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Full Length Article

Multilayered Zn-Ni alloy coatings for better corrosion protection of mild steel

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ABSTRACT

A simple aqueous electrolyte for the deposition of anti-corrosive Zn-Ni alloy coatings was optimized using conventional Hull cell method. The corrosion protection value of the electrodeposited coatings at a current density (c.d.) range of 2.0–5.0 A dm^{-2} has been testified in 5 wt% NaCl solution, as representative corrosion medium. The electrochemical behavior of the coatings towards corrosion was related to its surface topography, elemental composition and phase structure using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analyses, respectively. Among the monolithic coatings developed at different c.d.'s, the coating obtained at 3.0 A dm^{-2} was found to be the best with least corrosion current (i_{corr}) value. Further, the corrosion protection efficacy of the monolayer coatings were improved to many folds through multilayer coating approach, by modulating the cyclic cathode current densities (CCCD's). The composition modulated multilayer (CMM) Zn-Ni alloy coating with 60 layers, developed from the combination of CCCD's 3.0 and 5.0 A dm^{-2} was found to be the best with 3 fold enhancement in corrosion protection efficiency. The formation of multilayer coatings was confirmed using cross-sectional SEM, and the experimental results are discussed with tables and figures.

1. Introduction

Zinc (Zn) and it's alloy coatings are finding numerous applications in different industries like automotive, electrical, aerospace etc. as sacrificial metallic coatings for the protection of steel components [1]. Electroplated thick Zn coatings were used for many years to give protection for metallic parts economically [2], whereas nowadays the traditional the Zn coatings are replaced by its alloys due to its ineffectiveness in aggressive or high temperature environments towards corrosion [3,4]. The alloys of Zn with nobler Fe group metals (Ni, Co, Fe etc.) can give better protection efficacy than pure Zn coatings [1–6]. Apart from that, the alloys such as Zn-Ni can impart good mechanical properties like hardness, wear resistance etc, as compared with the pure Zn coatings [3–6]. Hence, it is widely accepted as an eco-friendly alternative to toxic coatings such as cadmium [3,6].

Amongst all the commonly electroplated alloys, Zn-Ni is the one which is most exploited in commercial applications [7–10]. Many reports are available on the corrosion protection efficiency of the Zn-Ni alloy coatings [7–13], whereas these coatings are prone to severe sacrificial dissolution to certain extend due to the less amount of Ni in the deposits [3,6,9]. In this regards, composition modulated multilayer (CMM) coatings are becoming more attractive to provide many fold improvement in corrosion protection [7–13], though the Ni content in the coatings are less. CMMA coatings can be developed by proper modulation in cathodic deposition current density (c.d.) periodically under optimal conditions from the same bath. The CMM coating contains many number of thin alternate metal/ alloy layers of different composition, and each of those layers plays an important role to achieve the preferred performance towards corrosion [7,14,15]. In the last decades, compositionally modulated multilayer alloy (CMMA) coatings have been widely investigated due to its economic and commercial importance [15–18]. Though there are many reports on the corrosion study of electrodeposited monolayer and multilayer Zn-Ni alloy coatings, no much reports were found on electrodeposited Zn-Ni alloy from a simple sulphate bath (without using any additive) operating under mild acidic conditions (pH = 6). Since the composition and pH of plating bath are crucial parameters, affecting the structure and morphology of the coatings, it plays an important role on its corrosion resistance properties as well. To the best of author's knowledge, no work is reported on the development of multilayered Zn-Ni alloy coatings from a simple sulphate bath. Hence, this study on CMM Zn-Ni alloy from a simple sulphate bath

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is first time to be reported here. The deposition conditions were optimized for good performance of the coatings towards corrosion.

2. Experimental

The electrolytic bath of Zn-Ni alloy was optimized through standard Hull cell method [19], without using any additives. The arrived composition of the aqueous electrolyte at optimal conditions of pH and temperature are given in Table 1. The alloy coatings at different deposition c.d.'s (2.0–5.0 A dm^{-2}) were developed on polished mild steel plates of 6.25 cm^2 exposed surface area. All depositions were carried out in a custom made plating cell of 250 mL solution capacity, by placing the electrodes ~5 cm apart from each other. Monolayer or homogeneous coatings (without modulation in composition) were deposited galvanostatically on pre-cleaned MS plates over a c.d. range of 2.0–5.0 A dm^{-2} from the proposed bath under optimal conditions.

