Corrosion protection of electrodeposited multilayer nanocomposite Zn-Ni-SiO_2 coatings

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Multilayer nanocomposite coatings of Zn-Ni-SiO_2 were deposited galvanostatically on mild steel (MS) from Zn-Ni bath, having Zn^{+2} and Ni^{+2} ions and uniformly dispersed nano-SiO_2 particles. The corrosion characteristics and properties of multilayered nanocomposite (MNC) coatings were evaluated by electrochemical polarization and impedance methods. Such deposition conditions as, bath composition, cyclic cathode current densities (CCCD's) and number of layers were optimized for peak performance of coatings against corrosion. A significant improvement in the corrosion performance of MNC coatings was observed when a coating was changed from a monolayer to multilayer type. Corrosion rate (CR) of MNC coating decreased progressively with number of layers up to an optimal level, and then started increasing. The increase of CR at a higher degree of layering is attributed to diffusion of layers due to a very short deposition time, failing to give the enhanced corrosion protection. The formation of layers, inclusion of silica particle in MNC coating matrix were confirmed by SEM and XRD study. At optimal current densities, i.e. at 3.0–5.0 A/cm^2, the Zn-Ni-SiO_2 coating having 300 layers, represented as $(\text{Zn-Ni-SiO}_2)_{3.0/5.0/300}$ is found to be about 107 times more corrosion resistant than a monolayer Zn-Ni-SiO_2 coating, developed from the same bath for the same time. The reasons responsible for the extended corrosion protection of MNC Zn-Ni-SiO_2 coatings, compared to corresponding monolayer Zn-Ni and (Zn-Ni-SiO_2) coatings were analyzed, and results were discussed.

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INTRODUCTION

Electrochemical deposition of metals and alloys is an integral process for the obtaining of nanosized features. Electrodeposition, electroless deposition, and displacement reactions used to deposit metals, alloys, and metal-matrix composite materials are controlled by electrochemical reactions. Electrochemically prepared nanomaterials are characterized by at least one dimension in the nanometer range, include nanostrutured thin-film multilayers, nanowires, nanowires with nanometric layers, nanotubes, nanosize particles embedded into metal matrices. Owing to the nanometric nature of the structure, the physical properties of nanomaterials can be significantly different from bulk materials having the same composition. Electrodeposition relates to the reduction of metal ions with an impressed current (or potential). In contrast, electroless and displacement processes occur without an impressed current (or potential). Magnetic compositionally modulated multilayered thin films and nanowires are typical examples of electrodeposited nanostructured materials [1]. Electrochemical deposition has appeared not only as a cost-effective alternative to vapor-deposition methods for thin films, but also as an atvantageous method for nanotechnology to deposit nanostructured layers onto irregular substrates and into deep recesses, enabling unique materials such as nanotubes and wires to be manufactured.

A new type of coating systems, the so-called compositionally modulated multilayer (CMM) alloy coatings, or alternatively, cyclic multilayer alloy (CMA) coatings has gradually became of interest amongst researchers, because these layered-structure coatings possess improved properties or novel phenomenon such as increased mechanical strength, micro-hardness, giant magneto resistance and corrosion resistance. CMM coatings consist of a large number of thin laminar deposits of metal/alloy layers, and each layer has its own distinctive role in achieving the preferred parameters. These multilayered or layer-by-layer deposits have attracted the attention of both the scientific and engineering communities due to their widespread applications. One of the first examples of CMMs was demonstrated by Blum in 1921, when alternate Cu and Ni layers, tens of microns thick, were deposited from two different electrolytes. The resulting Cu/Ni multilayer improved the tensile strength of the electrodeposits compared to elemental copper deposits [2]. Today, CMM materials that are of interest in other systems include not only mechanical properties [3–4] (e.g., fracture and tensile strength, hardness) but also magnetic and corrosion properties [5–7]. Among the various methods for producing metallic nanocomposite coatings, electrodeposition technique seems to be the most convenient, and today it meets the requirements of many new materials with improved properties. Further, the process design of

