NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2013, 4 (3), P. 409–416

ELECTROFABRICATION OF NANOSTRUCTURED MULTILAYER COATINGS FOR BETTER CORROSION PROTECTION

R. R. Vaishaka, A. C. Hegde*

Electrochemistry Research Laboratory, Department of Chemistry
National Institute of Technology Karnataka, Surathkal, Srinivasnagar-575025, India
*hegdeac@rediffmail.com

PACS 81.65.Kn

In an effort to improve the corrosion resistance of monolayer Zn-Ni alloy coatings, nanostructure multilayer coating (NMC) has been developed using a pulsed current. Successive layers of alloys with alternately changing compositions were deposited on mild steel (MS) by making the cathode current cycle between two values during deposition. Multilayer coatings with different configurations in terms of composition and number of layers were developed and their corrosion behaviors were studied by electrochemical methods. The effect of cyclic cathode current densities (CCCD's), and the number of layers have been studied, and coating configurations have been optimized for highest corrosion resistances. Multilayer coatings and their degradation during corrosion were confirmed by Scanning Electron Microscopy (SEM) analysis. The improved corrosion resistance of NMC in relation to monolayer alloy coatings, deposited from same bath has been analyzed and results were discussed in terms of increased number of interfaces due to layering.

Keywords: Zn-Ni alloy, Multilayer alloy, Corrosion study, SEM and XRD.

1. Introduction

A new type of coating system called the composition modulated multilayer alloy (CMMA), or alternatively, nanostructure multilayer coating (NMC) is gaining interest due to its improved functional properties, such as mechanical strength, micro hardness, giant magnetoresistence and corrosion resistance [1]. The NMC basically consists of alternating layers of metals/alloys in micro/nanometric scale deposited electrolyticaly by making the cathode cycle between two current densities (c.d.) at regular time intervals. The multilayered coatings exhibit enhanced properties (e.g. hardness, mechanical strength, wear and corrosion resistance) compared to the respective, simple monolithic coatings [2]. Deposition techniques such as evaporation, molecular beam epitaxy and sputtering are some of the common methods still in use for the development of multilayer coatings, although their higher costs and practical difficulties make the electrolytic deposition process more favorable. Though Zn-Ni alloy coatings offer better corrosion protection than pure Zn, the electrofabrication of multilayer coatings is more viable and is of distinct commercial interest.

The development of NMC consisting of Zn and Ni alloy as alternate layers was found to show the best corrosion protection. Kalantary et. al have demonstrated that the presence of high Ni content in Zn-Ni alloy is responsible for enhanced corrosion protection [3]. The first multilayer deposition was reported by Blum as early as 1921 [4], and later by Brenner [5]. Many attempts have been made to understand the reasons for improved corrosion performance of multilayer coatings [6, 7]. Kirilova et al. [8, 9] have reported the deposition of CMMA coatings of Zn-Co using a single bath technique (SBT). Tench and White fabricated Cu/Ni metal multilayers and studied their mechanical properties [10]. It was proposed that the presence of Ni

TABLE 1. The composition and deposition conditions of optimized bath

Bath ingredients	Composition (g/L)	Operating parameters
$ZnCl_2 \cdot 7H_2O$	27.2	Anode: Nickel
$NiCl_2 \cdot 6H_2O$	94.9	Cathode: Mild Steel
Boric acid, BA	27.7	pH: 4
NH_4Cl	100	Temperature: 303 K
Gelatin	5.0	
Glycerol	2.5	

in the deposited layers was responsible for the improved corrosion protection that was observed. Recently, Thangaraj et. al optimized a chloride bath for the galvanostatic production of CMMA Zn-Ni coatings, and showed that they are ∼45 times more corrosion-resistant than monolayer (bulk) Zn-Fe alloy coatings, even if deposited from same bath [11]. Though many reports are available with regard to the development of NMC of Zn-Ni alloy using different additives, no work has been reported for gelatin and glycerol, as additives. Hence the present work looks at optimization of deposition conditions for the development of NMC of Zn-Ni alloy which afford the best protection of mild steel (MS). The bath composition and operating parameters have been optimized by the Hull cell method. The process and products of electrolysis were analyzed using different instrumental methods, such as scanning electron microscopy (SEM) and X-Ray diffraction (XRD), and results are discussed. All electroplatings were carried out on pre-cleaned MS panels of 7.5 cm^2 active surface area at 303 K and pH = 4.0. A sensitive DC power source (N6705, Agilent Technologies) was used for pulsing the current during deposition. The modulation of composition in alternate layers was effected by periodic pulsing of the current. The power patterns used for monolayer and multilayer coatings are shown in Fig. 1. The corrosion behaviors of the coatings were evaluated using 5% NaCl (a representative corrosion medium). All coatings were carried out for 10 min (∼ 20 μm thickness) for comparison purpose.