Further, the CMA coatings with different number of layering were achieved by cycling the cathodic current densities through proper setting up of the power source [16]. The cyclic current densities were selected after the initial investigation on corrosion resistance and composition of the developed monolayer coatings, and the deposition time for each layer out of total time (600 s) was adjusted through the computer controlled DC power source (N6705A; Agilent Technologies, USA). The total deposition time for both monolayer and multilayer coatings were kept constant (600 s) for comparison purpose. The developed composition modulated multilayer alloy (CMMA) coatings with different number of layers are represented using the notation $(Zn\text{-}Ni)_{1.0/2.0/n}$. Where, '1.0 and 2.0' represents the first and second cyclic cathode c.d.'s (CCCD's), and 'n' represents the total number of layers.

Table 1
Composition and operating parameters of simple Zn-Ni alloy plating bath for the development of corrosion resistant alloy coatings.

Bath composition	Amount ($g\ L^{-1}$)	Operating parameters
Zinc sulphate heptahydrate	130.0	Temperature: 303 K (30 °C)
Nickel sulphate hexahydrate	15.0	Anode: Nickel
Sodium sulphate	40.21	Cathode: Mild Steel plate
Boric acid	15.31	c.d. range: 2.0–5.0 A dm^{-2}pH = 6.0

2.1. Characterization

The Zn-Ni alloy deposits were characterized for its surface topography, elemental composition and phase structure using scanning electron microscopy (SEM, JSM–7610F from JEOL, USA), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD, Rigaku Miniflex 600 X-Ray Diffractometer) analyses, respectively. The XRD patterns of the coatings deposited at different c.d.'s were recorded with in a scan range of 2θ = 20–65°, at a scan rate of 1° per minute. The electrochemical behavior of the alloy coatings developed at different c.d.'s towards corrosion was studied in 5 wt% NaCl solution. The corrosion resistance of the developed coatings were monitored by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques, using electrochemical workstation, Biologic SP-150, France. All electrochemical measurements were made using three electrode set up with developed coating (1 cm^2 exposed surface area) as working electrode, platinized platinum as counter electrode and saturated calomel electrode (SCE) as reference. The corrosion currents were obtained from the Tafel's extrapolation method using EC-Lab software in Biologic SP-150, France.

3. Results and discussion

3.1. SEM Study

The SEM images of the Zn-Ni alloy coatings obtained at different c.d.'s are depicted in Fig. 1. It may be noted that the microstructure