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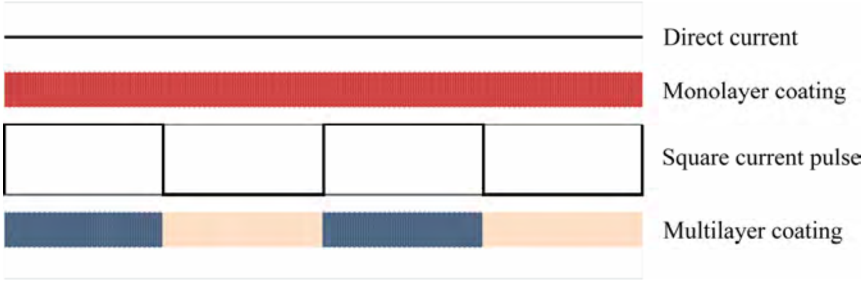


Fig. 1. Current pulses used for deposition of monolayer (direct current) and multilayer (pulsed current) coatings.

electrodeposition is guided by end applications and its corrosion protection behavior.

Generally, the corrosion resistant coatings on mild steel are represented by zinc based coatings. Although zinc coatings provide excellent corrosion protection, there is an increasing necessity for its improvement. Several methods are tested and proven to enhance the corrosion protection of normal Zn coating, like alloying with Ni. Fe, Co, Mn metals [6–8]. The corrosion performance of monolayer Zn-M (where M = Fe, Ni, Co and less commonly Mn) coatings have been improved substantially by CMA coating technique. Several reports are available for CMA Zn-M alloy coatings [6–9]. Fei et.al. have deposited CMA Zn-Fe coatings galvanostatically, and observed that they exhibit better corrosion protection than corresponding monolayer alloys. Venkatakrishna et.al, have reported the improved corrosion performance of CMA Zn-Co coatings compared to monolayer coatings. Chawa et.al. [10] reported the corrosion resistance of Zn-Co CMA coatings from zinc sulphate and nickel sulphamate baths demonstrating its better corrosion resistance, compared to monolithic Zn-Co coatings of similar thickness. Recently, Liao et al. [11–13] have studied both CMA coatings of Zn/Zn-Fe and only Zn-Fe systems. Kirilova et al. [14–15] reported CMA coatings of Zn-Co from single bath technique (SBT). Thangaraj et al. optimized a chloride bath for the production of Zn-Fe CMA coatings over MS, and showed that coating were found to have ~ 45 times better corrosion resistant than monolithic Zn-Fe coatings of the same thickness [9].

Deposition of many Zn-based composite coatings, such as Zn–TiO_2, Zn–Al_2O_3, Zn–yttria-stabilized zirconia, Zn–Ni–SiC, Zn–SiO_2 has been reported and their corrosion resistance was evaluated and results were found to be encouraging [16–17]. Experimental studies revealed that these coatings offer improved corrosion resistance in comparison with pure zinc coating. Though improvement in corrosion resistance of CMA coatings of Zn-M alloys were widely reported, very little was done with regard to optimization of the deposition condition of multilayered composite coatings. In the light of development of Zn-based composite coatings and multilayer coatings of Zn-Ni alloys, it has been tried to develop multilayer composite coatings of Zn-Ni. i.e. Zn-Ni-SiO_2 composite, by addition of nanosized SiO_2 particles into the electrolytic bath of Zn-Ni. Deposition conditions and bath compositions were optimized for production of MNC on MS for peak performance against corrosion. Experimental studies have been used to optimize the deposition conditions for peak performance of the coating against corrosion, and to analyze the factors responsible for enhanced corrosion protection. Electroplates were examined using SEM and XRD, and results were discussed.