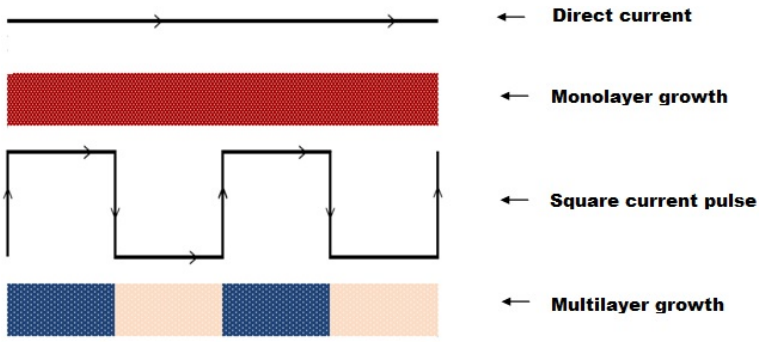

FIG. 1. Power pattern used for the deposition of monolayer (Direct current) and multilayer (square current pulse) coatings

2. Experimental

The optimal composition and operating parameters for the deposition of monolayer bright, uniform and homogeneous Zn-Ni alloy on MS were determined by the Hull cell method, and are given in Table 1.

The depositions were characterized by different analytical techniques, such as spectrophotometry, XRD, SEM and electrochemical methods. A standard three electrode system

was used for the corrosion study, at scan rate of 1 mV/s. The EIS measurements were made in frequency range of 100 kHz to 10 mHz in 10 mV perturbing voltage. The NMC's with alternate layers of alloys with different compositions are represented as: $(\text{Zn-Ni})_{1/2/n}$ (where 1 and 2 indicate the first and second cathode current density (CCCD's) and 'n' represents the number of layers formed during total plating time, i.e. (10 min).

3. Result and Discussion

3.1. Electrodeposition of Zn-Ni Alloy Coating

Zn-Ni multilayer alloy coatings were electrofabricated on polished MS with 7.5 cm^2 exposed area. Monolayer coatings were developed at different c.d.'s, 1.0 to 4.0 A/dm^2 and their corrosion rates (CR) were calculated by Tafel extrapolation method, corresponding data are given in Table 2. It may be noted that at 3.0 A/dm^2, the Zn-Ni alloy coating was found to be most corrosion resistant, and was selected as optimal configuration, represented by $(\text{Zn-Ni})_{3.0/\text{mono}}$. Under all conditions of the c.d. studied, the wt. % Ni in the deposit was found to be less than ca. 8.0%, which is much less than that in the bath (64.5 %). Hence, it may be inferred that the proposed bath followed an anomalous type of codeposition, characteristic of Zn-Fe group metal alloys [5].

TABLE 2. Corrosion data for Zn-Ni Monolayer Coatings

c.d. (A/dm^2)	Wt. % of Ni	Vickers hardness (V_{100})	$-E_0$ (V vs. SCE)	i_{corr} (μ A/cm^2)	CR $\times$ 10^{-2} (mm/y)
1.0	2.62	146	1.019	17.62	23.42
2.0	4.05	144	1.086	13.87	18.44
3.0	7.95	202	1.105	10.88	14.46
4.0	8.07	184	1.162	12.53	16.66

3.2. Optimization of Cyclic Cathode Current Densities (CCCD's)

The objective of the present work to improve the corrosion resistance of monolayer Zn-Ni alloy coating by multilayer technique is guided by three principles [12–14]:

i) The successive change in current density (c.d.) allows the growth of alloys having successive changes in its chemical composition.
ii) The corrosion resistance property of multilayer coatings or any functional property in general reaches its maximum value when the thickness of the individual layers reaches to optimum nanoscale.
iii) The layering of alloys having different noble metal content leads to the formation of distinct interfaces.