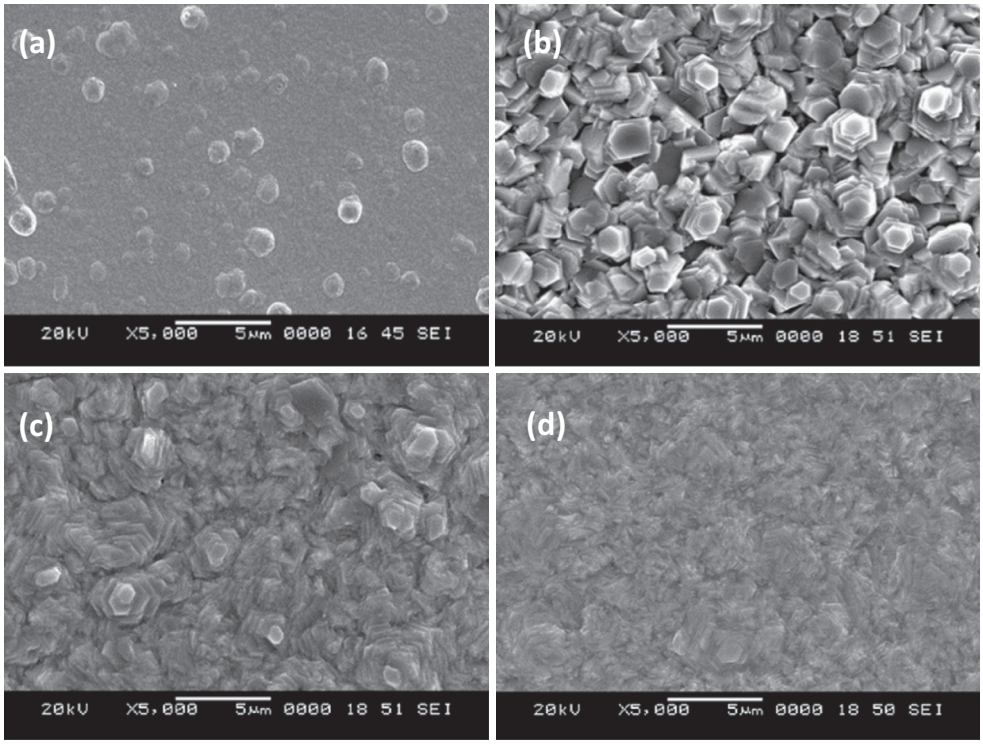

Fig. 1. SEM images of Zn-Ni alloy coatings deposited at different c.d.'s from optimal bath; (a) 2.0 A dm^{-2}, (b) 3.0 A dm^{-2}, (c) 4.0 A dm^{-2} and (d) 5.0 A dm^{-2}.

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of the coatings bears a close relationship with the deposition c.d., and the surface appearance changes remarkably with c.d. from flaky pyramidal structure at 3.0 A dm^{-2} to smooth porous structures at high deposition c.d. This variation in surface topography of the alloy coatings with c.d. was reflected in its anti-corrosive nature and decorative appeal.

3.2. XRD Study

The XRD pattern of Zn-Ni alloy coatings achieved at different c.d.'s from simple aqueous electrolyte is shown in Fig. 2. The phase structure changes, affected by compositional variations with deposition c.d. is clear from the obtained XRD patterns. It may be observed that, the XRD reflection corresponding to Zn (002) is found to be increased with increase in c.d. and the other reflections corresponding to Zn (101), (100), (102) and γ-(411) phases were found to be decreasing with increase in deposition c.d. [12]. The crystallite size of the coatings were calculated from the XRD data using Scherrer formula and was found to be decreasing with increase in deposition c.d. from 54 nm to 46 nm.

3.3. Compositional analysis and corrosion study

The monolayer Zn-Ni alloy coatings developed on MS substrate at different c.d.'s were tested for its elemental composition and corrosion resistance. The wt% of Ni was observed to be increased with deposition c.d. as reported in Table 2. Further the corrosion study results shows that the corrosion resistance of the coating increases only up to certain Ni content in the deposit and then decreases. This decrease in corrosion resistance of the coatings at higher c.d.'s are related to the porous morphology of the coatings as shown in Fig. 1. The compositional changes, corrosion rate and appearance of the coatings with deposition c.d. are given in Table 2.

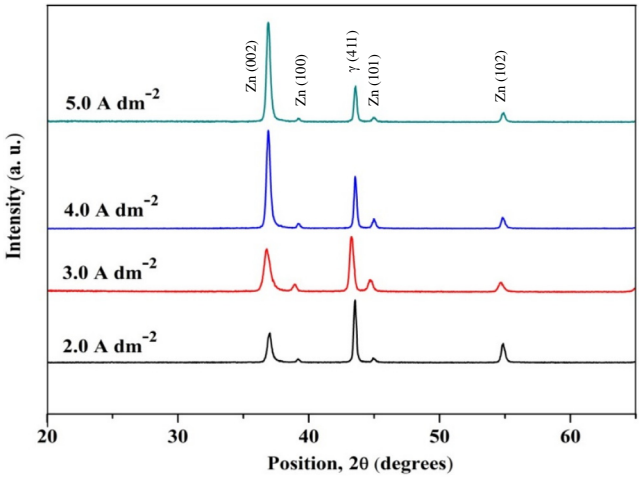

Fig. 2. XRD patterns of the coatings deposited at different c.d.'s from optimal bath.

The obtained corrosion data shows that the alloy coating deposited at 3.0 A dm^{-2} as the optimal coating with least corrosion current (i_{corr}) value (11.3 μA cm^{-2}), compared with coatings at other c.d.'s.

3.4. Optimization of cyclic cathode current densities (CCCD's)

Multilayer coating approach was adopted to further improve the corrosion resistance of the Zn-Ni alloy coatings through proper manipulation of the cyclic cathode current densities (CCCD's). As a preliminary examination of the effect of layering, CMMA coatings with 10 layers were developed by selecting two sets of CCCD's as reported in Table 3.

3.5. Optimization of total number of layers for better corrosion resistance

Among the different CCCD's tried, the CMMA coating developed at a combination of 3.0 and 5.0 A dm^{-2} was found to be the best (Table 3), with least i_{corr} values. Hence, this combination of c.d.'s were selected for further layering to produce CMMA coatings with 60, 120, 300 and 600 layers. The corrosion rates of the CMMA coatings with different number of layers are reported in Table 4.