1. EXPERIMENTAL METHODS

A Zn-Ni alloy bath was prepared using analytical grade reagents and deionized water. The composition of the bath used in the present study is: $NiSO_4.6H_2O$ 100g/L, $ZnSO_4.7H_2O$ 100g/L, sodium acetate trihydrate 75g/L, citric acid 2g/L and thiamine hydrochloride 0.5g/L. The bath pH was maintained at 3.0 ± 0.05 and adjusted using dil. H_2SO_4 and dil. NaOH. All depositions were accomplished over MS panels over known active surface area (25 mm × 30 mm). The optimization of plating parameters for deposition of CMA Zn-Ni coatings was reached by the method reported in [7–9]. The computer controlled DC Power Analyzer (N6705, Agilent Technologies) was used as a power source to develop the multilayer coating from single electrolytic bath. The compositional modulation in alternate layers was affected by pulsing the current. The present study is aimed at modulation in composition using square current pulses, shown in Fig. 1. The Zn-based composite coatings were electrodeposited by adding a fixed quantity (5 g/L) of commercial grade SiO_2 nanopowder (Sigma Aldrich). Zn-Ni bath after stirring with silica powder for 24 h (for homogenization) was used for electroplating. Later, depositions were carried out under steady conditions of agitation, using a circulation pump to avoid settling down of the composite particles due to gravity. The composition and deposition conditions were optimized by conventional Hull cell method [18].

Monolayer Zn-Ni-SiO2 coatings were developed at different c.d.'s and their corrosion resistances were evaluated in 5% NaCl solution, as a typical corrosion medium. All coatings were plated onto polished MS during 10 min (~ 20 µm thickness), for comparative purposes. After air drying the electroplated coatings were subjected to electrochemical corrosion tests using potentiostat/galvanostat (VersaStat-3, Princeton Applied Research). All potentials expressed in this work are measured with referring to saturated calomel electrode (SCE). The formation of MNC coatings was confirmed using Scanning Electron Microscopy (SEM, JEOL 6380 LA). The X-ray diffraction (XRD) study was used to analyze the phase structure of the deposits in alternate layers of nanocomposite coatings. MNC coatings with alternate layers of alloys having different composition are represented conveniently as: $(\text{Zn-Ni-SiO}_2)_{1/2/n}$ (where 1 and 2 indicate the cyclic cathode current density (CCCD's) and 'n' is the number of layers formed during total plating time. i.e. 10 min).

2. RESULTS AND DISCUSSION

2.1 Deposition of monolayer Zn-Ni coatings

Monolayer Zn-Ni alloy coatings were electrodeposited from the optimized bath using direct current (DC) without pulsating the cathode current. i.e., between c.d. 1.0 to 5.0 A/dm^2. The deposits were found to be bright and uniform and their corrosion characteristics were studied, It was observed that at c.d. = 3.0 A/dm^2, the monolayer Zn-Ni alloy was found to be more resistant to corrosion.

2.2 Deposition of monolayer Zn-Ni-SiO$_2$ coatings

A known quantity of SiO_2 (5 g/L) is dispersed into the optimized Zn-Ni bath. Similarly, monolayer Zn-Ni-SiO_2 composite coatings were developed from the bath at different c.d.'s using DC without modulation in composition over wide range of c.d.; and their corrosion behaviors were evaluated. The composite coatings were also studied for their composition, hardness and corrosion behavior, and are reported in Table 1. It shows the wt. % Ni in the composite coatings developed at different c.d.'s, in comparison with that in the monolayer Zn-Ni alloy coating (given in the parenthesis). It may be observed that monolayer coatings are harder than the corresponding binary alloy coating. It occurs due to the added mechanical strength to the coatings, caused by the embedded SiO_2 nanoparticles into the metal matrix. Further, the corrosion resistance of monolayer nanocomposite coatings is found to be slightly higher than that of Zn-Ni alloy. The improved corrosion resistance of the monolayer composite coatings may be attributed to the combined effect of its increased nickel content and presence of silica particles. [20] The silica particles are considered to act as the barriers for electron movement in corrosion process.

