular type. This supports the fact that modulation in composition of the individual layer is not the significant factor responsible for improved corrosion resistance; instead, the number of interfaces separating two compositions is of critical magnitude.

Acknowledgements

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