From the obtained results, CR of the CMMA coatings was found to be decreased only up to an optimal number of layers (60 layers) and then increased. The multilayer deposition results in the formation of new interfaces between the layers of different composition and hence increases the infiltration time of the corrosive medium to reach the substrate [10,17,20,21]. The penetration of the corrosion medium into the interfaces and subsequent spreading leading to the lag in corrosion rate as compared with its monolayer counterparts. Whereas, the layering effect is observed only up to optimal level due to the interlayer diffusion, which nullify the layering effect, with increase in the number of layers. At higher degree of layering (600 layers), the thin layers resulted from the very small deposition time may completely diffuse together to form a deposit, equivalent to its monolayer coating. This interlayer diffusion effect can be evident from the almost similar CR of the CMMA coating with 600 layers and optimal monolithic Zn-Ni alloy coating at 3.0 A dm^{-2}. However, the CMMA $(Zn\text{-}Ni)_{3.0/5.0/60}$ showed minimum i_{corr} value (4.3 μA cm^{-2}) as compared to the optimal monolithic Zn-Ni alloy coating (Table 2). Hence, $(Zn\text{-}Ni)_{3.0/5.0/60}$ has been obtained as the best configuration of CMMA coating for better performance against corrosion.

Table 3
Corrosion data of CMA Zn-Ni alloy coatings at different set of CCCD's (with 10 layers) at 303 K, pH = 6.0.

CCCD's (A dm^{-2})	$-E_{corr}$ (V vs SCE)	i_{corr} μA cm^{-2}
$(Zn\text{-}Ni)_{2.0/4.0/10}$	1.06	12.1
$(Zn\text{-}Ni)_{3.0/5.0/10}$	1.04	5.8

Table 2
The variation in Ni content, appearance and corrosion rate of monolithic Zn-Ni alloy coatings with deposition current density (c.d.) at 303 K, pH = 6.0.

c.d. A dm^{-2}	wt% of Ni	$-E_{corr}$ V vs SCE	i_{corr} μA cm^{-2}
2.0	2.31	1.05	18.1
3.0	4.62	1.04	11.3
4.0	6.86	1.04	16.7
5.0	7.91	1.02	19.2

Table 4
Corrosion data of CMA Zn-Ni alloy coatings with different number of layers.

CCCD's (A dm^{-2})	$-E_{corr}$ (V vs SCE)	i_{corr} (μA cm^{-2})
$(Zn\text{-}Ni)_{3.0/5.0/10}$	1.04	5.8
$(Zn\text{-}Ni)_{3.0/5.0/60}$	1.03	4.3
$(Zn\text{-}Ni)_{3.0/5.0/120}$	1.06	6.9
$(Zn\text{-}Ni)_{3.0/5.0/300}$	1.08	8.6
$(Zn\text{-}Ni)_{3.0/5.0/600}$	1.10	12.4

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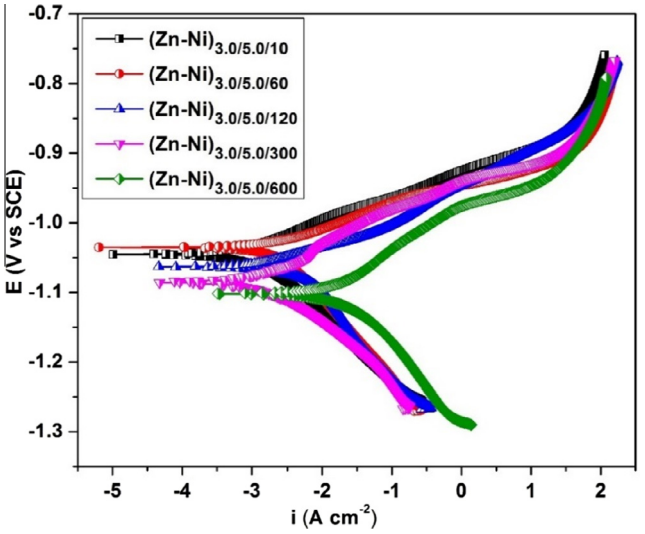

Fig. 3. Potentiodynamic polarization responses of monolithic Zn-Ni alloy deposits at different c.d.'s.