2.3 Deposition of multilayer nano-composite Zn-Ni-SiO$_2$ coatings

It is well known that in the case of electrodeposited Zn-Ni alloys a small change in the Ni content results in significant changes in properties, due to the change in phase structure, and many experimental investigations has supported this behavior [6–8]. Precise control of CCCD's, allows the development of layered coating with different compositions. It eventually leads to coatings with improved functional properties. Accordingly, to begin with, multilayer nanocomposite (MNC) Zn-Ni-SiO_2 coatings with 10 layers (5 sets each) at different CCCD's were developed and their corrosion protection efficiency was evaluated. A total of 10 layers have been arbitrarily taken for the comparison purpose. MNC Zn-Ni-SiO_2 coatings at different CCCD's combinations were developed, i.e. at 2.0/5.0 and 3.0/5.0 A/dm^2.

2.3.1 Optimization of CCCD's for nano-composite Zn-Ni-SiO$_2$ coatings

Among many combinations of CCCD's tried, the coatings developed with difference of 3.0 A/dm^2 and 2.0 A/dm^2 between C.D's were found to be more encouraging. In an effort to increase further the protection efficiency of MNC coatings multilayer coatings have been made in the range of 2.0–5.0 A/dm^2 and 3.0–5.0 A/dm^2 as CCCD's.

2.3.2 Optimization of the number of layers in multilayer coatings

Generally, improvement in the properties of electrodeposited multilayer coating depends upon a variety of factors, such as a choice of electrolyte, bilayer number and thickness of each layer. Accordingly, the corrosion performance of multilayer coatings can also be increased substantially by increasing the number of layers (usually up to an optimal limit), with no loss in demarcation between each layers. Therefore by selecting 2.0/5.0A/cm^2 and 3.0/5.0A/cm^2 as two sets of CCCD's, CMA Zn-Ni alloy and MNC Zn-Ni-SiO_2 coatings were developed with different number of layers. i.e. 20, 60,120,300 and 600 layers, for the comparative purposes. Tafel's extrapolation methods were used for determination of the corrosion potential, corrosion current density, i_c and corrosion rate, and are reported in Table 2.

It may be observed that the CR's of the coatings decreased progressively up to 300 layers in each set of CCCD's, and then started increasing to a higher number of layers. i.e. to 600 layers. The MNC coatings having $(\text{Zn-Ni-SiO}_2)_{3/5/300}$ configuration exhibited the least CR and has been taken as optimal con-

Table 1. Corrosion data and deposit characters of monolayer Zn-Ni-SiO$_2$ coatings at different current densities

Current density A/dm^2	Wt. % of Ni	Vickers hardness V$_{200}$	E_0 vs. SCE (volts)	i_c (µA/cm^2)	CR × 10^{-2} (mmy^{-1})
2.0	1.8 (1.1)	155	-1.015	9.69	14.34
3.0	2.3 (1.6)	170	-1.030	7.35	11.83
4.0	2.9 (2.1)	200	-1.038	8.74	13.93
5.0	3.5 (2.4)	210	-1.039	10.44	15.44

Table 2. Relative account of CR's of monolayer and multilayer coatings under different conditions of layering