Hence multilayer coatings having 10 layers (arbitrarily chosen) have been accomplished at different CCCD's, namely at 1.0/3.0 and 2.0/4.0 A/dm^2 using same binary alloy bath, given in Table 1. The coatings at different sets of CCCD's were developed to try different possible modulations in composition of individual layers, and their corrosion behaviors were studied, and corrosion data are reported in Table 3.

It was observed that the $(\text{Zn-Ni})_{1.0/3.0/10}$ and $(\text{Zn-Ni})_{2.0/4.0/10}$ showed the lowest corrosion rates when compared to $(\text{Zn-Ni})_{3.0/\text{mono}}$. However, for coatings at 2.0 and 4.0 A/dm^2, the differences between CCCD's were found to be more corrosion resistant. These CCCD's were employed for optimizing the number of layers for better corrosion protection.

TABLE 3. Corrosion rates of NMC Zn-Ni alloy coatings with 10 layers to set CCCD's

CCCD's (A/dm^2)	$-E_0$ (V vs. SCE)	i_{corr} (μ A/cm^2)	CR $\times$ 10^{-2} (mm/y)
(Zn-Ni)$_{1.0/3.0/10}$	1.085	8.416	11.18
(Zn-Ni)$_{2.0/4.0/10}$	1.108	6.606	8.78
(Zn-Ni)$_{3.0/mono}$	1.105	10.88	14.46

3.3. Optimization of Number of Layers in NMC's

The incredible claims of electroplating can be exploited for development of nanostructure multilayer coatings (NMC) for better corrosion protection. Hence, by choosing the above CCCD's, multilayer coatings with higher degrees of layering, i.e. with 10, 30, 60, 120, 300 and 600 layers, have been electrofabricated by proper setting up of the power source. The corrosion behavior of NMC's having different number of layers have been studied, and corresponding polarization behaviors are as shown in Fig. 2 (only representative). The corrosion data are reported in Table 4. It may be noted that the CRs decreased drastically with increase in number of layers in both sets of CCCD's.

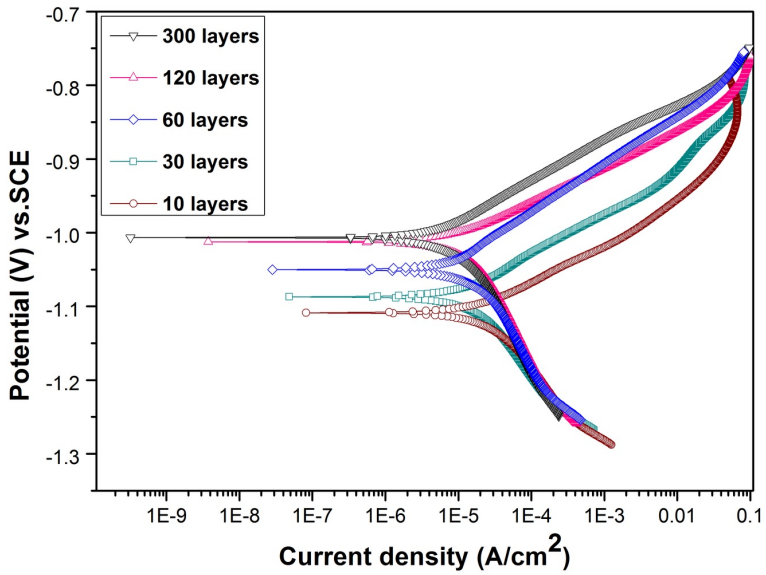

FIG. 2. Potentiodynamic polarization behaviors of NMC (Zn-Ni) coatintgs having different number of layers, deposited from optimized bath at 303 K

It indicates that the improvement in corrosion behavior of NMC's is not the unique property of individual layer; instead, the combined effect of composition modulation and number of layers. Further, the CR of multilayer Zn-Ni coating decreased only up to 300 layers and then started increasing, i.e. 600 layers as shown in Table 4. This decrease of CR at higher degrees of layering was due to less relaxation time for the deposition of metal ions on the cathode. In other words, at a very high degree of layering, multilayer coatings tend to become monolayer, showing higher CR's. Thus it may be stated that the amplitude of the composition modulation diminished.