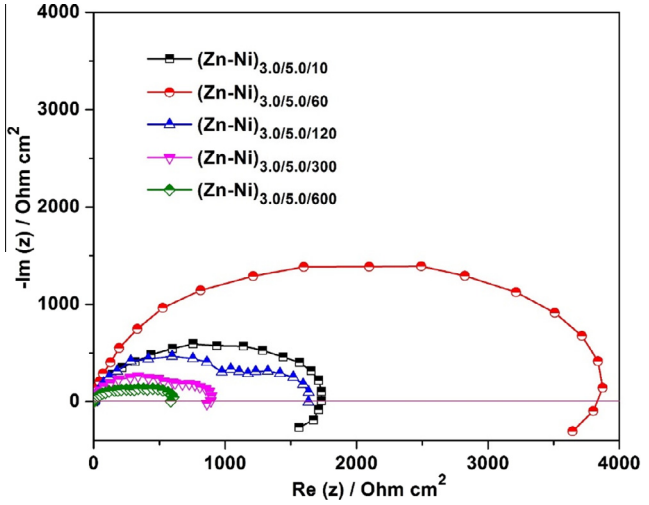

Fig. 4. Nyquist plots of CMMA Zn-Ni alloy coatings with different degree of layering.

3.6. Tafel's polarization study

The potentiodynamic polarization behavior of the Zn-Ni CMMA coatings were recorded in a potential window of ±250 mV from open circuit potential (OCP) at a scan rate of 1.0 mV s^{-1}. The polarization responses of $(Zn\text{-}Ni)_{3.0/5.0}$ CMA coatings with different degree of layering are shown in Fig. 3. The effect of layering towards corrosion rate was found to be encouraging only up to an optimal layering of 60 as evidenced from their i_{corr} values, reported in Table 4. Further, the corrosion rate of coatings were obtained from the Tafel extrapolation method and reported in Table 4. The polarization curves obtained for alloy coatings with different degree of layering are given in Fig. 3, which further supports the CMA $(Zn\text{-}Ni)_{3.0/5.0/60}$ configuration as the most anti-corrosive coating.

3.7. Electrochemical impedance spectroscopy

The double layer capacitance behavior of the coatings, which plays major role for the improved corrosion resistance, were analyzed using AC impedance spectroscopy study or EIS. The Nyquist responses of the coatings recorded within the frequency limit of 100 kHz to 10 MHz were plotted as imaginary impedance versus real impedance and given in Fig. 4. Impedance signals shown in Fig. 4 clearly indicates the increase in polarization resistance and decrease in double layer capacitance of the CMMA coatings up to 60 layers and its further decrease with layering. Further, the imaginary impedance (Z_{img}) attaining positive values at the lower frequency end (Fig. 4) is ascribed to the inductance behaviour of the alloy coatings due to the change in corrosion potential at the interface [13].

Further, an electrical equivalent circuit (EEC) was simulated from the fitment of Nyquist responses using EC-Lab software. The obtained EEC consists of solution resistance (R_s), polarization or charge transfer resistance (R_{ct}), constant phase element (CPE) pertaining to double layer capacitance, inductive resistance (R_L) and inductance (L). A representative fitment result and the obtained EEC are shown in Fig. 5.

The obtained EEC with high frequency (HF) capacitive loop (R_{ct}-CPE) can be attributed to charge transfer reaction. Since the Nyquist plots obtained in the real system represent a general behavior where the double layer at the metal solution interface

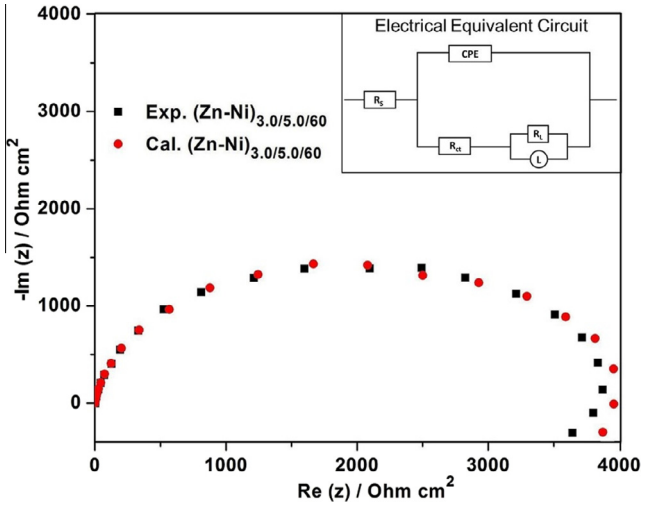

Fig. 5. A representative electrical equivalent circuit (EEC) fitment of Nyquist responses of multilayer Zn-Ni coating along with the obtained EEC in the inset.