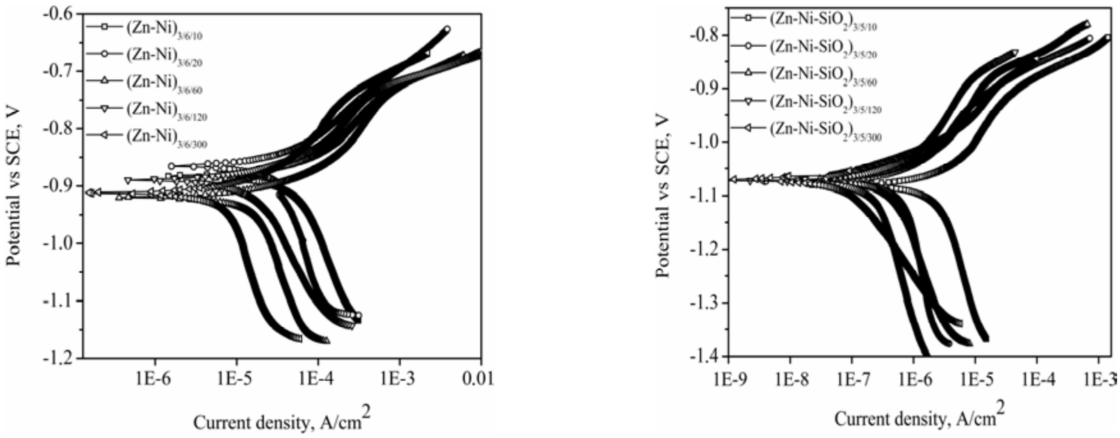
Coating configuration	Number of layers	E_0 vs. SCE (volts)	i_c (µA/cm^2)	CR × 10^{-2} (mmy^{-1})
Monolayer (Zn-Ni) alloy	–	-1.005	12.23	18.08
Monolayer (Zn-Ni-SiO$_2$) alloy	–	-1.030	7.35	11.83
CMA (Zn-Ni)$_{2/5}$	10	-0.881	10.2	13.6
	20	-0.864	9.46	12.6
	60	-0.919	7.42	9.88
	120	-0.889	4.97	6.62
	300	-0.911	0.92	1.22
	600	-0.919	8.87	11.8
MNC(Zn-Ni-SiO$_2$)$_{2/5}$	10	-1.048	3.744	5.53
	20	-1.050	2.019	2.98
	60	-1.053	1.646	2.43
	120	-1.049	1.148	1.69
	300	**-1.049**	**0.256**	**0.37**
	600	-1.030	7.371	10.89
MNC (Zn-Ni-SiO$_2$)$_{3/5}$	10	-1.081	3.061	4.53
	20	-1.073	1.495	2.20
	60	-1.072	1.251	1.84
	120	-1.072	0.419	0.62
	300	**-1.072**	**0.071**	**0.11**
	600	-1.082	6.490	9.60

figuration. It may also be noted even in CMA (Zn-Ni)$_{2/5}$ coatings, the CR decreased with an increase in a number of layers and reached its optimal value of 300 layers, shown in Table 2. The decrease CR at a higher degree of layering may be attributed to very short relaxation time for metal ions to set free from the effect of c.d., failing to bring clear demarcation between the layers [19]. Potentiodynamic polarization behavior of multilayer Zn-Ni alloy and MNC (Zn-Ni-SiO$_2$) coatings is given in Fig. 2a & 2b, respectively. The corrosion data given in Table 2 reveals that (Zn-Ni-SiO$_2$)$_{2/3/300}$ with 300 layers shows about 107 times higher corrosion resistance than a monolayer (Zn-Ni-SiO$_2$) coating, and it is 11 times higher corrosion resistant than even CMA (Zn-Ni) alloy coating.

The corrosion data on a monolayer and multilayer Zn-Ni-SiO$_2$ coatings in comparison with the data on the monolayer and multilayer Zn-based alloy coatings are given in Table 2. The potentiodynamic polarization behaviors of the monolayer and multilayer Zn-Ni-SiO$_2$ coatings are shown in Fig. 3a. The shift in i_{corr} value towards lower c.d. side indicates that the corrosion protection efficiency increases as coating changes from a monolayer to multilayer type. Decrease in corrosion rate at higher degree of layering may be explained through the electrochemical impedance study, using AC signal of small amplitude (±10 mV). The corresponding Nyquist diagrams, shown in Fig. 3b reveal that the polarization resistance of the coatings increases in the order of (Zn-Ni-SiO$_2$)$_{3/5/300}$ > (Zn-Ni-SiO$_2$)$_3$ > (Zn-Ni)$_3$. The impedance data points corresponding to MNC (Zn-Ni-SiO$_2$)$_{3/5/300}$ coating is modeled into an equivalent electrical circuit using Z_{simpwin} software (interfaced with the instrument) and is shown in Fig. 4. It may be observed that circuit elements like solution resistance (R_s), electrical double layer capacitor (C_{dl}) and charge transfer resistance, R_{ct} follows almost *Randles circuit* with an additional constant phase element (CPE), may be owing to an additional capacitor due to layering.