TABLE 4. Effect of layering on corrosion behavior of NMC $(Zn\text{-}Ni)_{1.0/3.0}$ and $(Zn\text{-}Ni)_{2.0/4.0}$ coating in comparison with monolayer $(Zn\text{-}Ni)_{3.0/mono}$ deposited from same bath at 303 K

Coating configuration	Number of layers	E_0 vs. SCE (volts)	i_{corr} (μ A/cm^2)	CR $\times 10^{-2}$ (mm/y)
$(Zn\text{-}Ni)_{1.0/3.0}$	10	1.085	8.416	11.18
	30	1.037	7.125	9.47
	60	1.056	4.531	6.02
	120	1.067	2.357	3.13
	300	1.041	1.319	1.75
	600	1.050	3.577	4.75
$(Zn\text{-}Ni)_{2.0/4.0}$	10	1.108	6.606	8.78
	30	1.085	4.989	6.63
	60	1.050	2.125	2.82
	120	1.007	1.056	1.40
	300	1.006	0.295	0.39
	600	1.036	1.975	2.61
$(Zn\text{-}Ni)_{3.0/mono}$	—	1.105	10.88	14.46

3.4. Comparison of Monolayer and Multilayer Coatings

The corrosion behaviors of monolayer and multilayer Zn-Ni alloy coatings, electrofabricated from the same bath for the same time (under optimal conditions) are shown in terms of DC and AC polarizations Fig. 3. Corrosion data revealed that NMC $(Zn\text{-}Ni)_{2.0/4.0/300}$ is about 37 (CR = 0.39×10^{-2} mm/y) times more corrosion resistant than $(Zn\text{-}Ni)_{3.0/mono}$ (CR = 14.46×10^{-2} mm/y) coatings.

3.5. Scanning Electron Microscopy Study

The scanning electron microscopy (SEM) image of $(Zn\text{-}Ni)_{2.0/4.0/10}$ coating is shown in Fig. 4. Figs. 4a and 4b show the surface morphology of the coating before and after the bend test (electroplated coatings on thin foil of MS were bent by 135 repeatedly), respectively. The fractured coating under SEM displays the layers, as seen in Fig. 4b (shown by arrow mark). The high corrosion resistance of multilayer coatings can be envisaged due to the formation of pores, crevices 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 multilayer coatings can be also explained in terms of formation of alternate layers of alloys with low and high wt. % of Ni as shown in Table 2.

3.6. Powder X-Ray Diffraction (XRD) Study

Figure 5 shows the XRD patterns of Zn-Ni alloy deposited at different c.d. from the same bath. A necessary requirement for better physicochemical properties of the multilayer coatings is compositional modulation, i.e. phase structure should vary with cyclic cathode current density (CCCD). In the present study, the deposits obtained at 1.0, 2.0, 3.0 and 4.0 A/dm^2 were found to exhibit a marked difference in phase structure as shown in Fig. 5. It has been reported that the phases obtained by the coatings with 0 to 13% nickel do not correspond to that reported on the thermodynamic phase diagram [15]. However, it may be noted that deposition at the optimal c.d., having about 7.95% Ni showed the highest corrosion resistance, due to Zn(101),