does not behave as an ideal capacitor, the obtained shape of the plots are not perfect semicircles. At the same time, the low frequency (LF) inductive loop R_L-L can be attributed to the relaxation process of the adsorbed chloride ions and protons. The R_{ct} values represents a measure of electron transfer across the surface and is inversely proportional to corrosion rate. The obtained fitting parameters are shown in Table 5. The data given in Table 5 shows that even though the solution resistance remains almost constant, the Rct values increases with layering up to an optimal level (60 layers) and then decreases. Thus, the EEC fitting results also supports the multilayered coating with coating configuration $(Zn\text{-}Ni)_{3.0/5.0/60}$ as the optimal coating.

3.8. Comparison between monolithic and CMM Zn-Ni alloy coatings

The overall corrosion study of the monolayer and multilayer Zn-Ni alloy coatings developed from the proposed bath shows that $(Zn\text{-}Ni)_{3.0}$ and $(Zn\text{-}Ni)_{3.0/5.0/60}$ as the optimal coatings, respectively (Table 6). The obtained corrosion data shows that the corrosion protection efficacy of the CMMA $(Zn\text{-}Ni)_{3.0/5.0/60}$ coating is ~3 times

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Table 5
Electrical equivalent circuit (EEC) parameters for the multilayered Zn-Ni alloy coatings with different number of layers.

Coating configuration	R_s (Ω)	R_{ct} (Ω)	R_L (Ω)	L (H)	CPE (μF)
$(Zn\text{-}Ni)_{3.0/5.0/10}$	1.8	1724	156	40.3	46.6
$(Zn\text{-}Ni)_{3.0/5.0/60}$	1.7	3846	192	58.6	21.5
$(Zn\text{-}Ni)_{3.0/5.0/120}$	1.8	1582	138	32.1	52.7
$(Zn\text{-}Ni)_{3.0/5.0/300}$	1.8	882	116	26.3	82.6
$(Zn\text{-}Ni)_{3.0/5.0/600}$	1.7	564	102	18.1	112.8

Table 6
Comparison of corrosion rates of $(Zn\text{-}Ni)_{3.0}$ (monolithic) and CMA $(Zn\text{-}Ni)_{3.0/5.0/60}$ coatings.

Coating configuration	$-E_{corr}$ (V vs SCE)	i_{corr} (μA cm^{-2})
$(Zn\text{-}Ni)_{3.0\ (Monolithic)}$	1.04	11.3
CMA $(Zn\text{-}Ni)_{3.0/5.0/60}$	1.03	4.3

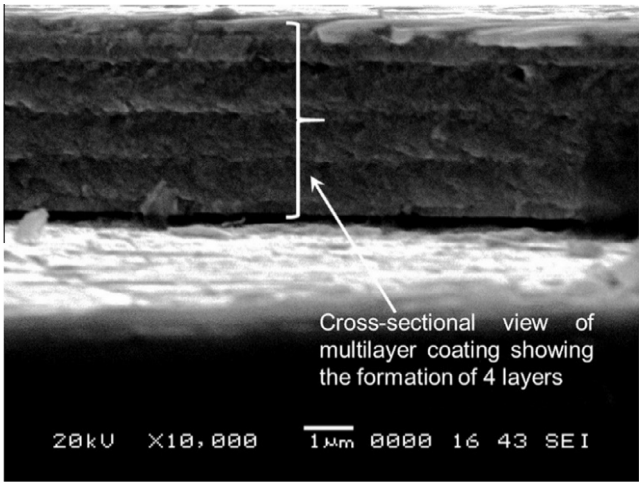

Fig. 6. Cross-sectional SEM image of CMMA $(Zn\text{-}Ni)_{3.0/5.0/4}$ coating shows the formation of layered coatings.

better than the optimal monolithic $(Zn\text{-}Ni)_{3.0}$ alloy coating developed from the same bath. It may be noted that the average thickness of monolayer Zn-Ni alloy coating (deposited for 10 min) is about 6 μm. Then the average thickness of individual layers of multilayer Zn-Ni alloy coating under optimal condition, i.e., $(Zn\text{-}Ni)_{3.0/5.0/60}$, deposited for same duration is estimated to be about 100 nm.