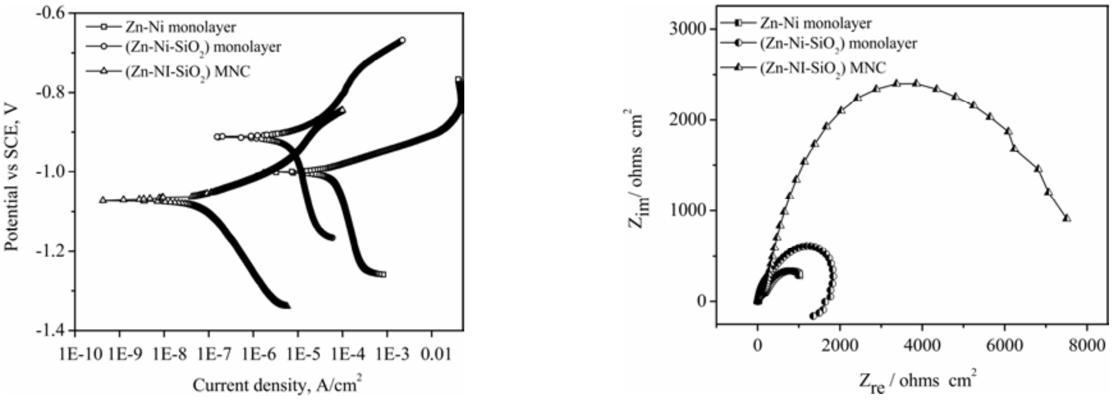
2.4 X-ray Diffraction Study

X-ray diffraction patterns of Zn-Ni alloy coatings developed at different c.d.'s used to produce their multilayer coatings are shown in Fig. 5a. At 2.0 A/dm^2 and 3.0 A/dm^2, γ-phase of the alloy and Zn$_{101}$ peaks is predominant. In the case of deposits obtained at 5.0 A/dm^2 and 6.0 A/dm^2, a clear sup-



(a) (b)

Fig. 2. Potentiodynamic polarization curves of (a) CMA Zn-Ni alloys and (b) MNC (Zn-Ni-SiO$_2$) at different degree of layering.



(a) (b)

Fig. 3. Comparison of potentiodynamic polarization behaviors (a), and Nyquist behaviors (b), of monolayer (Zn-Ni), (Zn-Ni-SiO$_2$) and MNC (Zn-Ni-SiO$_2$) coatings (all under optimal conditions).