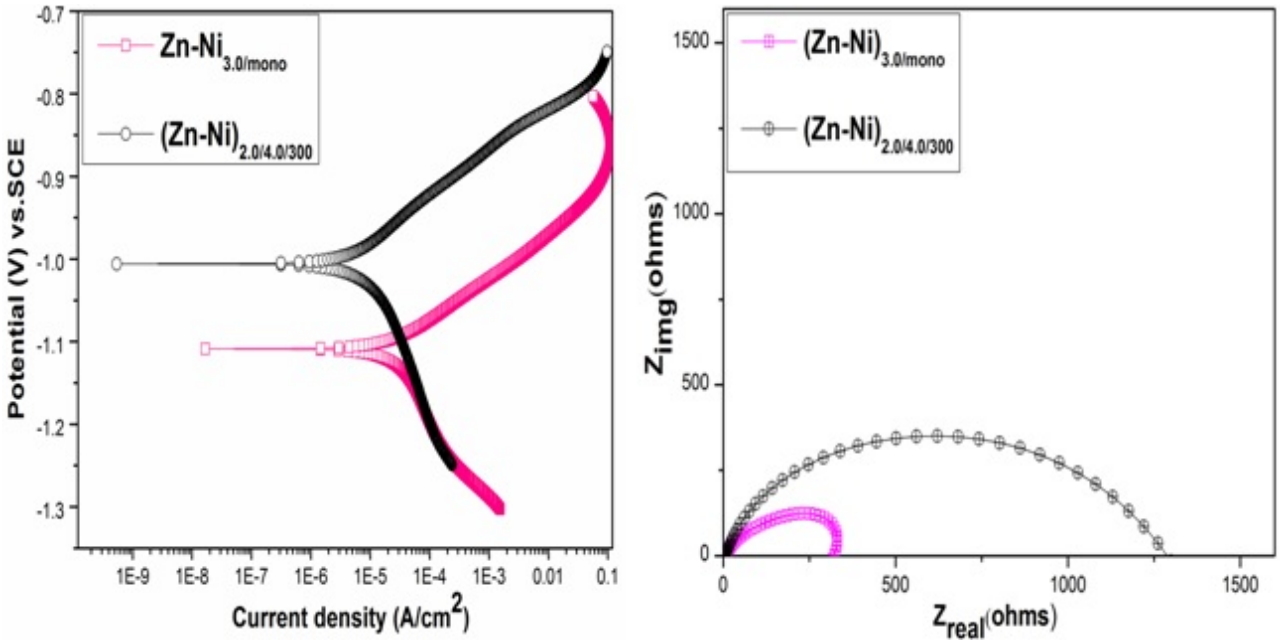

FIG. 3. Comparison of corrosion behaviors of monolayer and multilayer coatings of (Zn-Ni) alloy: a) Potentiodynamic polarization behaviors and b) Nyquist response under same frequency limit

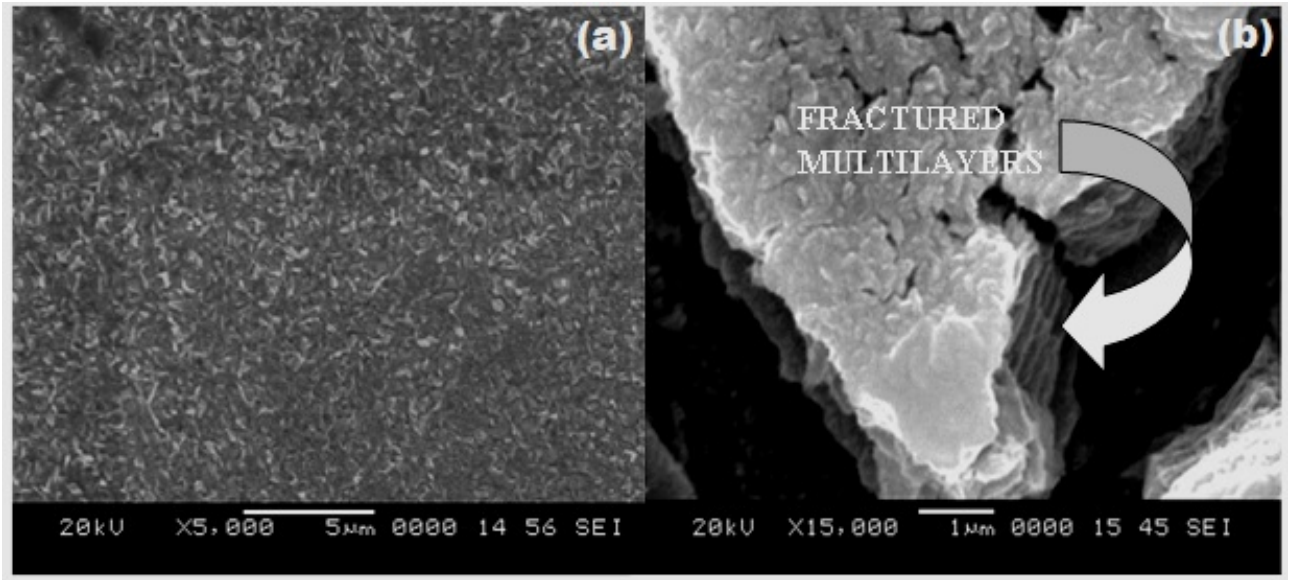

FIG. 4. SEM images of NMC $(Zn\text{-}Ni)_{2.0/4.0/10}$ coatings electrofabricated from optimized bath: (a) surface structure and (b) cross-sectional view after bend test