3.9. SEM analysis of multilayer coating

SEM analysis of the multilayered coating was performed to ascertain the alternate alloy layer formation with distinct composition. A multilayer, $(Zn\text{-}Ni)_{3.0/5.0/4}$, coating with 4 distinct layers and the formed interfaces in between sublayers are clearly visible in the cross-sectional SEM image shown in Fig. 6.

The enhanced anti-corrosion nature of the multilayered coating compared to its monolayer counterparts is ascribed to the formation of new interfaces, which allows the lateral spreading of the corrosive agent rather than directly penetrating into the substrate [9,17,21]. This lateral spreading of corrosion medium leading to lagging of corrosion rate in multilayered coatings, whereas it can penetrate directly to the substrate in monolayer coatings, as schematically shown in Fig. 7. Accordingly, the time required for the corroding medium to reach substrate by penetrating through monolayer (less time) and multilayer (more time than required for monolayer) coatings are different, and thereby the corrosion protection efficacy too.

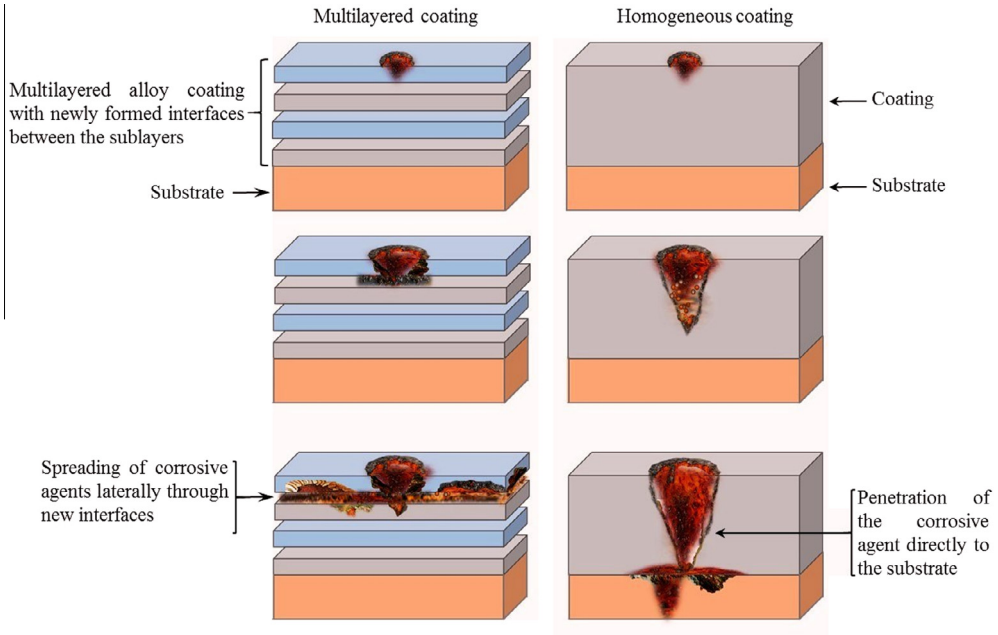

Fig. 7. Schematic of the corrosion mechanism in multilayer and monolayer alloy coatings.

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4. Conclusions

Based on the experimental results obtained for monolayer and multilayer Zn-Ni alloy coatings, the following conclusions have been made.

- A simple aqueous electrolyte has been optimized for the development of anti-corrosive Zn-Ni alloy coatings.
- The monolithic Zn-Ni alloy deposit achieved at 3.0 A dm^{-2} was found to be the best coating with least i_{corr} value (11.3 μA cm^{-2}) among the coatings developed at other c.d.'s.
- The enhancement in anti-corrosive nature of CMM Zn-Ni alloy coatings was observed only up to an optimal degree of layering and then decreased. This decrease in anti-corrosive property of multilayered coating at higher degree of layering is attributed to the inter-layer diffusion resulted from the extreme thinning of layers, where multilayer becomes monolayer.
- The CMMA coatings developed using square pulse with configuration $(Zn\text{-}Ni)_{3.0/5.0/60}$ was found to exhibit approximately 3 times better corrosion resistance compared to optimal monolithic $(Zn\text{-}Ni)_{3.0}$ alloy, deposited from same bath, for same length of time.
- The corrosion resistance of monolayer alloy coatings can be increased to many folds of its magnitude by multilayer technique.

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