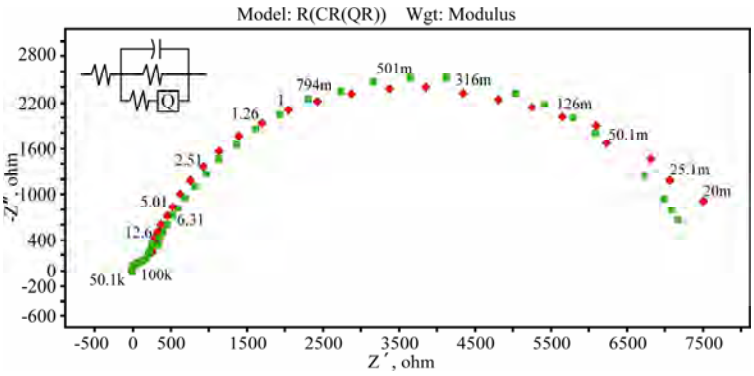
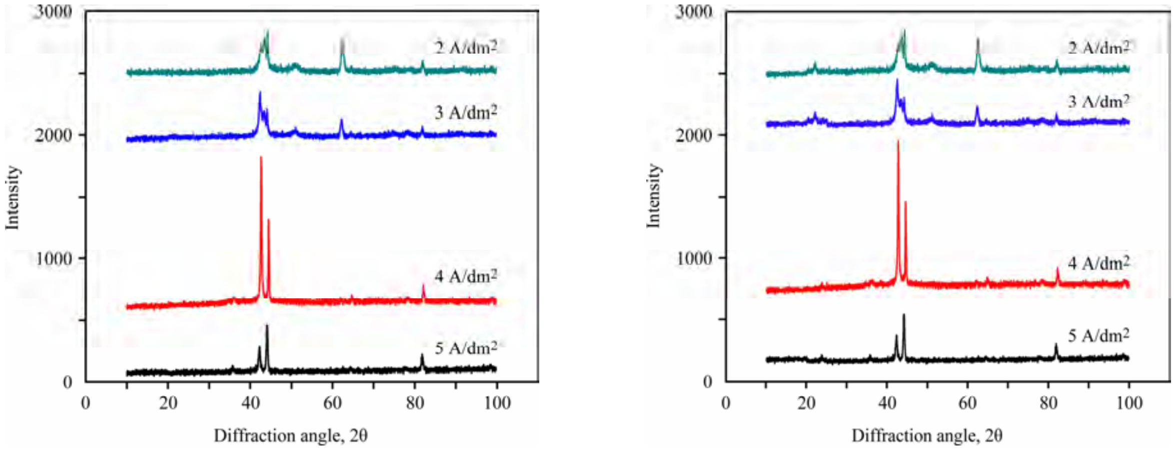
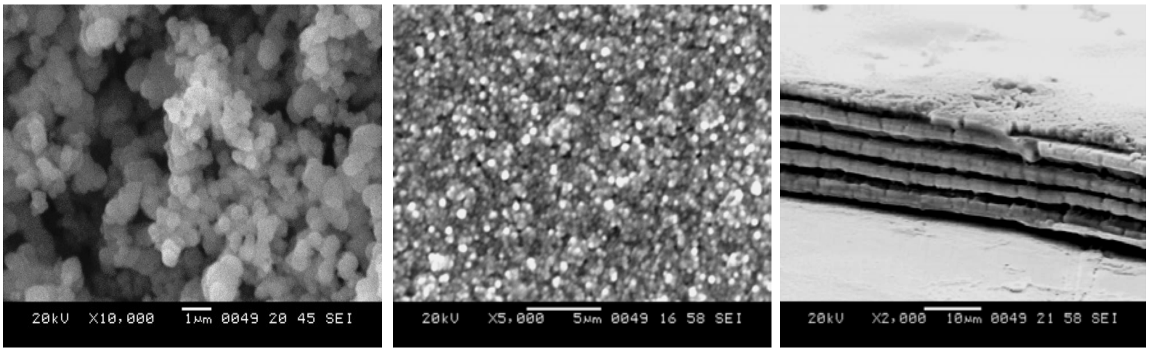


Fig. 4. Equivalent circuit modeling for Nyquist plot of MNC Zn-Ni-SiO$_2$ coating using $Z_{simpwin}$ software.



(a) (b)

Fig. 5. Powder X-ray diffraction patterns of (a) monolayer Zn-Ni alloy and (b) monolayer Zn-Ni-SiO$_2$ composite coating.



(a) (b) (c)

Fig. 6. SEM images of (a) SiO_2 nano powder; (b) surface morphology (Zn-Ni-SiO_2) showing SiO_2 particles and (c) cross section of MNC coatings of (Zn-Ni-SiO_2) having 10 layers.

pression of γ-phase may be observed, with appearance of two new $Zn_3Ni_{22\,(006)}$ and Zn_{102} phases. This evidences to the influence of the c.d., and hence the nickel content of the alloy on a phase structure of the alloy in the individual layers.

The deposition of an alloy coating with an individual layer thickness in nano/micrometric level is responsible for the improved corrosion resistance. In the case of Zn-Ni-SiO_2 nanocomposite coatings, as shown in Fig. 5b, the presence of SiO_2 in the coating matrix is indicated by low intensity peak that appeared at a reflection angle, 2θ in the range of 20–25°, irrespective of the c.d. at which they are deposited. Hence, it may be inferred that the phase structure of the nanocomposite coating remains unaltered with c.d. It indicates that the phase structure of the MNC caused only by silica is not altered by deposition parameters like c.d., and concentration. Further, the improved hardness and corrosion behavior of the MNC coatings is due to the inclusion of silica partials in the layered structures of the coatings [20].