γ-phase (Ni_5Zn_{21}), Zn(103) phases and a small amount of Ni_3Zn_{22}(335). This particular ratio of phases was found to be responsible for the uniformity and brightness of the coating at the optimal c.d. (3.0 A/dm^2). In the case of coatings at 1.0 and 2.0 A/dm^2, the reflection corresponding to γ-phase and Zn(101) phases are highly suppressed. The above experimental observation reveals how the cathode current density (CCD) can be used as tool for compositional modulation of individual layers, and how their duration can be used for controlling the thickness

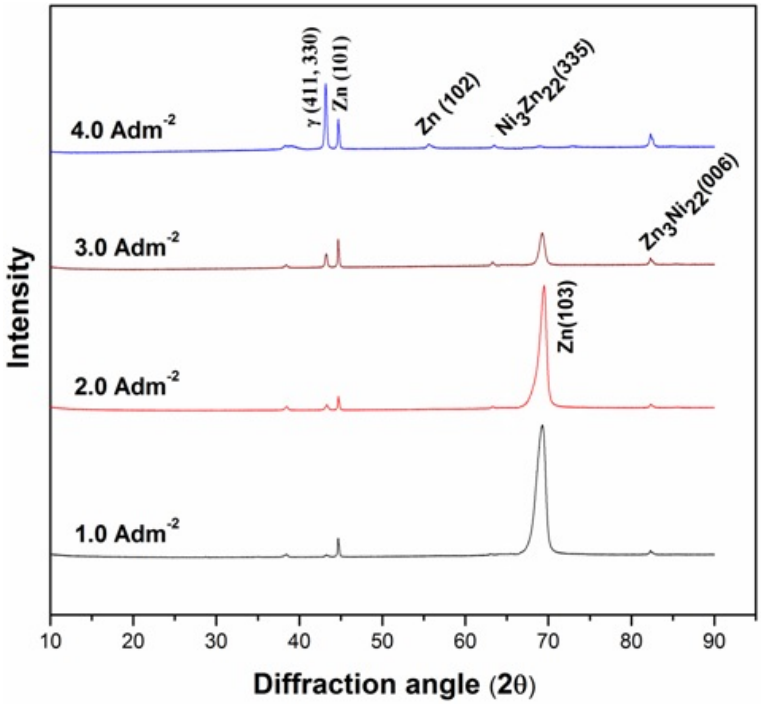

FIG. 5. XRD patterns of Zn-Ni alloy coatings at different c.d.s.

of layers. Hence, layered coatings having distinct compositions were responsible for modulation in composition, as evidenced by XRD study.

4. Conclusions

- The proposed Zn-Ni bath followed an anomalous type of deposition, i.e. the wt. % Zn in deposit is more than that in the bath at all deposition c. d.'s.
- At different c.d., Zn-Ni alloy coatings of different phase structures have formed, which enabled the compositional modulation in layered coating, as evidenced by XRD and SEM analysis.
- The amplitude of the compositional modulation diminished rapidly when layer thickness falls below certain limit, i.e., less than 1000 Å. Hence, NMC's fail to offer the improved properties at higher number of layers.
- Improved corrosion behavior at a different set of CCCD's revealed that improvement is not specific to individual layers, instead it is a combined effect of compositional modulation and number of layers.
- The extended protection of NMC's is due to fact that the failure during the single layer deposition process is masked or neutralized by the successively electrofabricated layers. Hence, the path for the corrosive agents is extended or blocked.
- Under optimal conditions, multilayered Zn-Ni alloy coatings were about 37 times more corrosion resistant than corresponding monolayer alloy electrofabricated from the same bath at the same time.

Acknowledgment

Mr. Vaishaka R. Rao acknowledges National Institute of Technology Karnataka (NITK), Surathkal for supporting this research in the form of Institute Fellowship.

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