2.5 Scanning Electron Microscopy Study

The surface morphology and cross sectional view of electrodeposited MNC coatings of (Zn-Ni-SiO_2), as examined under SEM is shown in Fig. 6. Spherically shaped particles in Fig. 6a show nano/submicron size of the silica particles used in the present study. Fig. 6b is the surface morphology of electroplated monolayer (Zn-Ni-SiO_2) coating, demonstrating the occlusion of silica particles into the coating. In Fig. 6c, the cross section SEM image of MNC (Zn-Ni-SiO_2) with 10 layers coated on mild steel is shown. The layers with different composition/phase have appeared with clear contrast. The bright regions represent layers of one composition and the dark regions represent another set of layers.

CONCLUSIONS

- An electrolytic bath has been optimized for the deposition of Zn-based alloy composite coating on MS in terms of its bath composition and operating parameters.
- Zn-Ni-SiO_2 can be electroplated successfully onto MS by dispersing SiO_2 particles into Zn-Ni bath using proper bath ingredients.
- The corrosion resistance of the monolayer Zn-Ni-SiO_2 composite coatings can be improved with multilayered coating technique by optimizing CCCD's and number of layers.
- The analysis of electroplates confirmed the incorporation of SiO_2 nanoparticles in the coating matrix, supported by SEM and XRD studies.
- Under optimal conditions, the MNC Zn-Ni-SiO_2 coatings are found to be about 107 times higher corrosion resistant than the monolayer Zn-Ni-SiO_2 coatings, which are about 1.5 times higher corrosion resistant than the monolayer Zn-Ni alloy coatings.
- Decrease in CR at higher degree of layering is attributed to less relaxation time for redistribution of metal ions in the diffusion layer during plating.
- The constant low intensity peaks corresponding to SiO_2, observed in each c.d.'s confirm that its phase structure is not altered by deposition parameters like c.d., concentration. Hence, the improved hardness and corrosion behavior of the MNC coatings are due to the inclusion of silica partials in the lattice structure.

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Реферат

Многослойные нанокомпозитные покрытия из Zn-Ni-SiO_2 осаждались гальваностатическим методом на низкоуглеродистую сталь (НС) из ванны с Zn-Ni в присутствии $Zn^{+2}Ni^{+2}$ ионов и равномерно диспергированных нано-SiO_2 частиц. Коррозионные характеристики и свойства многослойных нанокомпозитных (МНК) покрытий оценивались электрохимической поляризацией и методом импедансов. Условия осаждения такие, как состав ванны, циклическая плотность катодных токов (ЦПКТ) и количество слоев были оптимизированы с целью получения максимально коррозионностойких покрытий. Значительное улучшение антикоррозийных свойств многослойных нанокомпозитных покрытий наблюдалось при замене монослойных покрытий на многослойные. Скорость корродирования (СК) МНК покрытий уменьшалась поступательно в соответствии с количеством слоев до оптимального уровня, а затем начинала увеличиваться. Увеличение СК на более высоком уровне наслаивания связано с диффузией слоев из-за короткого времени осаждения и невозможности создания антикоррозийной защиты. Формирование слоев, включения силиконовых частиц в матрице МНК покрытий было подтверждено с помощью SEM и XRD анализов. При оптимальных значениях плотности тока, то есть 3,05–5,0 А/$см^2$, покрытие из Zn-Ni-SiO_2 состоящее из 300 слоев, обозначенных как (Zn-Ni-$SiO_2)_{3.0/5.0/300}$, в 107 раз превосходит по антикоррозийности монослойное покрытие из Zn-Ni-SiO_2, образованное в той же самой ванне и за то же время. Причины увеличенной защиты от коррозии МНК покрытий из Zn-Ni-SiO_2 по сравнению с соответствующими монослойными покрытиями из Zn-Ni и (Zn-Ni-SiO_2) проанализированы и результаты описаны.